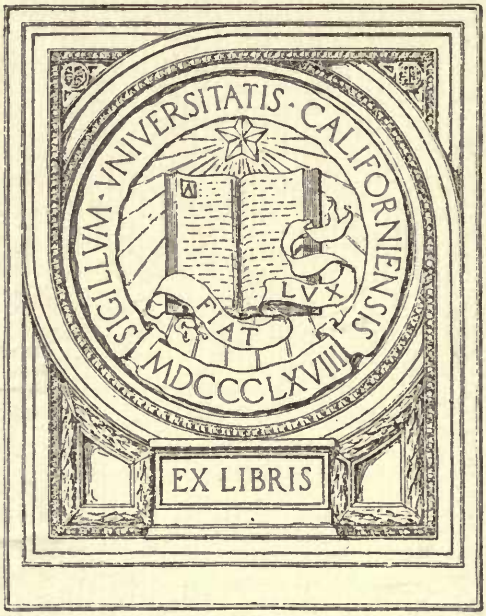
MODERN GASWORKS CHEMISTRY

GEOFFREY WEYMAN


SIGILLVM · VNIVERSITATIS · CALIFORNIENSIS
FIAT LVX
MDCCCLXVIII
EX LIBRIS

MODERN GASWORKS CHEMISTRY

MODERN GASWORKS CHEMISTRY

BY

GEOFFREY WEYMAN, D.Sc., F.I.C.
CHIEF CHEMIST TO THE NEWCASTLE-UPON-TYNE AND GATESHEAD GAS COMPANY

LONDON
BENN BROTHERS, LIMITED
8 BOUVERIE STREET, E.C. 4
1922

Printed in Great Britain at
The Mayflower Press, Plymouth. William Brendon & Son, Ltd.

PREFACE

In recent years it has come to be recognised that the Gas Industry is essentially a chemical industry. For this reason the chemist is rapidly being incorporated as an essential part of the controlling organisation.

It is of national importance that coal—our greatest national asset—should be treated at all times with due regard to the fact that the supply is by no means unlimited.

While coal is chiefly valued from the thermal standpoint it has to be remembered that it is also the only raw material from which many important substances can be obtained on a commercial scale. The Gas Industry is responsible for the primary treatment of a very large quantity of coal each year, and besides supplying the public with heat, light, and power it stands as an intermediary between the colliery and the chemical trade.

Every year it becomes more and more important that there should be a definite collaboration between modern research and commercial practice. Time is always a factor to be considered, and to permit research work to lie neglected for many years, buried in a mass of literature with its significance unappreciated, is a sign of gross national inefficiency. It is for the chemical organisation to ensure that the application of research work to practical conditions follows quickly upon the advance of knowledge.

This volume has not been written with the intention of discussing the chemical and physical theories which form the basis of the various processes carried out and the relative merits of various types of plant. Rather is it intended to describe the methods of controlling plant and processes in everyday use, in the hope that those who are endeavouring to introduce scientific control may be saved much time and trouble.

It is assumed that the reader has perused the important work of Vivian B. Lewes on *Carbonisation of Coal*, and that he will not have neglected to refer, for description of plant and processes, to Alwyne Meade's *Modern Gasworks Practice*, which is now recognised throughout the world as a standard work of reference. It is also hoped that advantage will be taken of the reference books and papers quoted at the end of each chapter. Although these form only a selection they have been chosen as the more important of those having a bearing on the text.

The author has made use of many of the books and papers quoted, in particular of Archbutt and Deeley's *Lubricants and Lubrication* and of the brochure compiled by the South Metropolitan Gas Company and made available to the author by the courtesy of E. V. Evans. This brochure consists of methods of sampling and analysis carefully selected with respect both to their accuracy and to their suitability for control work. While taking advantage of the information thus placed at his disposal the author has considered it inadvisable to quote *in extenso* in the hope that the publication of the brochure as a whole will not be delayed much longer.

Reproductions of the illustrations has been facilitated by the courtesy of the Society of Chemical Industry, the Institution of Gas Engineers, Messrs. Alexander Wright & Co., Ltd., Messrs. Baird & Tatlock (London), Ltd., The Cambridge and Paul Scientific Instrument Company, Ltd., The Sturtevant Engineering Company, Ltd., Messrs. Townson & Mercer, Ltd., and in particular Messrs. Brady and Martin, Ltd., of Newcastle-upon-Tyne, who have not only lent many blocks but also special forms of apparatus for personal trial.

The writer owes a very great deal to his friends of the Newcastle Chemical Industry Club, and to the Club Library. His friend, H. Dunford Smith, has criticised and helped very materially in every portion of the book. To Dr. H. G. Colman the author has always been indebted. The genial advice of his friend, Alwyne Meade, and the publishers must also be acknowledged.

Finally, the writer gladly recognises the assistance of those who have worked with him on the Staff of the Newcastle-upon-Tyne and Gateshead Gas Company.

GEOFFREY WEYMAN.

NEWCASTLE-UPON-TYNE,
September, 1922.

CONTENTS

CHAPTER I

INTRODUCTION

CHAPTER II

COAL

CHAPTER III

CARBONISATION

CHAPTER IV

COKE

CHAPTER V

MAINTENANCE OF HEATS

CHAPTER VI

REFRACTORY AND INSULATING MATERIALS

CHAPTER VII

TAR

LIST OF ILLUSTRATIONS

TABLES

MODERN GASWORKS CHEMISTRY

CHAPTER I

INTRODUCTION

It is inspiring to feel that the development of the processes for the manufacture of coal gas is a record of British industry. Had the same amount of thought and work been given to the recovery, manufacture, and utilisation of the other products of the carbonisation of coal as has been devoted to the manufacturing plant for the production of gas the position of the industry as a user of our chief national asset—coal—would have been impregnable. As it is to-day the increase in the cost of raw materials and wages has outstripped the reduction in costs due to improvement in plant and process. It is more economical in some cases to use raw coal as a fuel directly than to use it indirectly in the form of products of a gasworks. Could coal be so treated that the value of the by-products would allow the gaseous therm to be distributed as cheaply as the therm in the form of raw coal, the increased efficiency with which the former may be used would render carbonisation of extreme importance and would go far to stabilise the industrial conditions in this country.

The Chemist. To an industry dependent on chemical reactions and processes a technical staff trained to observe, to record, to analyse, and to synthesise is all-important. It is not so much knowledge that is required as the training to acquire knowledge quickly, to know what to look for, how to observe it, and the power to reason why. The boundary line between chemistry and physics disappears. The chemist must be prepared to utilise knowledge of any of the sciences that has a bearing. Fortified with a broad training in chemistry, mathematics, physics and even geology the chemist will be in a good position to deal with the complex factors which influence the direction and extent of the various reactions.

To a large extent the technical chemist is a product of recent years. Often enough he is superimposed upon an existing organisation, and without definite position or authority is expected to show substantial increases in economy. To the qualifications of training and ordered knowledge must, therefore, be added one of tact. With personality and the exercise of tact the difficulties will disappear, and the chemist will become an authority to whom the workmen will take their practical observations and difficulties. In the long run, from a person who is variously regarded as a nuisance, as a necessary evil to be tolerated as far as may be, as a sort of spy in charge of "tell-tale" instruments or as an amusing trickster, the chemist must trust to the result of his work to make his position one of reference by both workman and manager; until, from being an excrescence, the laboratory takes its place as the nerve centre of the works.

Work of the Chemist. The work of the chemist consists in obtaining and recording detailed information of the different factors which influence the extent and direction of the various processes, and it must always be remembered that "snap" information is never so reliable and is more likely to give false impressions than average information collected by observation over a period of time. Just as no analytical result should be accepted without some approximate check of its correctness, so no information should be passed on until it has been decided after careful consideration to be within the bounds of possibility. In particular, the position of the decimal point should be the subject of strict scrutiny.

Chemical Control. Chemical control may be placed in four divisions: (1) the valuation and determination of the physical and chemical properties of raw materials; (2) the observation and determination of the behaviour of various grades of raw material in the plant; (3) the observation and determination of the relative value of the different factors which influence the working of the plant with a given raw material; (4) the determination of the chemical and physical properties of the products. To these classes may be added a fifth, consisting of what may be styled "applied research." This consists of isolating different factors and studying each as far as possible independently of others, and then in re-combining the factors so as to clearly view the influence of one upon another. In this way a mental picture can often be formed which is of the greatest value in interpreting the results of large scale practice.

It is very necessary that in all organisations which include more than one laboratory, and in all cases where results are to be collectively averaged, there should be unity of method of sampling and analysis. This has in fact led the South Metropolitan Gas Company to compile the "*Brochure on Analytical Methods,*" already referred to.

Economy and Efficiency. The aim of chemical control is to obtain the maximum economy. By economy is meant the reduction in over-all costs to a minimum. There must be economy of raw material, of plant, of process, of labour, and of products. Economy is always expressed in money values. The ideal would be to produce something for and from nothing; consequently 100 per cent. economy is never reached. Economy is not to be confused with efficiency. By the latter is meant the ratio of that taken to that obtained. Efficiency may have relation to material, energy, heat, light, labour, and so on. Increase in efficiency usually, but not always, leads to increase in economy. It may not pay to increase efficiency beyond a certain point, as the extra cost involved may more than counterbalance the value of the extra yield obtained. It may also pay to sacrifice efficiency in one respect in order to gain it in another. Efficiency expressed as money value is economy.

Costs. It will be obvious that the chemist must always consider his results in relation to process costs, and a systematic costing is of essential importance. Chemical control itself is an expense, and this must be reckoned with in calculating economy. Often a full chemical control may not be worth while instituting, and the chemist must in the first place value the results which may be obtained and the cost of control before entering upon it.

In industry generally there has been a great tendency to preserve costs of manufacture as something private, on no account to be divulged to subordinates. It is difficult to see the value of the elaborate costing systems often found if this policy is pursued. Obviously no real attempt at further economy can be made unless the operator in charge of plant knows in what items the chief expense lies and how, if he cuts one expense, another will be affected. There is no doubt that exposed records lead to very great reduction in costs. The policy of the Government in circulating costs of different plants under their control during the war was most valuable. In an industry like the gas industry, where the operations of one concern do not directly interfere with those of another, there appears every incentive for exposing records of cost and efficiency.

Organisation. The organisation of the chemical staff rests with the chief chemist and depends on individual circumstances. In some cases those concerned actually with observation and control of plant are divided from those engaged in analytical and physical work. This arrangement suffers disadvantage in the tendency of the works staff to lose contact with the laboratory staff and to fail taking advantage of the laboratory equipment. There may be delay in the application of laboratory results. On the other hand, it is preferable that those engaged in refined analytical work should be constantly practised in such work. Errors will be more frequent if a chemist has to alternately make rough tests and accurate analyses. It would seem the best plan, where possible, to place one responsible chemist in the laboratory to take charge of the more refined work and check analyses. The remainder of the staff are distributed over the works, with the laboratory as their headquarters, and are responsible for the routine analytical work necessary to their particular control. In many cases the organisation has to include supervising and shift chemists, and some care must be taken to prevent the introduction of dual control.

Laboratories. It is to be hoped that in the future expense in fitting out controlling stations and laboratories will not be grudged any more than the capital expenditure on plant and buildings. Seeing that adequate control is a first essential to the success of any plant, one would have thought that the capital expenditure necessary to secure the former would have been included in the latter. At the present time it is usually considered an extra item to be added at some future date when the success of the plant has already been assured. It is a bad policy to stint laboratory space. If one apparatus has to be taken down to make room for another at short intervals much time will be lost and breakages will be more frequent. Cramped quarters always lead to waste in apparatus. The work of a gasworks' laboratory covers a wide range and therefore plenty of accommodation for apparatus is essential. Space must be found for special instruments, physical and chemical apparatus, to be used to examine various gases, coal, coke, liquor, tar, oils, refractory materials, oxide of iron, materials containing sulphur, besides the usual equipment necessary in every laboratory for general analytical work.

Owing to the large area covered by the works, and the fact that many materials do not lend themselves well to transference, it is customary to have control stations at different places close to the plant. Thus in the vicinity of the retort house may be placed a small laboratory suitable for rough gas analysis and containing instruments for checking the quality of the gas made. It is often necessary to equip suitable places with the required recording instruments close to the gas mains so that the length of lead and connections may be as short as possible.

These control stations must be well designed ; for it is better not to have instruments at all than to instal them in places which it is impossible to keep clean and which are subject to rapid alternations in temperature, just as it is useless to expect good work in a foul atmosphere or one subject to extremes of cold and heat. A respectable working bench, supplied with gas and usually with water, good light, means of heating and ventilation, are essentials.

Main Laboratory. The main laboratory serves as the centre of chemical control and the place in which most of the analytical and physical work will be done. It is conveniently divided into a sampling room, a testing room, an analytical and physical room and an office. In the first all the rough samples are received and reduced to a convenient size, preferably with the aid of mechanical means ; bottled, corked, and sealed and sent to the laboratory or elsewhere, or stored, as the case may be. Small scale experimental work, furnace work and the rougher analytical operations are made in the testing room, while the more refined work is performed in the analytical room where the instruments are also installed.

Labour will be saved by giving a service of compressed air, electricity, suction, and high-pressure gas. All these are usually to be obtained on the works, and short leads will not be expensive. A small motor and blower in place of compressed air service will also drive a shaft off which may be taken the power for driving a ball-mill, crushing or grinding machine, miniature centrifuge and stirring gear for calorimeter and other apparatus.

Attached to the main laboratory may be a small chemical store in which a stock of apparatus and reagents is kept. This will enable purchasing to be done at considerable intervals and in quantities which should command the grant of special terms from dealers. Possibly, also, sufficient repair work may be accumulated to justify the periodical attendance of an expert glass-blower. Considerable expense may sometimes be saved in preparing reagents from commercial products for special purposes. Waste reagents may also occasionally be economically recovered. A soldering outfit, a little soft solder and a solution of zinc chloride will often enable small repairs to instruments to be made when otherwise the delay and expense of returning the whole apparatus to the makers would be necessary.

It will probably be found convenient to stock at the laboratory store, reagents, thermometers, accumulator acid, test papers, disinfectants, first-aid materials, and various sundries used by other than the chemical staff proper. The cost is periodically debited to the departments concerned.

Checking Stores. It is very necessary that all new volumetric apparatus, thermometers, hydrometers, and the purity of reagents should be checked before issue for use. A set of thermometers and hydrometers covering the range used, a set of weights, a burette, and possibly pipettes, may be sent to the National Physical Laboratory for standardisation and then reserved for checking purposes. A carborundum pencil can be used to mark each piece of apparatus as having been checked and found correct to certain limits. Apparatus with the graduations appreciably out of the truth are better returned to the makers. This also applies to instruments and apparatus issued to the works, in particular to thermometers. In respect to the latter, it is often advisable before checking to anneal them for some time at the temperature at which they will be used. Gas burettes and large instruments will usually be supplied with certificates, but may be similarly checked.

For the details of methods of checking volumetric apparatus the reader must be referred elsewhere, but it may be noted that such details should be available for every member of the staff so that they may know the proper conditions to observe in their use, in particular as regards drainage time and rate of delivery.

Absorption Vessels and Gas Generating Apparatus. Apart from the usual forms of apparatus, the gas chemist is particularly concerned with gas absorption vessels and gas generating apparatus. In respect to the former, the vessel for general use should embody three essentials. It should provide intimacy of contact between gas and liquid, it should be such as can be readily washed out and precipitates removed, and it should be fairly robust. Owing to the necessity for gas tightness, ground glass connections are preferred, but often rubber stoppers may be used, especially if coated with a layer of vaseline on the under-side of the cork to prevent action of the gas upon the rubber.

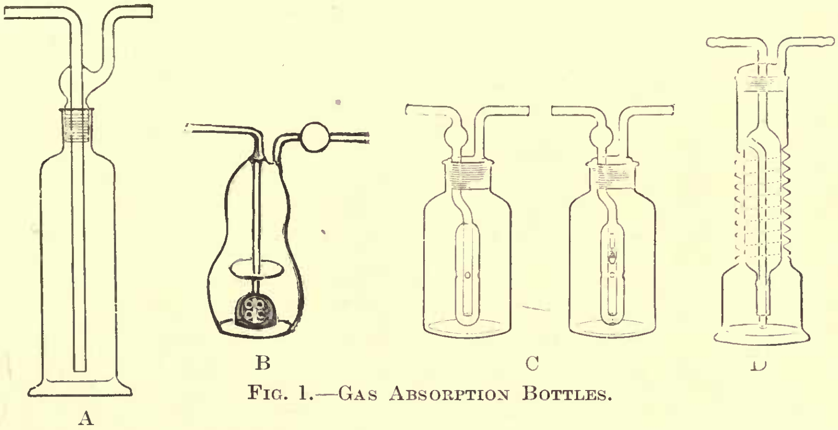


Fig. 1.—Gas Absorption Bottles.

Drechsel's form (Fig. 1—A) is very generally applicable although not very efficient in its scrubbing action. The closed-up variety, by G. Stephenson (B), is more efficient and can be usefully used where the contents are always liquid and it is desired to weigh the vessel and contents. Allihn's form (C) is more complicated but very efficient. The spiral form shown in the figure (D) cannot be too highly recommended for general work. It is most efficient, robust, and fairly easily cleaned out.

A suitable generator for producing comparatively large quantities of hydrogen sulphide, carbon dioxide, and hydrogen has been designed by F. Hirsch. It is free from a large number of cork and tube connections, is easily filled with large lumps of material, and gives an even generation of gas. The reacting solution is kept overhead in the vessel (Fig. 2) and its admittance to the solid reagent in the tapered tube is controlled by the tap. The liquid and gas work downwards through the column of solid material to the spent liquor reservoir at the base, from which the gas and spent liquor can be continuously withdrawn.

Standard Solutions. Too much attention can hardly be given to the preparation and use of standard solutions. Inaccuracy in this respect leads to great confusion and loss of time. A system such as the following may well be adopted. The solutions in common use are made up in reasonable quantities at definite intervals, when the surplus from the previous period is discarded. Each solution is carefully standardised. Of the quantity made up a portion—say, one litre—is reserved for checking purposes only and is carefully preserved in stoppered bottles in a cool, dark place. The remainder is used as working solution. At frequent intervals, and always before some important work is undertaken, the working solution is checked by titration against the reserved standard. Any error due to inadvertent contamination is then at once detected. It is well to entrust the standardisation to one competent individual and to record for all to see the details of the method employed, such as the end points of the indicator used, the temperature of titration and the time allowed for reading burettes, and the approximate total volume of the liquid titrated. The ultimate standard may conveniently be sodium carbonate, although sodium oxalate has been suggested on the ground that it may be prepared in a purer state. The conversion to carbonate may, however, present some difficulty. Acid so standardised is then used for adjusting the strength of the alkalis and so on. The warning might here be given that in calculating the strengths and in general work the full atomic weights should be used and not "rounded" off numbers. It is also advisable before making up standard solutions to check the acidity, ammonia content and presence of sulphur and chloride in the distilled water to be used.

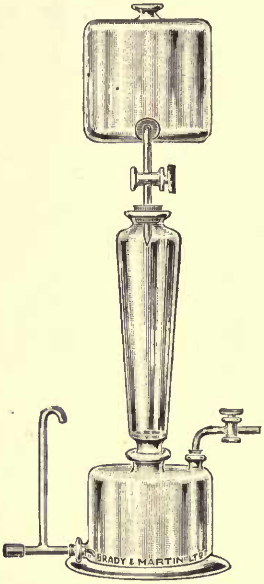


Fig. 2.—The Hirsch Gas Generating Vessel.

6*a*. *Standard Sodium Carbonate.* The purest sodium carbonate (or bi-carbonate) is used. When 5 grams of the carbonate are dissolved in 250 c.c. of water there should be no residue, only a slight opalescence when one-half of the solution is acidified with nitric acid and silver nitrate added, and no precipitate with excess of hydrochloric acid and barium chloride to the boiling solution of the remaining half.

The pure sample is dried by placing a sufficient quantity in a platinum crucible immersed in a sand-bath to the level of the carbonate, and heated with occasional stirring at 270–300° C. for 30 minutes. It is then cooled and weighed. If on further heating for 15 minutes the weight is constant it is enclosed in small portions in weighing bottles and stoppered up. Three portions of 2·5 grams each are exactly weighed out, dissolved separately in about 100 c.c. of water and titrated cold against the normal acid to be standardised, using methyl orange as indicator. The end point may be judged by the final red coloration and 0·05 c.c. deducted in order to avoid neutral tints which are variously appreciated by different observers. If the three titres do not give an agreement to ±0·05 c.c. the process is repeated till this accuracy is attained in three consecutive readings. A drainage time of, say, 15 seconds may be allowed before reading the burette, and the temperature of the solutions should be within a degree or so of 15° C.

7*a*. *Standard Acids.* About 150 c.c. of pure hydrochloric acid or 26–27 c.c. of sulphuric acid is diluted to one litre and checked against the sodium carbonate, as detailed above. The strength may then be adjusted to a strictly normal one, or a factor may be used. Thus if 2·100 grams of sodium carbonate neutralises 39·00 c.c. of acid, instead of the correct 39·62 c.c. for a strictly normal solution, the remaining acid may be diluted to $\frac{(1000-39) \times 39{\cdot}62}{39} = 976{\cdot}3$ c.c., or a factor may be used $\frac{39{\cdot}62}{39{\cdot}00} = 1{\cdot}0159$ by which the volume of acid used is multiplied in subsequent use. The former method is preferable in a works laboratory in the case of stable solutions.

To prepare acids of weaker strength aliquot portions of the normal acid are carefully diluted and then checked against proportionately smaller quantities of the pure sodium carbonate.

7*b*. *Standard Caustic Alkali.* Caustic soda purified by alcohol may be used. The "granulated" form is usually more pure than the "stick" soda. Usually, as methyl orange is used as indicator, small amounts of carbonates do not affect the results, but when phenolphthalein is used precautions should be taken to exclude carbonates. As a rule, it is sufficient to make up a very strong (50 per cent.) stock solution of good commercial caustic soda which is kept carefully corked up with a rubber stopper. Carbonate and other impurities will then separate as a sludge and the clear liquor may be decanted from the top substantially free from carbonate. A portion containing about 50 grams of the stock caustic soda are diluted to one litre and three successive portions titrated with standardised acid. The strength may be then adjusted, as in the case of the standard acid, and again checked. The correction factor is made as before. Resistance glass is best used for the strong solution.

7*c*. *Standard Permanganate and Sodium Oxalate.* A standard solution of potassium permanganate is best kept in blue glass bottles to protect it from the action of daylight. The distilled water used for preparing it usually contains oxidisable matter. Permanganate will also attack filter paper. It may not be used for solutions containing chlorides unless these are in small amount, when the addition of manganese sulphate will restrict action on the chloride. Permanganate N/10 is best prepared by weighing out about 3·2 grams of the purest crystals obtainable and dissolving the bulk in about 600 c.c. of boiling water. The remainder, a very small amount, is dissolved in, say, 500 c.c., and subsequently used to dilute the bulk. The boiling of each solution is continued for 15 minutes, and the solutions then cooled.

The stronger solution is decanted into a litre flask, and made up to the correct titre with the weak solution. It may be standardised with pure sodium oxalate which has been previously dried at 100° C., and cooled in a desiccator over calcium chloride. The oxalate is weighed out in quantities of 0·2 gram dissolved in 100 c.c. of water to which an excess (about 10 c.c.) of sulphuric acid is added. The solution is warmed to about 60° C. and titrated with the permanganate.

$$5\,Na_2C_2O_4+K_2Mn_2O_8+8\,H_2SO_4=K_2SO_4+2\,MnSO_4+10\,CO_2+5\,Na_2SO_4+8\,H_2O$$

If necessary, the purity of the sodium oxalate may be checked by conversion on heating to carbonate and titration against standard acid, using methyl orange as indicator. Permanganate solution can also be checked with pure iron wire. A weighed portion of the wire is dissolved in sulphuric acid out of contact with the air, and an aliquot part of the solution containing an excess of acid is titrated with the permanganate. The fine iron wire usually used contains about 99·7 per cent. of iron.

8*a*. *Standard Iodine and Thiosulphate.* Iodine can be obtained sufficiently pure and dry to enable it to be weighed out directly for a standard solution. If not considered pure it may be purified by sublimation with potassium iodide. Exactly 12·69 grams are weighed out in a stoppered weighing bottle and dissolved in about 50 c.c. of a solution of 15 grams potassium iodide and made up to one litre. This will give an N/10 solution.

If the purity of the iodine is not assured, pure arsenious oxide can be used to standardise the iodine solution. The pure oxide is dried over conc. sulphuric acid, weighed out, and dissolved in water containing about twice its weight of sodium bi-carbonate at boiling-point. A further addition of bi-carbonate is made before titration with the iodine. (Cf. **100***d*.)

$$As_2O_3+2\,I_2+2\,H_2O=As_2O_5+4\,HI$$

A thiosulphate solution containing 24·83 grams of pure sodium thiosulphate ($Na_2S_2O_3{\cdot}5\,H_2O$) per litre should check very closely. The thiosulphate should dissolve without turbidity, give no precipitate of sulphate, or carbonate with barium chloride, and should be free from sulphide and chloride. The solution is more permanent if standardised after keeping a month. The titration is carried out by adding the thiosulphate to the iodine solution until only a faint tinge of yellow is observed, when 0·5 c.c. of fresh cold starch solution—prepared by making 1 gram of soluble starch into a cream with water and pouring into 100 c.c. of boiling water—is added. The titration is continued until the blue colour just disappears.

$$2\,Na_2S_2O_3{\cdot}5\,H_2O+2\,I=2\,NaI+Na_2S_4O_6+5\,H_2O$$

8*b*. *Standard Silver Nitrate and Thiocyanate.* An N/10 solution is prepared by weighing out exactly 16·989 grams of the pure silver nitrate crystal dried at 130° C. for an hour. A thiocyanate solution, containing approximately 10 grams of the pure salt in one litre, is standardised against the silver nitrate by placing 25 c.c. of the latter in a porcelain dish with 25 c.c. of water and running in the thiocyanate till most of the silver has been precipitated. Five c.c. of a solution of ferric alum (10 per cent.) is added. The titration is continued with vigorous stirring until the red colour of the ferric thiocyanate persists. $AgNO_3+KCNS=AgCNS+KNO_3$

If the silver nitrate is not regarded as being sufficiently pure, the solution may be standardised by precipitating 25 c.c. diluted to 100 c.c., with excess of dilute hydrochloric acid, filtering, washing, drying, and weighing the silver chloride. (Cf. **95***a*.)

$$AgNO_3+HCl=AgCl+HNO_3$$

REFERENCES

G. Lemmens. What the Manufacturer Expects of his Chemists (address). *J. Inst. Chem.*, 1922, *pt. 2*, 151.

T. Hardie. Presidential address, Inst. Gas Engineers, 1922. *Gas World*, 1922, **76**, 526.

H. T. Wright. Organisation Applied to Industrial Problems. 1920.

F. M. Lawson. Industrial Control (exposed records). 1921.

G. Lunge and C. A. Keane. Technical Methods Chemical Analysis, Vol. I, Pt. I. (Standard Solutions.) 1911.

F. Sutton. Volumetric Analysis. 1922.

Prideaux. Theory and Use of Indicators. 1917.

GENERAL BIBLIOGRAPHICAL WORKS

Cripps. List of Gas Literature. *Trans. Inst. Gas Eng.*, 1894.

Chester. Bibliography (to end of 1891).

A. V. Hendrickson and others. *Trans. Inst. Gas Eng.* (yearly abstracts from 1891).

Various. Society of Chemical Industry. Annual Reports on Applied Chemistry—Section Gas—Destructive Distillation—Tar Products—yearly from 1916.

Note.—Papers referred to in the *Trans. Inst. Gas Eng.* will also be found in the " Institution " numbers of the *Gas World* and the *Gas Journal* of that year.

Abstracts of papers appearing in foreign journals appear in the *Journal of the Society of Chemical Industry* ; attention is also directed to the excellent "*Abstracts*" published fortnightly by the American Chemical Society.

CHAPTER II

COAL

The economy of a gasworks depends very largely upon the chief raw material—coal. The ease with which it may be converted into gas, the yield of gas and its quality, the quantity of coke and other products and the respective yields are governed by the composition and properties of the coal in the first place. It is true that by suitable treatment inferior coals can be made to yield large volumes of gas, but the quality is poor and the yield of other products small.

Without entering into a discussion on the constitution of coal, it must be pointed out that a knowledge of the work which has been done in this respect is essential to a proper appreciation of the value of coal for gas-making. It is customary to speak pessimistically of our knowledge of the constitution of coal for the reason that as yet the known facts cannot be crystallised into a set formula. At the same time a very large amount of work has been done which is capable of being put to considerable use by the technical chemist.

For our present purpose it will suffice to regard coal as a complex mixture of hydrocarbons which on heating decomposes yielding gaseous, liquid, and solid products. It is with the relative proportions of these products and the distribution of carbon between them that we are primarily concerned. So far as the constitution is revealed it can be said that the class of compounds known as "cellulosic" decompose with elimination chiefly of hydrogen and carbon monoxide. This decomposition reaches a maximum at about 750° C. and leaves the residue non-coking. Another class of constituents known as "resinic" are soluble in pyridine and phenol and is responsible for the coking property and the richer constituents of the gas. The most practical theory of to-day is developed by S. R. Illingworth, who regards the coking property of coals as in the first place due to the amount and composition of the resinic compounds. The decomposition of these furnish films of carbon which bind the residue to coke. If, during the time these compounds are undergoing decomposition, other matter—cellulosic compounds—are also evolving gas, the coke becomes accordingly of an open and expanded character. The character of the coal therefore depends not only on the relative amounts of the resinic and cellulosic materials but also on their relative stability and manner of decomposition.

There is no doubt that the resinic matter affects more or less the complete liquation of the coal substance and forms a plastic mass of varying consistency. On the property and composition of this plastic mass depend the rate at which coal can be carbonised. While there appears to be no dividing line between a gas coal and a coking or steam coal, an essential characteristic of a gas coal is in the formation of a plastic layer which is thin and of low viscosity. Coking coals, on the other hand, form highly tenacious layers which are very resistant to the penetration of heat. Cannel coals possess constituents dissimilar to the resinic compounds of coal, which on melting form comparatively mobile liquids and do not liquate the whole mass. The coal on carbonisation approximately retains its shape, and while the pieces may adhere the coke is poor and fragile. Anthracite coals contain little or no resinic compounds and on heating retain both shape and appearance.

The selection and valuation of coal has always been a difficult matter and methods vary largely, but the question is too serious to justify any but a chief place in the work of the chemist. It is necessary to examine the coal in various ways. Having tabulated the results a summarised opinion may be expressed.

Variation. Coal varies in its properties largely in the different coal-fields. Yorkshire coal as a rule provides an excellent gas coal, giving high yields of fair quality gas with a minimum of trouble. Durham coal, on the other hand, requires more severe treatment, but given such, the results often surpass the coal of other coal-fields. There are, of course, coals from Durham which are as easily carbonised as those from Yorkshire, and the variation from coal-field to coal-field is covered by variation in the seams of one coal-field. In collieries of the same area variation is largely due to the mixing of different seams at the pithead. This is very troublesome if the mixing is spasmodic. At the present time it is necessary to identify the coal by the pit at which it originates, and to closely observe and note those cases in which the coal is evidently a variable mixture.

The coal substance from the same seam does not vary much so long as the depth of the seam from the surface and its geological horizon does not materially alter, and very often coal from the same pit remains remarkably constant in its character. Over distances of many miles seams divide, are lost, or sometimes change their character. Seams which in Durham are good coking coals pass to gas and steam coals if followed north. Trade coal sold under a trade name is usually a mixture of coal from neighbouring pits and may include coal from several seams.

11*a. Visual Examination.* By careful visual examination much work can be avoided, for as a rule it is possible to tell those consignments which differ from previous lots from the same pit. Such coal, and any other coal which is out of the ordinary or at all suspicious, is sampled. Further trouble may be saved in the after examination, which may be restricted to such analysis as seems necessary. The chief points noticed are the *size, hardness, fracture, lustre, homogeneity, presence of pyritic material, extraneous ash, fusain, and moisture.* Coals may be bought as unscreened, small, or nuts; and this part of the specification is accordingly checked. Should a serious case of excessive quantity of dust and small be observed, a screening test is instituted and the consignment held up until the result is known. Hard coals are as a rule suitable, but soft coal even if large to start with will form a good deal of dust before reaching the retorts. A large proportion of fusain is also detrimental in this respect. Visual analysis is also useful in selecting coal suitable for storage.

11*b. Specific Gravity.* The real specific gravity of clean coal is fairly constant at about 1·30–1·34. The specific gravity is chiefly of importance in connection with storage accommodation and the estimation of coal stocks. For this purpose the apparent specific gravity of the coal in bulk is required. This varies considerably (from 1·0 to 1·3), according to the size and moisture content of the coal. A convenient method consists in levelling the top of the coal in one or two coal wagons of suitable shape and marking the level on the truck. The trucks are then weighed and tipped. The empty trucks are measured to find the volume occupied by the coal and the truck is tared back to find the weight of coal occupying that space. Or, a box measuring exactly one cubic foot internally may be tared, filled, and weighed. (See also **45***a*, **45***b*, **45***c*, **46***a*, **46***b*.)

12*a*. *Sampling.* Coals selected for sampling are best dealt with at the time of tipping. A shovelful at a time is taken at frequent intervals and stored in a covered-in receptacle till a large representative sample is obtained. Or, a bucket or funnel may be arranged to divert coal from the stream of coal as it is tipped. With unscreened coal it is best to screen a ton or two, weigh separately and sample each grade. The size of the larger is reduced by quartering and coning. Finally, the two grades of approximately equal size are mixed in the proportions ascertained. The mixing must be done very thoroughly, preferably by passing through a machine.

The " Metro " procedure consists in sizing the gross sample on a half-inch screen, weighing each portion. The rock, shale, and foreign matter are picked out of the " large " portion and after weighing are examined, crushed to less than half-inch in size and the whole then thoroughly mixed, first with the " small " coal, and finally with the " large," which has been previously reduced to less than one inch. The whole is then reduced by methods cf ridging, coning, and quartering.

Sometimes it is impossible to sample while tipping, in view of the fact that at this stage it is convenient to effect the mixing of coals for the retort house. Sampling from the trucks then becomes necessary. The amount of the sample to be taken depends on the facilities, which should be used to the limit. Unless the sampling is properly done subsequent work may be positively dangerous in view of the misapprehension caused. If possible, a whole truck is passed through a machine for automatically grinding, crushing, and selecting a portion. If this is impossible, each truck may be dealt with as follows : Coal trucks are usually filled from hoppers and the coal to some extent sizes as it flows into the truck—the large falling to the outside. A trench is therefore dug at least one-third of the depth of the truck from end to end. From the bottom of this trench a sample of about 1 cwt. is taken by the shovel. Care is taken to include the large and small just as it happens to come. This sample may then be put through a mechanical sampler. One of these machines is illustrated (Fig. 3), which not only reduces the coal to a small size but automatically selects a proportion, say 10 per cent., which is discharged separately as the sample. If a machine is not available the coal is crushed and quartered down in the usual manner until a sample of perhaps 56 lbs. is obtained. The maximum size of the coal should not exceed a half-inch. The sample is removed to the laboratory and there divided into halves by quartering. One half may be reserved for the coal-testing plant or may be rejected, and the other is ground and sampled down, preferably by machine, until a portion of about 1,000 grams entirely passes through a 4-mesh screen. This is then divided, one portion forming a reserved sample is sealed up and the reduction of the remainder is carried down to such a size that the whole of the remaining sample (about 50 grams) passes a 60-mesh screen. This is then placed in a stoppered bottle for immediate analysis.

It is particularly necessary to be careful that at any stage the sample *all* passes through the appropriate screen. When crushing by hand no hard particles are allowed to fly off, and, also, the amount of dust formed must not be excessive. A hammer and polished steel plate are usually preferable to mortar and pestle until the final stages are reached.

Moisture. Apart from the question of the nett weight of coal received a heavy moisture is undesirable. While the moisture has some chance of being removed during storage in the retort house prior to being charged, very wet coal may retain sufficient moisture to cause trouble with conveyor and charging machinery. Besides altering the weight of coal charged the moisture gives a severe shock to the settings, retards carbonisation and may produce abnormal amounts of carbon dioxide and carbon monoxide. It is also inadvisable to stock wet coals. Unless the coal is "washed" the moisture should not exceed about two or three per cent.

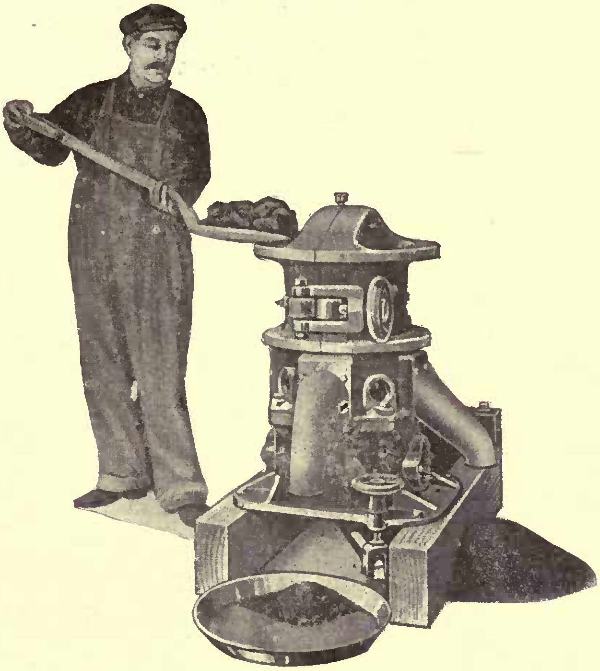


Fig. 3.—The Sturtevant Coal Sampling Machine.[1]

13*a. Moisture.* With very wet coals a special moisture sample is taken. In some cases the best plan is to take separate samples from the base and from the top of the trucks which appear to be the worst in this respect and those which appear to

---

[1] As made by the Sturtevant Engineering Company Ltd.

be the best, and to report the moisture for these particular cases. It is practically impossible to obtain an average moisture sample from a truck dripping with water except at the time of tipping. In any case the sample is reduced quickly on a non-absorbent surface to a half-inch size and transferred to the laboratory, where it is crushed quickly (not ground) on a steel plate to a size which would appear to pass a 4-mesh screen. A kilogram is then weighed out on to a porcelain or celluloid tray and exposed to the atmosphere in a thin layer until the moisture has been reduced sufficiently to allow of the sample being handled. It is again weighed and the loss added to that obtained in the final moisture determination as detailed below.

A reasonably dry coal (e.g. with less than 1·5 per cent. moisture) which does not appear at all wet is sampled down and treated at once for the final moisture on the sample as reduced to pass a 4-mesh screen.

14*a*. *Final Moisture.* A portion of the sample passing a 4-mesh screen is reduced quickly by hand to pass a 60-mesh screen. Ten grams are weighed out into a wide stoppered weighing bottle. The bottle and stopper are then separately placed in a jacketed oven maintained at 105° to 108° C. for an hour, when the stopper is replaced, the whole cooled in a desiccator and weighed as soon as sufficiently cool. Sometimes one gram of the sample is used. In some cases a further heating is required, and with coals which have been unduly exposed to the atmosphere the time of heating is shortened and repeated till the coal shows signs of gaining in weight. The jacket of the oven may contain toluene, glycerine and water, or some oil of appropriate stability, and is provided with openings at the back and front for ventilation. The American Chemical Society recommend passing air dried over sulphuric acid through the oven. Occluded gases are reckoned as moisture.

14*b*. *Final Moisture.* A good method which is not in general use consists in weighing 5 grams of the coal into a U-tube. Pads of cotton-wool are placed above the coal to prevent dust being carried away. The U-tube is suspended in a beaker containing water and glycerine or in a toluene oven and heated to 105° C. in the presence of a slow current of dry hydrogen. To the outlet is attached a calcium chloride drying-tube previously filled with hydrogen and weighed. Several hours are required to complete the transference of the moisture to the calcium chloride. The gain in weight of the calcium chloride tube then represents moisture. The calcium chloride must not contain free alkali.

Volatile Matter. The comparative amounts of volatile matter provide a first means of appraising a gas coal. The usual limits are a minimum of 28 per cent. and a maximum consistent with the production of a sufficiently good coke. Bituminous coals on the lower side are usually too highly coking to permit of being rapidly gasified, while coal very rich in volatile matter usually give a poor and soft coke. Oxidised coal may give a high volatile matter, but the gas yielded is poor. Cannels range higher, and in this case it may be thought that the large yields of rich gas may compensate for poor coke.

14*c*. *Volatile Matter.* The method of analysis usually used is some slightly modified form of the " American method." Exactly 1 gram of the fresh sample ground to pass a 60-mesh screen is weighed into a platinum crucible with tightly fitting lid which holds about 15 c.c. and weighs altogether 20 to 30 grams. The crucible is then placed on a silica triangle 6 to 8 cm. above the top of a No. 4 Méker burner. The gas pressure is adjusted so that when burning freely the flame has a length of 20 cm. The heating is maintained at full pressure for seven minutes, when the top of the crucible lid should be free from soot and the under-side well blackened. The crucible with lid still upon it is then cooled in a desiccator and weighed. The loss in weight, less moisture, represents the volatile combustible matter.

Coal Testing. It is often advisable to test coals experimentally in a model plant, and this is particularly so where the works plant is in large units and it is difficult to carry out large scale trials. The size of test plants range from those dealing with $\frac{1}{1000}$ part of a ton to those which are small scale manufacturing plants. The increase in size, while possibly reducing some errors, also produces limitations. The amount of each individual coal required becomes a serious matter and the time required to attain constant conditions is lengthened. Under skilful supervision model plants may be set up as a standard for the works.

The most common size is that dealing with $\frac{1}{1000}$ part of a ton. Very considerable experience and care is required to obtain comparative results, and the conditions must be standardised and rigidly adhered to. The results are of no use unless the details of the conditions obtaining are known, and hence published results must be considered very cautiously.

From such tests carried out under standard conditions the yield and quality of the gas and coke are the most important of the figures obtained. The tar and liquor cannot be measured with any accuracy unless the tests on one coal are unduly prolonged. The yield of gaseous therms calculated per ton from the results may form a basis of valuation which may be " corrected " by figures representing other properties.

15*a. Coal Testing Plant.* A typical arrangement[1] is shown (Fig. 4). The retort, about 3 inches by 6 inches by 18 inches long, has usually been cast in iron and faced up to give a good joint with the lid, which closes on a hinge and is screwed up against a ring of asbestos tape. Cast-iron retorts have a very short life at the best of times, and are also very variable in their behaviour. Recently the author has used retorts cast of nickel chrome steel which have been found to last in a much more satisfactory manner, and to be less expensive in the long run. The temperature is easily maintained constant as there is little or no scaling of the metal, and may be raised as high as 1100° C. on the inside. From the top of the retort near the door an ascension pipe leads to a seal pot and tar drain. The retort is placed in a " setting " and heated by a row of burners, using a well-governed gas supply. The gas off-take is continued to a pair of condensers, which may consist simply of a number of inclined or vertical pipes connected at the top and bottom by bends. The latter are provided with drain pipes sealed in water. There should be means of varying the number or length of pipes in use so as to vary the condensing power. The condensers may conveniently be enclosed in a casing through which a draught may be maintained. Alternatively, a water-cooled condenser may be used. In this case, instead of constantly circulating fresh water through, a proceeding which would be too drastic, the cooling water

---

[1] As made by Messrs. Alexander Wright and Co., Ltd.

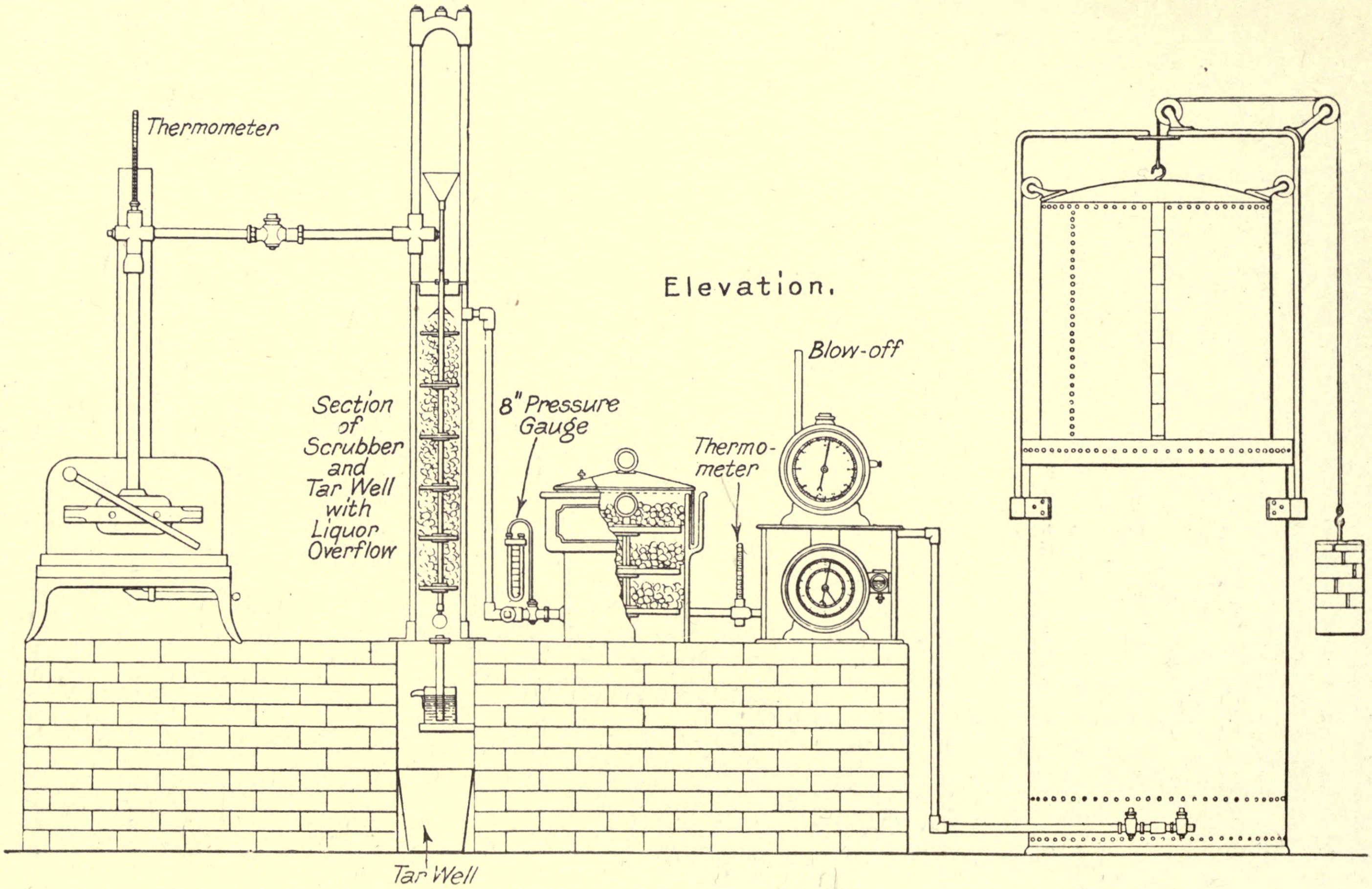


Fig. 4.—Model Coal Testing Plant.

should be circulated through a small heater by which its temperature may be regulated. From the condensers the gas passes through a small scrubber consisting of, say, a 6-inch pipe about 5 feet long, arranged vertically. This is filled with carefully sized coke, which is kept moist by a water drip from the top. The liquor is taken off by a seal at the base. The gas outlet at the top passes to a set of small purifiers containing three or four layers of bog iron ore 2 inches deep resting on grids about 15 inches square. Two of these in series at one time will usually be sufficient. A meter follows the purifiers and the gas then passes to a 20 cubic feet test holder, two of which will be required. It is unfortunate that the plant contains so much dead gas space which has to be cleared in each test, but attempts to reduce the capacity have not been altogether satisfactory.

17*a*. *Coal Testing.* The plant is first tested for gas tightness under pressure and vacuum. This can be done by passing some gas into the holder, closing the retort and altering the weights used to counterbalance the weight of the holder. The meter index will then show any leakage. The vacuum is then adjusted to $\frac{1}{10}$ of an inch w.g. at the retort gas valve by altering the counterbalance weights. The temperature of the retort is maintained at, say, 1050° C., and is kept steady by adjustment of the pressure of the gas supply to the burners. The coal sample having been previously broken to a size passing a 2-mesh screen, a charge of 2·24 lb. is weighed on to an iron tray. The trays may be 3 inches wide, 2 inches deep, and 12 inches long. The charge is quickly inserted into the retort and pushed to the far end. The door is clamped tight and the gas valve above is opened. Water is turned on to drip down the scrubber. Attention is then given to the regulation of the temperature gradient between the retort and the outlet of the scrubber so as to give a gradual fall to about 20° C. It is most important to keep the concentration of the hydro-carbon vapour in the cooled and purified gas in some definite proportion to that of the gas issuing from the retort. The charge is run off until a predetermined volume of gas has been collected, or until the rate of gas evolution has fallen to some minimum value. This will take from 30 to 50 minutes, depending on the coal. The gas valve at the retort is then shut and the coke withdrawn on the tray. The red heat is taken off the coke by spraying with a minimum quantity of water. When cooled it is weighed and sampled for analysis. As the plant contains 4 or 5 cubic feet of gas space, at least three charges from the same coal are necessary to obtain a quality of gas corresponding to the coal tested. Each charge is run to the same volume of gas so as to obtain concordant results for the quality. The gas is therefore passed to another holder and the plant made ready for another test. During the succeeding tests the gas from the previous charge is examined for its specific gravity, calorific value, and in such other way as appears advisable. The nitrogen should not be allowed to exceed 3 per cent. in the gas from the last charge. From the calorific value and yield of gas corrected for temperature and pressure the therm yield per ton can be calculated. The time required to obtain each 4 cubic feet of gas, or the gas evolved each 5 minutes, is also noted and compared with the other means for appreciating the rate of carbonisation. The coke may also be examined for volatile matter, calorific value, ash, sulphur, nitrogen. (See pp. 44–53.)

Tube Distillation. In the absence of a coal-testing plant, valuable information of the same nature may be obtained by distillation in a tube. The conditions are again standardised. The results may be taken as comparative only. It is hardly advisable to translate the figures obtained into results to be anticipated on a large scale. Such experiments are more reliable when taken in conjunction with a coal test. The chief trouble lies in the hydrocarbon content being of a variable nature, and it is impossible to do much in the way of gradual condensation. Probably, in view of this, it is best to wash out all the hydrocarbons in heavy paraffin or creosote and estimate them by distillation of the wash oil. If this is done the calorific value calculated from gas analysis becomes reliable. The gas may be collected in a small test holder or aspirator bottle.

18*a*. *Tube Distillation.* The apparatus and method is essentially that evolved by G. Beilby and W. A. Bone. A retort tube (Fig. 5) of silica closed at one end, about 60 cm. long with an internal diameter of about 20 mm., is placed in a 25-burner Bunsen combustion furnace. At the closed end is placed 15 grams of the coal, which is kept in position by an asbestos plug. This is followed by about 10 cm. length of loose, broken silica or fire-brick lumps, followed by another asbestos plug. At the front end against the cork, which is inserted to close the tube, is placed a small, weighed wad of dry cotton-wool. The side-tube is arranged to hang down and is directly connected to a trap-bulb tube which may be immersed in liquid at 105° C., to prevent condensation of water. At the outlet of this vessel is placed another wad of cotton-wool to retain tar fog. The whole is weighed before being connected. The outlet of this tube may be connected to absorption vessels containing dilute sulphuric acid to absorb ammonia, and, if required, to vessels for absorbing hydrogen sulphide, carbon dioxide and hydrocarbons. Finally, the apparatus is connected to an aspirating device for collecting the gas and for providing a constant vacuum on the retort tube. That illustrated of the Fuel Research Board's design may well be imitated. The gasholder E contains

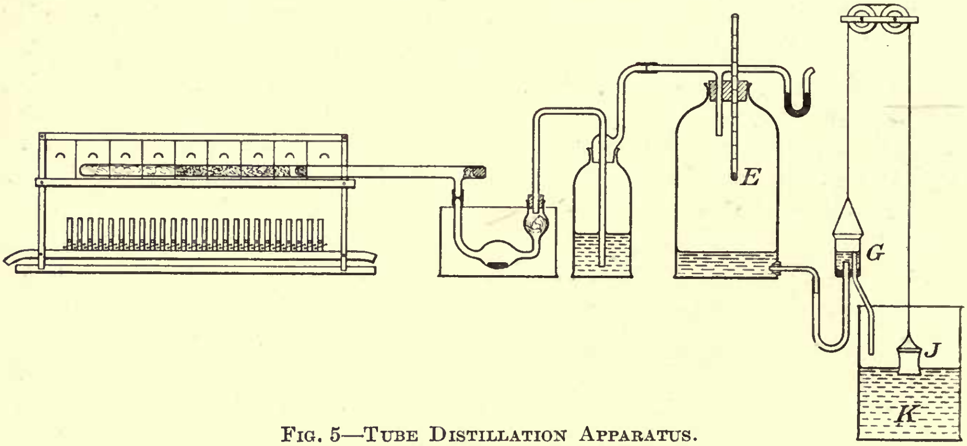


Fig. 5—Tube Distillation Apparatus.

either a mixture of glycerine and water or an almost saturated solution of magnesium chloride, or may simply contain acidified water. It is connected to a reservoir G by an india-rubber tube, which is suspended over a pulley and counterbalanced by the weight J floating in the tank K. The vessels E and K should have the same diameter, when, as the level in E falls, the level in K will rise to the same extent, thus providing a constant pressure in the gasholder.

The tube is so arranged in the furnace that while the front end is at a temperature of not less than 100° C., the cork and connections are not heated sufficiently to char. The whole of that part of the tube containing the coal is over the burners.

19*a*. *Distillation.* When the apparatus has been tested for gas tightness, the first five burners are lit under the silica brick till this part of the tube has been heated to about 900° C. A burner is then turned on, passing towards the coal, at the end of each 10 minutes till all the burners are on. When the distillation is finished the apparatus is disconnected at the tube and holder. A sample of the gas may be taken from the holder for analysis. Clean coal gas is then drawn through the absorption vessels till the test gas left in them has passed through the absorption train. The cotton-wool plug at the end of the tube is used to wipe out the tarry end of the tube and is added to the first absorption vessel. The tar may then be estimated by weighing the absorption vessel. The ammonia and other constituents absorbed in the remaining absorption vessels may be estimated by appropriate methods. (See **93***a*, **114***b*.)

Other Carbonisation Tests. The information obtained from the tests already described is not of much value in indicating the physical behaviour of the coal in the retorts. This aspect is most important and may be studied in several ways.

Rate of Carbonisation. The author has suggested that the rate of gas evolution may be taken as a criterion of the rate at which the coal may be carbonised. Such an indication is of the greatest service in warning those in charge of both vertical and horizontal retort plants what may be expected of a particular coal, and which of several coals it may be particularly advisable to mix.

19*b*. *Apparatus.* A furnace is used which may be built up of loose silica blocks cut or shaped to fit loosely in an iron casing. The aperture inside may be 8 inches diameter and the space between the brick and casing is filled with asbestos lagging. A hole in the side admits a Keith injector burner for heating, while the hole in the block forming the cover admits the distillation tube. In the centre of the furnace is placed a nickel-chrome steel pot 6 inches diameter. In this is placed a small supporting block on which rests a nickel-chrome-steel crucible 3½ inches high and 1 inch external diameter (Fig. 6). The walls may be ⅛ inch thick. This contains sufficient lead to make the total weight 600 grams. The distillation tube is of steel, 12 inches long, ½ inch diameter, with one end welded up. It is closed at the top end and connected to a bubbling bottle and gas meter. It should be sufficiently weighted or clamped to sink in molten lead.

19*c*. *Rate of Gas Evolution.* A volume of 50 c.c. of the coal previously passed through a 40-mesh screen and resting on a 60-mesh screen is placed in the tube which is connected to the bottle and meter. At a given moment, when the temperature as measured by a pyrometer inserted in the furnace just inside the crucible has been maintained constant for 10 minutes at 950° C., the gas burner is shut off and the pyrometer is removed. The distillation tube is then immediately thrust down into the molten lead and a stopwatch is started. The gas meter index is then read every half-minute for 10 minutes, by which time the gas evolution will have practically ceased. The results may then be plotted in form of a curve with the time horizontally and the gas yield vertically. Coals with a sharply rising curve and with a high maximum at the end of the 10 minutes can be recommended as easily carbonised. The experiment is repeated with at least one other grade of the coal, say that passing a 100-mesh screen.

20*a*. *Resistance of Coal during Carbonisation.* G. E. Foxwell has suggested a method which shows the properties of the plastic mass of coal undergoing carbonisation in a somewhat different way. While the method remains to be worked out in detail, it roughly consists of packing a quantity of the carefully graded coal in a silica tube to a length of, say, 6·5 cm., which is placed in a sand-bath of a gas-heated furnace. Gas from a reservoir is arranged to pass through the layer at the rate of 20 c.c. per minute per square cm. area of coal, and the gas pressure required to effect this is not further altered. The coal is then heated so that the temperature rises at the rate of 5° C. per minute. The pressure as read by a sensitive gauge placed at the inlet of the tube gradually rises and is read every two minutes. The flow of gas dies away as the coal passes through the plastic stage and recommences as coke is formed. The results of the readings of the resistance as measured by the back pressure may then be plotted against the temperature and the time. Those coals which give hard cokes (coking coals) give the highest resistance, while gas coals give less and non-coking coals still less. As a rule, the temperature at which the resistance is highest is lower for coals containing more volatile matter.

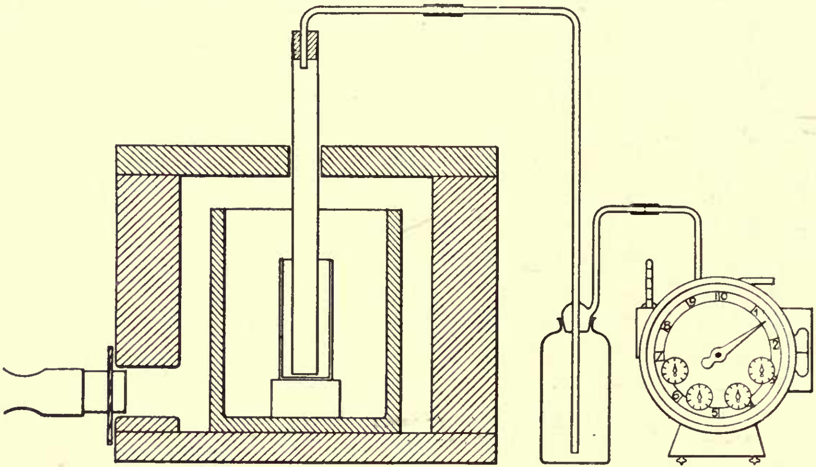


FIG. 6—APPARATUS FOR DETERMINING THE RATE OF GAS EVOLUTION.

21*a*. *Coking Test.* A coking test such as that advocated by R. Lessing gives information as to the relative amount of expansion or frothing which is likely to occur. One gram of coal is heated in a special silica tube in an electric furnace. Under this treatment the coal takes an expanded form, according to its type, and may be sufficiently voluminous to pass out of the heating zone. For this reason silica plungers of variable weight are placed on top of the coal before the test to compress the carbonising mass. The method may be used to determine the volatile matter by cooling and weighing the tube after the coking, and possibly the agglutinating value may also be determined with the apparatus.

Agglutinating Power. The modified Campredon method has been used with considerable success in evaluating the coking power of a coal. As a rule, the higher the coking power the more the trouble likely to be experienced in carbonising the coal as quickly as is desired in a gasworks, but, naturally, some coking power is necessary. Coal suitable for coke ovens has an index from 15–20 ; gas coals will fall below this. Probably the best way to utilise the results is to regard those coals as suitable which have both a high volatile matter and a high coking index.

21*b*. *Sinnatt's Modification.* Finely powdered electrode carbon, as suggested by J. T. Dunn, which passes a 60-mesh sieve and is retained on a 90-mesh sieve, is mixed in gradually increasing proportions with coal which has been ground to pass a 60-mesh sieve. One gram of the mixture is then coked, as in the determination of volatile matter. (See **14***c*.) The button of coke is removed from the crucible and upon it is placed a 100-gram weight. When the button just gives way under the pressure the agglutinating value is reckoned as the number of times the weight of inert matter admixed exceeds the weight of the coal. As noted by H. D. Smith it is important rigidly to exclude air. The crucible is therefore packed inside one of larger diameter, the space between being filled with charcoal.

Extraction with Solvents. In view of the importance that the amount of resinic matter extractable by solvents has been shown to have on the coking of coal, methods may be used to effect such an extraction. The extraction is carried out in a Soxhlet apparatus in a special atmosphere, and takes several days to effect the complete extraction of 5 to 10 grams of coal. Either pyridine or phenol may be used. As a rule the process will be too tedious and not sufficiently significant for ordinary use, but the reader may be referred to the methods described by W. A. Bone, and Parr and Hadley.

Oxygen. It is unfortunate that we possess no means of estimating what is perhaps the most important impurity in the coal substance. There is no doubt that the oxygen content of a coal affects its value very materially, and if a certain limit of oxidation is exceeded a coking coal becomes non-coking. The presence of oxygen in the coal substance is far more detrimental than it may be when inadvertently admitted during carbonisation, but the effect is much the same. Hydrogen is eliminated as water leaving the carbon : hydrogen ratio larger in the residue, while the tar has a high pitch content. The gas is readily evolved, but is rich in carbon dioxide and of low calorific value. The coke yield is higher and the binding power of the resinic materials is weakened. Oxygen present, whether absorbed or in a firmer state of combination, tends in the same direction, as it will most certainly appropriate hydrogen, which is required to keep carbon in a gaseous form.

While the oxygen can be estimated by an ultimate analysis by difference of the determined amounts of carbon, hydrogen, ash, sulphur, moisture, nitrogen, and occluded gases from 100, it is obvious that under any circumstances the result is of doubtful accuracy. Apart from the value of the oxygen figure an ultimate analysis involving the determination of the carbon and hydrogen is of little practical use. Although elaborate schemes of classification of coals have been founded on such analyses they are only capable of interpretation in a very general sense.

22*a*. *Apparatus*: *Ultimate Analysis.* A combustion tube, which may conveniently be of porcelain, 20 mm. in diameter and 80 cm. long, is filled as detailed below and arranged in a combustion furnace of at least twenty-five burners. There should then be a space of 2 or 3 inches of tube overlapping the burners at each end, so that rubber corks, used for connection to the absorption and purifying train, are not affected by the heated portion of the tube. First is introduced into the tube a spiral of copper gauze wound round a central copper wire about 10 cm. long and loosely fitting into the tube. A space is left for the porcelain or platinum boat on which the coal is placed. A short roll of copper gauze is next inserted to act as a "stopper" for granulated, freshly ignited copper oxide, which is filled in to occupy about 30 cm. length of the tube. Another gauze "stopper" is followed by about 15 cm. of granular lead chromate free from dust. Another "stopper" may be followed by a little silver asbestos or pumice obtained by soaking the material in silver nitrate solution and igniting, or room is left for the insertion of a spiral of copper gauze 10 cm. long, which before use is reduced by heating and dipping in a little alcohol in a basin and then drying off. This end of the tube is closed by a rubber cork through which is directly connected the first calcium chloride tube of the absorption train. The train consists of a calcium chloride tube filled with calcined chloride free from dust and previously saturated with carbon dioxide; two absorption vessels filled with conc. caustic potash solution, and finally a calcium chloride guard-tube for taking up moisture carried over from the potash vessels. All these vessels and tubes are such as can easily be weighed and are provided with rubber tubing and glass-rod stoppers, so that they may be closed up when not in use. They are weighed after standing over calcium chloride for an hour. The oxygen used, as well as the air, is purified by passage through caustic potash solution followed by conc. sulphuric acid. The connections are so arranged that either oxygen or air may be passed through the tube without altering the connections. The apparatus is connected up and proved for gas tightness. If preferred, a silica combustion tube may be used with platinised asbestos or platinised silica in place of copper oxide.

22*b*. *Ultimate Analysis.* A blank test is usually necessary, and in any case the tube is carefully heated and proved free from moisture and carbonaceous matter. Before introducing the coal the tube is heated to a dull red and then all but the central part is allowed to cool. Dry coal, say 0·30 gram, is introduced on the boat by removing the copper spiral, which is afterwards replaced. Connection is made to the air-oxygen supply. The freshly reduced copper spiral is introduced at the other end and connection made to the absorption train. A stream of oxygen is admitted at the rate of one to two bubbles per second. The copper oxide is heated up to a red heat and the chromate to a very much lower temperature. The copper spiral behind the boat is then heated, and gradually the heat is spread along to include the boat. As soon as the combustion is well under way the reduced copper spiral is heated. When the coal is burnt off, air is substituted for the oxygen to sweep the products forward and the tube allowed to cool. The absorption vessels are then disconnected, wiped with a chamois leather, and allowed to stand an hour over calcium chloride before weighing. The increase in weight of the first calcium chloride tube gives the weight of water equivalent to the hydrogen, while the increase in weight of the potash vessels and guard tube that of the carbon dioxide from the carbon.

Sulphur. The distribution of the sulphur between the products of carbonisation is naturally very important, but as it depends more on the conditions under which the coal is distilled rather than on the form in which the sulphur occurs in the coal it is difficult to produce any figures of great practical value. The distribution may be obtained under the conditions of the tube distillation by determining the total sulphur, the sulphur evolved as hydrogen sulphide and the sulphur remaining in the coke and coke ash. Similar figures may be obtained from the coal-testing plant. From a gasworks point of view it seems preferable to obtain as much as possible of the total sulphur evolved as hydrogen sulphide, since it may be conveniently removed in this form. A high sulphur content in the coke, particularly if it is largely volatile on combustion, is very detrimental, and chiefly for this reason coal with a high total sulphur, say over 2·5 per cent., is to be avoided.

23*a*. *Total Sulphur from Bomb Washings.* The calorific value is carried out in the usual way. (See **26***a*.) The bomb is previously washed out with water containing sodium carbonate and used wet. About 5 c.c. are added to the water equivalent to correct for this. The bomb is afterwards allowed to remain closed up for an extra 10 minutes, and the pressure is released gradually. The cover is unscrewed and the whole bomb washed out about ten times with small quantities of distilled water. A few drops of bromine water may be added and the solution is then strongly acidified with hydrochloric acid, boiled down to a syrup, placed on the water-bath and baked for an hour or so. The residue is taken up with a little acid, diluted with water and filtered. The residue is washed and the sulphur precipitated from the filtrate by addition of barium chloride to the boiling solution. The boiling is continued for 30 minutes, and after settling a short time is filtered hot through a low ash filter paper and washed till free from chloride. The wet filter and precipitate are removed from the funnel; the top of the paper folded over and the whole placed in a tared crucible. It is then slowly charred and burnt off. Finally, the crucible is maintained at a red heat for 10 minutes, cooled, and the residue weighed as barium sulphate.

$$S \rightarrow H_2SO_4 \rightarrow BaSO_4.$$

23*b*. *Sulphur by Eschka Method.* One gram of the dried sample is weighed into a platinum dish, together with 0·5 gram of anhydrous sodium carbonate, and 1 gram of calcined magnesia. This is intimately mixed with a spatula, levelled and covered with 0·5 gram of magnesia. The latter amount is increased if the dish is a large one. The dish is then placed on an asbestos plate with a small hole cut in the centre to nearly fit the dish, or it is put into a cold muffle, and cautiously heated till the volatile matter has been driven off. There should be no spurting or frothing. A full red heat is finally given for an hour or so, with occasional stirrings with a platinum wire sealed into the end of a glass rod. When finished there should be no sign of black carbonaceous matter. The contents are transferred to a beaker, a little bromine water is added and the basin washed out with dilute hydrochloric acid. The solution is acidified with hydrochloric acid, evaporated to dryness, baked for an hour or so at 100–105° C., taken up with water and acid, filtered and the sulphur precipitated as barium sulphate, as already described. (See 23*a*.)

Extraction of the sintered mass with water only, followed by filtration and precipitation, usually gives low results. On the other hand, the method described gives high results in presence of much iron unless the latter is removed before addition of barium chloride.

The reagents used invariably contain sulphur. A blank test is made for each new batch of sodium carbonate or magnesia brought into use, by weighing the amounts normally used of these reagents into a platinum dish and exactly repeating the methods given above, omitting only the coal. The amount of barium sulphate found is subtracted from the total weight found in subsequent determinations.

24*a*. *Method using Lime.* If desired, pure calcium oxide may be used in place of the sodium carbonate and magnesia, and in this case a porcelain dish may be substituted for the platinum. One half of the calcium oxide is slaked with water to form a dry powder and this is then ground with the remaining half. One gram of the powdered coal is mixed with 1 gram of the lime, moistened with 1 c.c. of water, rapidly dried, covered with a further weighed quantity of lime, cautiously heated to drive off the volatile matter, and finally burnt off in a muffle and then cooled and extracted with water. Bromine water is added, followed by hydrochloric acid. The whole is boiled, filtered, the residue washed and the filtrate raised to boiling-point, when barium chloride is added, and the same procedure followed as given above for the Eschka method.

Nitrogen. The larger the content of nitrogen the better. Most gas coals contain from 1·5 to 2·5 per cent. Like the sulphur, the proportion of the total nitrogen that will be volatile, and particularly the amount which will appear as ammonia, depends chiefly on the conditions under which the coal is carbonised. Although the distribution of the nitrogen may be obtained by estimating the total nitrogen and that evolved as ammonia in a distillation test together with that remaining in the coke, it is for this reason not of very practical importance. It seems, in fact, possible that with complete gasification and in presence of hydrogen and steam all the nitrogen may be obtained as ammonia.

24*b*. *Nitrogen by Modified Kjeldahl Method.* One gram (or 1·4 gram) of the dried coal that has passed a 60-mesh screen—or preferably that has been ground to a flour in an agate mortar—is weighed into a conical glass flask, or "Kjeldahl" flask, of about 300 c.c. capacity. About 30 c.c. of a mixture of fuming and ordinary conc. sulphuric acid (2:3) are added, with or without about 0·5 gram of metallic mercury. After standing on a hot plate for about 15 minutes, 10 grams of anhydrous potassium sulphate is added to raise the boiling-point. The heating is continued at a gentle simmer for an hour after the solution has become colourless. An inverted crucible lid is placed loosely over the top of the flask. Sometimes potassium permanganate is also added, but there seems to be no need to add to the number of reagents used. The solution is cooled, diluted, and washed into a distilling flask to make a bulk of about 250 c.c. Excess of caustic soda is added and then, if mercury has been used, sufficient sodium sulphide (about 20 c.c. of a 4 per cent. solution) to precipitate all the mercury as black sulphide. A few particles of zinc are added to prevent bumping, and the ammonia distilled off into 25 c.c. of N/10 sulphuric acid. A splash bulb is necessary at the head of the flask and the distillate is condensed in four-bulb Liebig condenser arranged vertically. The excess of acid is then found by titration with caustic soda in the cold, using methyl orange or methyl red as indicator. The reagents, including the distilled water, should be free from all but a trace of ammonia. A blank test is usually advisable, in which pure cane sugar is substituted for the coal used. The ammonia equivalent of the acid neutralised by the distillate is calculated, and from this the nitrogen.

$$N_2 \rightarrow 2\,NH_3\,;\;2\,NH_3 + H_2SO_4 = (NH_4)_2SO_4$$

The various modifications of the Kjeldahl method have been considered accurate for many years and the method has received the support of several investigators, but recently Simmersbach, Sommer and Ernst Terres consider that the results are far too low and that a modified Dumas (combustion method) should be used.

This is also the opinion of the Gas Investigation Committee of the Institution of Gas Engineers, who recommend the following modification of the Dumas method.

25*a*. *Dumas Method.* Carbon dioxide generated from previously boiled marble chips and a 40 per cent. solution of hydrochloric acid is washed with sodium carbonate solution and passed into a combustion tube containing (*a*) a platinum boat holding 15 grams of potassium chlorate, (*b*) 3 cm. length of freshly ignited copper oxide, (*c*) 10 cm. of an intimate mixture of freshly ignited copper oxide powder and 1 gram of the coal sample, (*d*) 30 cm. of freshly ignited copper oxide and a roll of 15 cm. of reduced copper gauze. The chlorate end of the tube is heated in the last stages of the combustion and the oxygen generated completes the oxidation. The products of combustion swept out by the carbon dioxide are collected over potash solution. Any free oxygen and carbon monoxide are finally removed in an Orsat, or other gas analysis apparatus, and the residual nitrogen is measured volumetrically, at known temperature and pressure, and calculated to a percentage by weight on the coal substance. This method gives results 0·5 per cent. higher than obtained by the Kjeldahl method, and it is obviously imperative that the method used should always be stated in reporting results.

Calorific Value. The calorific value of a coal is not any indication of its suitability for gas making, except in so far as it provides an indication of the calorific value of the coke. The latter is usually some 6 to 8 per cent. lower than that of the coal. The volatile matter of the coal possesses a smaller heat of combustion than the coke for equal weights, hence coals rich in volatile matter are not those with the highest calorific value. If the calorific value of the coal, coke and gas from a coal test be determined the calorific value of the tar may be obtained by difference. Usually it is sufficient to obtain the calorific value of the coke, estimating the sulphur at the same time.

In the comparison of different coals it is convenient to reduce the calorific value of each to an ash and moisture free basis. The calorific value so obtained gives a relative value for the coal substance. Partially oxidised or badly weathered coals give low values. A similar procedure in the case of the volatile matter is, however, hardly justified, as an increase in ash content for the same or similar coal does not always correspond with an equivalent decrease in the volatile matter. The calorific value of a good gas coal is usually about 13,500 B.Th.U. per lb.

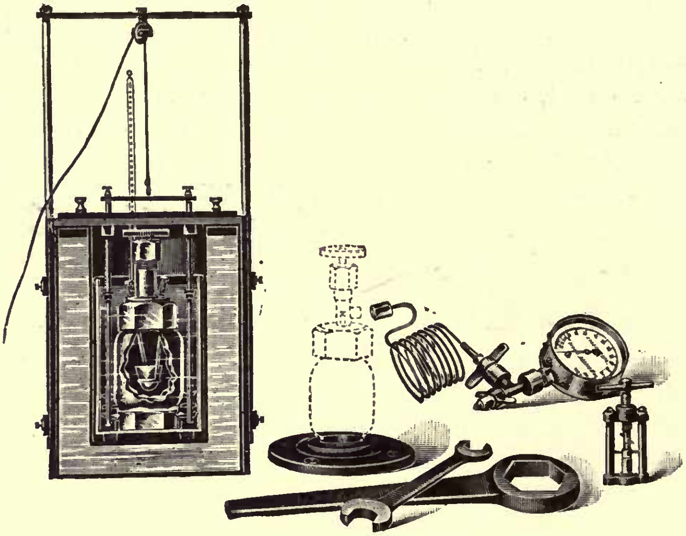


FIG. 7—MAHLER-COOK BOMB CALORIMETER.

26*a*. *Bomb Calorimeter.* The use of forms of calorimeter which do not embody a bomb cannot be recommended. Several excellent types of bomb calorimeters are on the market, and with careful treatment will last many years of constant use. One of the Mahler-Cook type (Fig. 7) has been used by the author for some ten years, and save for a few small spots on the lining, and the loss of the nickel-plating, it is as serviceable as ever. It is hardly necessary to describe the apparatus and method of use, since very excellent instructions are sent out by the makers with the instruments. One or two details of operation, however, may be of service. The jointing of the bomb cover and bomb is made with a soft lead wire wrapped round in a shallow groove. This needs re-packing occasionally and makes an absolutely tight joint under a pressure of 25 atmospheres. It is unnecessary to use a platinum crucible; a silica crucible may be substituted. Fine iron wire may then be used for firing. The bottom of the crucible may be protected by a little calcined magnesia. The iron wire is weighed and that left, if any, is also weighed and deducted. The weight used multiplied by the calorific value (1600 cal.) is deducted from the gross calorific value obtained (in cal.). It is particularly necessary that the combustion should be so rapid as to virtually amount to an explosion. For this reason the firing is best made off the electricity power supply, using a water voltameter to protect the service wiring. The iron wire is connected between the terminals and looped so as to be in actual contact with the coal. The latter is dried, screened through a 60-mesh screen and made into pellets. A loose powder, or even a liquid, may not completely burn unless it is surrounded with oxygen. The pressure of oxygen used is usually between 20 and 25 atmospheres, but may be somewhat lower in many cases. The amount of water used in the calorimeter is sufficient to cover the bomb to the top, but not to reach to the terminals, which are kept dry. The total, including the water equivalent of the calorimeter, may amount to 2500 grams. The water is best weighed directly in the copper vessel. The stirring may be made by hand with a string passing over the pulleys, but must be done at a regular rate. Readings for 10 minutes before the bomb is fired, and for 10 minutes after the temperature has reached a maximum, is sufficient for the radiation corrections. Although the radiation correction is reduced by starting with the water a few degrees below atmospheric temperature, it is not so constant as it is when a start is made with water at the atmospheric temperature. The correction is based on the fact that the cooling is proportional to the difference of temperature between the inside and outside of the calorimeter. The correction in the form of an addition to be made to the observed thermometer readings can be obtained from a formula such as the following:

$$(n-1)\,a+\frac{a+b}{2}$$

where a is the average difference in temperature readings per minute after the rise, and b that before the rise, n is the number of minutes during which the temperature rises. The value b may be positive or negative. (*Metro.*) Or the temperature change during the period before the start, and also during the period after the maximum observed reading has been obtained, may be plotted against the respective temperatures. A straight line drawn between the two points will give a curve showing the radiation loss at each temperature. This can be added to each observed thermometer reading and will give the corrected temperature. The maximum temperature will then be the mean of the corrected temperature of the final period, which should be practically constant. The difference in temperature between this value and that at the moment before firing, multiplied by the total water equivalent of calorimeter and contents, gives the gross heat effect for the coal taken. Deductions may be made for the iron wire used and for the acids formed. Nitrogen does not in the ordinary way burn to nitric acid, but is completely oxidised in the bomb, and it is usually considered, perhaps erroneously, that while the sulphur only burns to sulphur dioxide in the air, in the bomb the oxidation is complete, and therefore an allowance is made by deducting a proportionate number of calories from the gross value obtained. The bomb washings are boiled to expel carbon dioxide, and titrated with N/10 barium hydroxide solution, using phenolphthalein as indicator. The barium sulphate precipitated is removed by filtration, and the filtrate containing barium nitrate is treated with N/10 sodium carbonate solution in excess. Barium carbonate is precipitated and removed, and the excess of sodium carbonate in the filtrate is determined by titration with N/10 hydrochloric acid using, methyl orange as indicator. (*Metro.*) 1 c.c. of N/10 nitric acid is equivalent to 1·43 calories, and 1 c.c. of N/10 sulphuric acid to 3·57 calories.

When it is also required to estimate the sulphur in the coal it will be preferred to titrate the bomb washings with N/10 caustic soda to obtain the total acids, and then to precipitate the sulphate as barium sulphate in the usual way. The nitric acid is obtained by difference. The weight of sulphuric acid, multiplied by 725, will give the extra amount of heat liberated by the complete instead of partial combustion of the sulphur, while the nitric acid found, multiplied by 227, will give the heat liberated by the oxidation of the nitrogen. These deductions having been made the remaining calories can be calculated to one gram of coal. The factor for conversion to B.Th.U. per lb. is 1·8.

It is necessary to obtain an accurate water equivalent and to re-determine this occasionally. It can best be made by determining the calorific value of a substance of known calorific value just as in the case of one of unknown value, and calculating back the calories absorbed by the apparatus. Pure naphthalene (calorific value= 9,668 cal. per gram) is very convenient and an additional check is to use benzoic acid (calorific value=6330 cal. per gram). Both are made into pellets and used in the same manner as for coal.

Ash. Great attention has been recently focussed both on the content of ash and its composition. The lower the amount of ash the less the weight of material to be handled and the more valuable is the coke. The possible catalytic effect of the ash has yet to be demonstrated. The composition of the ash is of more importance as regards the coke, and is dealt with later.

28*a*. *Estimation of Ash.* One gram (or the residue from the determination of volatile matter) is accurately weighed out into a tared crucible of wide shape and is covered with a lid. The whole is heated gradually over a Bunsen until the volatile matter has been expelled. The lid is then removed and the coke is gradually burnt off, raising the temperature gradually. From time to time it is stirred gently with a platinum wire sealed into the end of a glass rod. When the ash is quite free from black specks the crucible is cooled in a desiccator and weighed. The final burning off is conveniently made in a muffle furnace, but it is a mistake to use too high a temperature in an endeavour to quicken the combustion.

The method of burning off in a tube in presence of oxygen cannot be recommended for coal, but an atmosphere richer in oxygen than the air may be used in a muffle by admitting oxygen at the back and nearly closing the front, or a current of air may be slowly drawn through the muffle to hasten the oxidation.

Intrinsic Ash. It is often useful to select a piece of coal as pure as can be found and to determine the ash. This may be compared with the average ash and provides an indication of the extent to which the coal has been "cleaned." An intrinsic ash of over 6 per cent. is hardly likely to provide an average ash of reasonable dimensions.

This may also be applied to coals in respect of sulphur.

29*a*. *Chlorine*. In view of the corrosive properties of chlorine and its compounds in the retort and the trouble which may arise from stoppages due to ammonium chloride in foul mains, etc., the chlorine in the coal may usefully be estimated. The total chlorine may be found by burning the coal in a platinum dish with lime, as in the method for sulphur. (See **24***a*.) The sintered mass is digested with water, filtered, the residue washed with hot water till free from chloride. The filtrate is acidified with nitric acid, and a measured quantity of N/10 silver nitrate solution is added in excess. The silver chloride is filtered off, washed with warm water, and the excess of silver nitrate in the filtrate is determined by titration with thiocyanate, using 1 or 2 c.c. of a solution of ferric alum as indicator.

$$NaCl+AgNO_3=AgCl+NaNO_3$$
$$AgNO_3+NH_4CNS=AgCNS+NH_4NO_3$$

Arsenic and Phosphorus. The only importance of these impurities in the coal is due to their presence in the coke, and they are dealt with under that heading.

29*b*. *Coal Valuation*. It has already been said that the determination of any single property of coal will not fix its value for gas-making purposes. The valuation of coal consists, therefore, in summarising the information acquired by many, at least, of the foregoing methods of examination. The total value of the products which may be obtained can only be made a figure of comparison if the cost of producing these can also be appraised. A coal rich in gas-making constituents is of little use unless the gas can be obtained from it within certain limits of time.

The matter is a very difficult one. If all the factors are taken into consideration their relative importance is liable to be confused. Probably the best method is to lay down a specification of a standard coal similar in most respects to that of a coal which is known to be fairly constant in its properties and which has given good all-round results in practice. A warning here might be given of the erroneous impressions often obtained in practice owing to retort house conditions lagging behind in their response to the introduction of a fresh coal. Often it happens that excellent results are obtained from a coal owing to the fact that the heat of the settings is being maintained by the coke from another coal previously carbonised. By the time the new coke finds its way to the producers and reacts unfavourably, another coal has been charged and receives heat treatment below the average.

The properties of a standard coal being known they have to be translated into figures so that they may be rendered additive and so expressed in a single phrase. It will be found necessary in many cases to multiply or divide the analytical figures so as to bring the various properties into their relative importance. For example, the ash of a standard coal may be fixed at 6 per cent. Another coal contains on an average 10 per cent. It is obvious that the latter is inferior in commercial value to the former by more than 4 per cent. Twice this amount is, perhaps, not a sufficient expression of the inferiority.

The system of valuation must largely depend on local circumstances, but the tentative suggestion is made that the yield of therms per ton in gaseous form of not less than the declared calorific value should be taken as a basis. To this figure is added or subtracted "corrections" for other characteristics, in particular for the relative rate at which it may be carbonised. It must be realised, of course, that *figures arrived at in this way represent nothing more than a considered opinion.* The following is an example of one method of valuation. In the first place, certain minimum requirements are stipulated, and any coal is rejected which comes below these requirements. No coal would be acceptable if it gave less than 30 per cent. of volatile matter, contained more than 8 per cent. of ash or more than 2·5 per cent. of sulphur. The coals meeting these requirements are valued in a relative manner on the results of examination. A standard coal, giving under known conditions 70 therms per ton, with a gas yield in unit time expressed as a figure of 50, and yielding a coke of hardness expressed by a figure of 30, has an ash content of 6 per cent. The valuation consists in obtaining similar relative values for test coals, and summating the figures as follows:

(Therms per ton) + (Time factor−50) + (Coke hardness) + 2 (6−Ash).
The standard coal gives: $(70) + (50-50) + (30) + 2(0) = 100$.

Examples.

Coal	A	B	C
Therms per ton	72	65	68
Time factor	48	55	35
Coke hardness	25	15	30
Ash	7	8	6
Valuation figure	93	81	83

REFERENCES

STOPES and WHEELER. Monograph on Constitution of Coal (with bibliography). 1918.
WALCOT GIBSON. Coal in Great Britain. 1920. (Geological distribution.)
W. A. BONE. Coal and its Scientific Uses. 1918.
S. R. ILLINGWORTH. Theory of Coking. *J.S.C.I.*, 1920, 111 T, 133 T.
U.S.A. GEOL. SURVEY. Report on Coal-Testing Plant. *Bull.*, 323. 1906. (Methods of Sampling and Analysis.)
J. S. S. BRAME. *Fuel*, 1917. (Methods of Analysis.)
F. S. SINNATT. Notes on Coal Analysis. *Bull.*, 4. (Lancashire and Cheshire Coal Owners Res. Assoc.)
T. GRAY and J. C. KING. Assay of Coal for Carbonisation Purposes. *Fuel Research Board Tech. Paper I.* 1921. (Tube distillation.)
G. WEYMAN. Rate of Carbonisation. *J.S.C.I.*, 1921, 300 T., and *Gas World*, 1922, **76**, 565.

G. E. Foxwell. Resistance of Carbonising Mass and Travel of Gas. *J.S.C.I.*, 1921, 193 T.

R. Lessing. Apparatus and Results of Coking Test. *Gas World*, 1912, **56**, 842; *J.S.C.I.*, 1912, 465.

F. S. Sinnatt. Agglutinating Power. *J.S.C.I.*, 1920, 83 T.

D. White. Effect of Oxygen in Coal. U.S.A. Geol. Survey, *Gas Journal*, 1909, **108**, 618.

P. P. Bedson. Extraction of Coal with Pyridine. N.E. Inst. Min., Eng., 1899. *J.S.C.I.*, 1908, 147.

Parr and Hadley. Extraction of Coal with Solvents. Illinois Univer. Exp. Station, *Bull.*, 76. *Gas Journal*, 1915, **129**, 260.

Burgess and Wheeler. Extraction of Coal with Solvents. *J. Chem. Soc.*, 1911, **99**, 649.

W. F. K. Stock. Sulphur and Lime Method. *J.S.C.I.*, 1897, 305.

O. Simmersbach and F. Sommer. Nitrogen determination. *J.S.C.I.*, 1916, 102; *Stahl v. Eisen*, 1905, **35**, 601.

E. Terres and Colleagues. Nitrogen determination. *J.S.C.I.*, 1919, 399A; *J. Gasbeleucht*, 1919, **52**, 173; 192.

Gas Investigation Comm. Inst. Gas Eng. Fourth Report (Nitrogen by Dumas method). *Trans. Inst. Gas Eng.*, 1920, 311.

Coste and Andrews. Fuel: Gaseous, Liquid and Solid. 1914. (Correction for Calorimeter determinations.)

CHAPTER III

CARBONISATION

Mixing Coal. In very few works will it be possible to obtain sufficient of one kind of coal to last for more than a few days. Usually it is necessary to tip several kinds of coal in the course of twenty-four hours. Not only the chemical, but also the physical character of the coal used may change in the course of a few hours, and unless some careful mixing of the coal is made it will be impossible to maintain economical conditions. Screened coal (nuts) may be tipped one hour followed by a small dusty kind the next, and those engaged in charging the retorts will find themselves faced with great difficulty in maintaining regular charges of the desired size. It has been recently pointed out that heavy coking coals which give considerable trouble when small in size can be dealt with more easily when in the form of nuts. Previous knowledge of the coal is essential for proper mixing and grading, and it is preferable that time should be given for an examination of coal before it enters the retort house. Unfortunately very few works are provided with facilities for doing this. As a rule the coal store is isolated, and once coals are put into stock they are not used until some emergency arises. It is preferable to work all coal through the store, which may be divided into compartments. This admits of the possibility of obtaining a regulated mixture even from coals varying widely in character.

Experimentally, it appears that a mixture of coal of even size will give no better average result than the average of the components, but the advantage of dealing with a raw material of unvarying composition in practice is enormous.

By mixing, properties such as excessive " swelling " may be neutralised by a coal which forms a poor coke. Dusty coals may be mixed with screened coals ; coals of a type approaching steam coals will give excellent results when mixed with those approaching coking coals in type. Wet coals may be made workable by mixing with dry coals ; coals with high ash can be distributed among coals with low ash. In fact, probably there is no better direction in which the chemist can help in promoting economy than by attention to the mixing of the coal.

Control of Carbonisation. The control of carbonisation consists in the appreciation of a number of factors each of which contribute in its own way to the general result. Unfortunately the general result cannot be expressed in a single figure. The chief objects aimed at may be thermal output of gas per ton and per retort per day, but these are limited by the necessity of keeping other factors within certain limits. For example, the quality of the gas is more or less fixed at a certain minimum quality ; the coke must not be unduly depreciated ; high yields of ammonia and tar are desired; while undue formation of scurf, naphthalene and other sources of annoyance are to be avoided.

Methods by which these factors may be observed and appreciated are given below with particular reference to the working of horizontal retort plants, but the results are to be considered jointly and not independently.

Very much the same methods apply to vertical retort plants. A few essential differences will be pointed out later.

The Time Factor. The time taken to carbonise the average mixture of coal is checked in the first place by a determination of the volatile matter left in the coke. (See **47***d.*)

Examination of the coke from individual retorts and a selection of samples from portions which have obviously been on the outside and inside of the charge will give an indication as to whether the thickness of the charge is greater than is warranted by the temperature of the heating flues. Residual volatile matter in excess of, say, 5 per cent. will raise doubt as to whether the coal is being completely carbonised. In such circumstances the heats may be raised or the time given to carbonise may be increased. The latter alternative is not a convenient one, and the former may not be possible. The weight of the charge may be altered, and this will have the effect of altering the conditions under which the primary products are "cracked," which may be undesirable.

It is a curious fact that the maximum output of gas per retort per day corresponds closely to the maximum output per ton of coal carbonised, the temperature being constant. The maximum thermal output of gas per day and per ton correspond also so long as the secondary decompositions are held within limits.

If the charges are very much overspent a low output per day is accompanied by a low volatile matter in the coke. This may be counteracted by increasing the weight of charge. Analysis of the gas during the last stages of carbonisation will show by excessive amounts of hydrogen or inerts if the charge is spent before the time comes to discharge it.

It is naturally most important that the amount of coal dealt with per day should be known, and some expense to attain this is fully warranted by the smaller wastage that will follow.

The Yield Factor. The cost of the raw material—coal—forms such a large proportion of the total cost of manufacture, that it is essential to obtain the maximum output of suitable products per ton. Just as the maximum output per day corresponds very largely to the maximum output per ton, so the maximum output of therms per ton varies as the freedom of the retort-house gas from nitrogen. The reason for this appears to be in part due to the fact that oxygen will preferentially combine with hydrogen forming a condensible product—water; and partly owing to the fact that, wherever a leak occurs which admits air or furnace gases, loss of coal gas takes place owing to its superior diffusive power, in particular as regards its hydrogen content. The loss more than counterbalances the gain of volume due to the nitrogen gaining admittance, while from both the causes given there is a loss of therms and no gain. Over-pulling as a means of either increasing the volume or thermal output cannot be admitted, even though the quality of gas would otherwise be above that required. With retorts in bad repair analyses of the gas will show abnormally low hydrogen content. The carbon dioxide may be very little higher than usual, but will tend to increase with bad mouthpieces. Only in very abnormal cases, as for example when the seals are broken under a heavy vacuum, will the carbon dioxide and carbon monoxide show a heavy increase. Oxygen is very rarely found in retort-house gas above 1 per cent., although it may from the analysis be obvious that far more than the corresponding amount of air has been drawn in. Oxygen is absorbed by tar at comparatively low temperatures, and gradually diminishes in quantity as the gas passes to the scrubbers.

The extent to which the tar and hydrocarbon vapours are " cracked " by contact with hot surfaces and radiant heat exerts an important influence on the volume output per ton, as well as per day. The effect is seen by an increase in the hydrogen content of the gas to 50 per cent. or more and reduction of hydrocarbon vapours. If the " cracking " is confined to the breaking up of paraffin bodies which would otherwise condense as tar oil, the thermal output in the gaseous form may also be increased, but when the olefine bodies and methane are appreciably reduced it is doubtful if any gain in thermal output results. Scurf is formed and a considerable amount of carbon, which otherwise would appear in the gaseous form, is left as a residue in the retort. Increasing the output by this means is in any case limited by reduction of the gas below the standard of quality ; by the decrease in the recovery of ammonia and by the appearance of undesirable impurities, such as cyanogen and naphthalene.

The formation of scurf is to be closely watched from this point of view, as well as its possible interference with the discharging of the coke. The analysis is made as in the case of coke, and for true scurf will indicate 95 per cent. of fixed carbon.

Besides the indications of the extent to which the " cracking " process is being carried, furnished by gas analysis, periodical determinations of naphthalene in the gas and examination of the tar for naphthalene, benzol, and paraffin are made and provide valuable information as to the conditions obtaining in the retorts.

Retort House Stoppages—Ascension Pipes. As a rule deposits formed in ascension pipes are caused by the partial oxidation of tar constituents. Air drawn in through the mouthpiece is absorbed by the tarry vapours, hydrogen is eliminated and pitch is thrown down. The pitch may, if a large amount of air is admitted, be coked and then forms a deposit similar to scurf. The pitch in any case contains a large amount of " free " carbon. Sometimes coal and coke dust may be detected in the deposit, but dust is very seldom a prime cause of the blockage. Naturally, as the charge becomes carbonised and the gas passing through the pipe is smaller in quantity, the pipe tends to become hotter through conduction as well as owing to the gas coming from the retort higher in temperature. Leakages are accentuated and the deposit has every chance of hardening. For these reasons, if the coal is carbonised before its proper time, stoppages are more frequent.

Analysis of the deposit, coupled with temperature and pressure readings at the ascension pipes and analyses of the gas, will indicate how a remedy can be most easily applied.

Stoppages in Mains. Deposits of thick pitchy tar in mains are usually due to an extension of ascension pipe trouble—sometimes to the deposition of solid ammonium chloride and sometimes to both causes. A deposit of pitch free from oxidation products is rare, if it ever occurs. Circulation of tar or liquor will relieve such trouble to the detriment of the liquid used. It is better to find and remove the cause. Insertion of thermometers or pyrometers at different positions along the main, and analysis of the deposit will provide an indication of the cause and remedy. The temperature gradient in the neighbourhood of the boiling-point of water and vaporisation of ammonium chloride should be made as rapid as possible.

Vertical Retort Plants. The control of continuous vertical plants is very much simplified by the provision of easy means of regulating the time factor. Because they are more delicate in operation the results obtained are more dependent on the skill employed in regulation. The extent to which the coke has been carbonised is more or less visible and is the first criterion for regulation of the extractor. The hourly readings of the volume of gas and a record of its calorific value enable a balance to be easily struck between the rate and yield of gas, or therms, per ton of coal carbonised.

The penetration of heat into the charge appears to be considerably more rapid than in the case of horizontal retorts. The movement of the charge tends to break up the plastic zone and allows convection currents of hot gases to carry heat inwards. In spite of the appearance of paraffin hydrocarbons akin to those produced in low temperature work, and a less proportion of benzene and naphthalene, the hydrogen content is rarely less than 50 per cent. and often as high as 60 per cent. Carbon monoxide is as a rule 2 or 3 per cent. higher than in horizontal retort gas—no doubt owing to steam admitted at the bottom castings of the retort to keep the metal cool and prevent explosion when the discharging doors are open. Steaming proper increases the amount of carbon monoxide, but should not be allowed to cause more than a slight increase in the content of carbon dioxide.

The third chief factor—the extent to which the primary products are decomposed—can also be regulated with fair exactitude by alteration of the level of heat between the top and bottom of the retort. The formation of scurf is of greater importance, as it prevents the even movement of the charge downwards.

The most disturbing factor, and therefore the most important, is the effect of variation in the coal supply. The fact that the makes of gas will drop off by 25 per cent. or more coincidently with the introduction of a different class of coal is sufficient reason for very careful consideration being given to the selection and mixing of the coal.

The control is exercised in a similar manner to that of horizontal retorts. Analysis of coke, gas, and tar provide essential information. Temperature readings of the gas in retort mains and off-take pipes will rise quickly in response to oxidation or a hanging charge.

Steaming can be controlled with some certainty by constant determination of the carbon dioxide in the gas by means of recording instruments. A rise above, say, 3 per cent. indicates that the temperature conditions, necessary both for the decomposition of the steam and for the carbonisation of the coal, are not being maintained. This indication will be seen before a fall of temperature can actually be observed in the heating flues, and suggests the immediate advisability of reducing the steam admitted. Once the reserve of heat has been exhausted, as shown by a fall in temperature of the heating flues, it is very difficult to restore it for some space of time.

Analyses of Various Gases

Selected for Purposes of Illustration

No.	CO_2	O_2	C_nH_m	CO	CH_4	H_2	N_2
A	2·4	0·0	2·4	5·6	34·8	51·9	2·9
B	2·6	0·2	1·8	6·8	23·5	56·3	8·8
C	7·0	0·4	0·6	9·8	9·9	33·4	38·9
D	1·0	0·2	1·8	6·4	32·2	50·1	8·3
E	1·8	0·1	2·2	7·5	28·8	52·6	7·0
F	2·0	0·0	1·0	7·6	21·3	61·0	7·1
G	3·0	0·0	1·4	11·4	24·5	52·3	7·4
H	8·7	0·0	—	25·5	1·7	3·6	60·5
I	4·6	0·2	—	25·9	0·9	12·8	55·6
J	8·5	0·5	—	17·1	1·6	18·4	53·9
K	4·4	0·0	—	39·8	1·1	48·9	5·8
L	3·9	0·1	6·6	35·5	8·3	42·2	3·4

A—Typical horizontal retort gas, 2½ hours after the last charge; 12-hour charges. B—The same, 7 hours after charging. C—Sampled at one end of a single retort mouthpiece in bad condition, dip-pipes unsealed. D—Sampled at the same time at the other end, dip-pipes sealed. E—Typical continuous vertical retort gas, without extra steaming, moderate heats. F—The same with high heats. G—Continous vertical retort gas with moderate steaming. H—Dry semi-direct producer gas. I—Duff producer gas. J—Mond producer gas (without ammonia recovery). K—Blue water gas. L—Carburetted water gas (about 2¼ gallons of oil per 1,000 cubic feet).

Sampling. Retort-house gas is necessarily drawn off against a vacuum, and precautions are taken not only to eliminate all chances of contamination of the sample by air, but also that the sample is a representative one. Snap samples are required for the purpose of finding the conditions at a particular time in a more or less restricted zone. Average samples are also needed for the purpose of checking the conditions over a more extended period, and as a means of determining the ultimate average composition. The latter do not indicate abnormal occurrences during the period of sampling, and to obtain records of such, an infinite number of snap samples are required. In such cases hand sampling and analysis are replaced by recording instruments.

36*a*. *Sampling Connection.* In all cases the sampling connection between the sample tube or apparatus for analysis is made as short as possible. This necessitates very often working in the most inconvenient surroundings, and the exercise of some ingenuity. The tube into the gas main or gas stream is of sufficient length to penetrate about one-third of the diameter and terminates at right angles to the gas stream. A convenient arrangement is shown in Fig. 8. It consists of a solid 2-inch plug with a $\frac{3}{8}$-inch piece of tube screwed into each side; the plug being bored right through. This may then be inserted in the gas main in place of a 2-inch plug. If left in place it is provided with a socket and plug to close it up when not in use. The outlet tube is provided with a T-piece, to one limb of which is connected the gas sample tube filled with liquid, the other end of the T-piece being connected to an aspirator.

37*a*. *Snap Samples.* In taking snap samples the aspirator is set in operation, and after an interval the cocks of the sample tube may be opened and a portion of the gas stream drawn into it. Care must be taken not to let the liquid run out of the sample tube below the level corresponding to suction of the gas main. To avoid this possibility the lower end of the sample tube may be connected by rubber tubing to a levelling-bottle containing water. When the sample is to be kept for any length of time the sample tube is made in pipette form without taps, and is provided with rubber tubing and clips at each end so that the tube may be removed when the sample is taken and sealed up over a flame at constrictions previously made near each end.

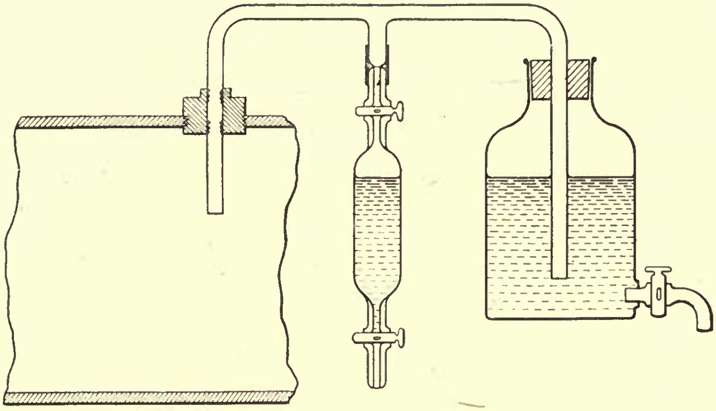


Fig. 8.—Gas Sampling Connection.

It is imperative that all conditions operating at the time of taking snap samples are noted—such as the vacuum, time in hours after retorts are last charged, and so on.

If the temperature of the gas is much above 300° C. the sampling tube may be jacketed with a loose tube and the interspace filled with insulating packing. It is slightly inclined towards the sample tube. A better plan is to run a smaller diameter tube of silica through the iron tube described, which then forms a protecting tube.

In most cases it is sufficiently accurate to use as the confining liquid water rendered acid with sulphuric acid and coloured with methyl orange.

37*b*. *Average samples.* Various methods are used for obtaining average samples. The gas may be purified in the usual way and sampled on the pressure side of the exhauster in the manner described with purified gas. Or the gas may be passed through a miniature purifying train to recording instruments. This method, while it may give an earlier indication of the quality of the finished gas, is subject to considerable "lag" owing to the time taken in passing from the retort house to the exhauster and in passing through the purifying train. Variations are also to a considerable extent reduced by the mixing of the gas on the way. Often gas from one retort house is mixed with gas from another, or with water gas.

38*a*. *Miniature Exhauster.* In some cases small exhausters have been introduced to pull a small stream of gas away from the main stream and pass it through a small purifying train to sampling holders and recording instruments. While samples may by this method be taken from the retort house, there is still a lag on the results due to the time taken for the comparatively small stream to pass through the connections. It is advisable to place the exhauster as close up to the origin of the sample stream as possible, to avoid chance of air being drawn in, and to enclose the machine in an oil bath. The chief trouble, however, is in respect to condensation in the pipe system, which is difficult to control and which may substantially affect the results.

38*b*. *Glass or Metal Aspirating Systems.* A large number of different forms of aspirators have been designed to take average samples in the retort houses, whence the containing vessel is removed to the laboratory for examination of the sample. Large metal tanks are difficult to move and handle, and do not seem to give any more accurate results than samples taken in comparatively small glass vessels. Whatever the arrangement adopted it must be capable of drawing the gas in at a constant rate over a period of, say, 12 hours; it must allow of the sample being withdrawn easily; it must be gas-tight and automatically shut off when the full sample has been taken. To obtain a constant rate of inflow the apparatus must be free from all constrictions and regulating cocks on the gas side, or it will surely be unreliable owing to deposits of tarry matters from the gas.

An apparatus which has given very satisfactory results is illustrated (Fig. 9). It consists of two glass vessels of approximately the same size, *A* and *B*, arranged at different levels. A syphon is arranged from *A* to *B* through a small seal tube *S*, which will prevent the contents of *B* getting back to *A* in the event of all the water running from *A* to *B*. The bottle *A* is filled at the start with a suitable liquid, and

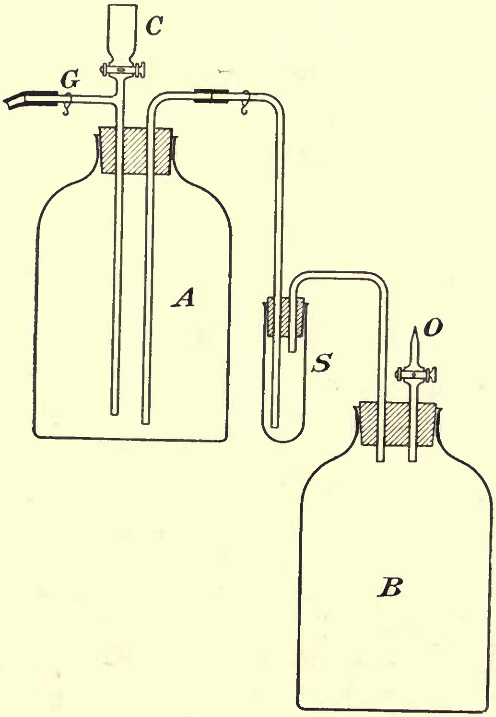


FIG. 9.—APPARATUS FOR TAKING AVERAGE SAMPLES UNDER VACUUM.

the syphon established by admitting liquid from the cup *C*. The connecting tube *G* to the source of the gas sample is filled at the same time, and the air in *B* is put under pressure. As water is then allowed to flow to *B* gas is drawn into *A*. There is a constant pull on *G* owing to *A* functioning as a " Marriott's bottle." The rate of inflow is regulated by the escape of air from the bottle *B* by the size of the orifice *O*. As the pressure is constant throughout the system the rate of efflux is constant. It will be seen that there are no constrictions except on the air escaping from *B*, which is clean and free from dust. By closing cocks or clips the bottle *A* may be disconnected and removed to the laboratory. It is first put under pressure by admitting liquid from *C*. For the collection of a fresh sample it is simply necessary to interchange the vessels *A* and *B*.

39*a*. *Orsat Apparatus*. When only partial analysis is required an Orsat apparatus may be directly connected to the sampling tube. For the estimation of carbon dioxide, oxygen, unsaturated hydrocarbons and carbon monoxide, a five-pipette apparatus is needed, as two pipettes are necessary for the proper extraction of carbon monoxide. Sometimes a Hempel or other form of explosion bulb is added to complete the analysis. This addition largely nullifies the one advantage of the apparatus—its portability. The use of the Orsat apparatus is described under the analysis of producer and waste gas, for which purpose it is better fitted.

39*b*. *Hempel*. In spite of many varying forms of apparatus which have been designed there is still no more suitable apparatus for crude gas analysis than that of Hempel. The ease with which broken parts can be replaced and the very general use which it can be put to renders it very serviceable. The results are sufficiently accurate for almost all technical work, and great rapidity can be acquired with practice. The disadvantages of the long levelling tube and unstable wooden base are overcome by the variation shown in Fig. 10. The burette is mounted on a board firmly fixed to an iron retort stand. The levelling tube is mounted beside it and connected by a T-piece which also leads to a small levelling bottle. Between the burette and levelling tube is placed a milk glass scale with horizontal markings which enables the eye to follow the level of the liquid from one tube to the other. Mercury may replace the acidified water but is not usually necessary. To the top of the measuring tube a capillary bore tap is fused or connected on by thick-walled rubber tubing, a bend connecting a piece of glass capillary tubing sufficient to reach to the pipettes when the latter are mounted upon the usual wooden table. Each pipette has a rubber connecting piece and stout clip. All rubber connections, except the one end to connect to the burette, are wired on with copper binding-wire. The apparatus including the pipettes are proved to be gas-tight. Occasionally it is found that the rubber tubing

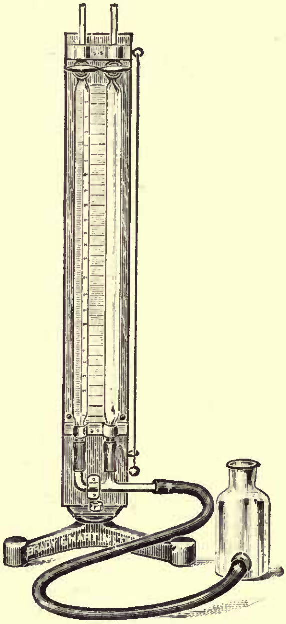


FIG. 10.—HEMPEL BURETTE (MODIFIED).

used has a small pin-hole, which is extremely difficult to detect unless particular care is used in the examination for soundness. The pipettes are preferably of the four-bulb type. (Fig. 11.). The bulb nearest to the burette is filled with the reagent by attaching a suction tube to the fourth bulb and inverting the pipette so that the tube of the first bulb dips into the reagent. The third bulb is then filled with water. When gas is forced into the first bulb the reagent displaces air from the second. This forces water from the third bulb, which finds a temporary accommodation in the fourth. Each set of bulbs should be of the same capacity. If preferred, pipettes may be obtained with a filling aperture at the base of the first bulb, through which the reagent may be introduced. Six pipettes are required filled with solutions of caustic potash, pyrogallol, bromine water, cuprous chloride (two), and acidified water. (See **127**.) Usually the methane and hydrogen are determined by explosion over mercury in a special bulb, or the residue from the absorption of carbon monoxide is transferred to other apparatus for the completion of the analysis. (See **134***b*, **134***c*, **135***a*.)

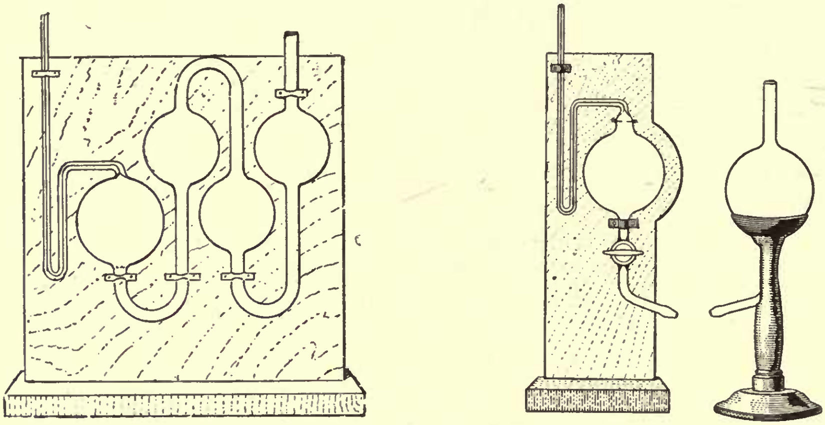


FIG. 11.—HEMPEL PIPETTE AND EXPLOSION BULB.

40*a*. *Method of Analysis*. The sample is introduced after the burette has been completely filled with water. The air in the capillary above the tap of the sample tube, and the rubber connection which is adfixed thereto, can be displaced by squirting water from a small jet into it. It is slipped on to the burette and the lower end of the tube having been immersed in a beaker of water, the gas can be drawn in by opening the cocks and lowering the levelling bottle. When over 100 c.c. have passed in the cocks are closed and the sample tube disconnected. The levelling bottle is then raised until the volume of gas corresponds to exactly 100 c.c., when the flexible tube at the base of the burette is nipped tight and the cock at the top opened momentarily to the atmosphere. There should then be 100 c.c. exactly at the atmospheric pressure and temperature. The gas is passed successively into the pipettes, shaken for three minutes with the reagent and returned to the burette for measurement. Care is taken to leave the reagent standing at the same level in the outlet tube of the pipette as it was in the first place, and to avoid as far as possible any passage of the reagent over into the burette. Before the gas is withdrawn a few drops of liquid from the burette may be forced into the pipette to displace drops of the reagent at the entrance of the outlet tube. If it is desired to absorb hydrogen sulphide separately from the carbon dioxide a two-bulb pipette containing cadmium chloride (a 10 per cent. solution made just slightly acid) is used. Shaking in this case is to be avoided. The gas is next passed to the caustic potash pipette for the absorption of carbon dioxide, followed by the pyrogallol pipette for the oxygen.[1] The unsaturated hydrocarbons are then absorbed in bromine water, which should be sufficiently strong to leave a distinct red colour in the gas. To remove this the gas is passed back to the burette and then to the potash bulb, and after returning to the burette it is measured. The bulk of the carbon monoxide is removed in the first cuprous chloride pipette. The gas is returned to the burette and measured before passing to the second pipette for the final absorption. The residual gas is then stored in the acidified water pipette. The burette is cleaned, if necessary, and care taken to wash out the connecting tube with acidified water. The explosion bulb is rinsed out with acidified water and filled with mercury to the end of the capillary tube. From 12 to 14 c.c. of the residual gas is drawn into the burette and measured. The levelling bottle is lowered and the cock at the top of the burette opened so that air is drawn in until the level of the water drops to below 90 c.c. The cock is then quickly closed, and the gas-air mixture measured. It is forced over to the explosion vessel and enclosed by a screw clip. The explosion bulb is left open to the levelling bottle to take up the force of the explosion and the mixture is fired by a spark from an accumulator and sparking coil. The explosion should be sufficiently vigorous to give only a momentary flash. Partial ignition is marked by a visible travel of the flame from the spark gap. A brilliant white flash is also to be avoided, or nitrogen may be oxidised. The gas is then passed back to the burette and the contraction measured. The carbon dioxide formed is afterwards absorbed in the potash bulb and the gas returned to the burette for measurement. As a check the oxygen may be absorbed in pyrogallol and the excess of air can be calculated. As methane forms its own volume of carbon dioxide, the amount present in the gas taken for explosion is easily observed. For every volume of carbon dioxide thus formed there are two volumes of " contraction " (due to condensation of water). The remaining contraction in volume after explosion is due to hydrogen, which gives two volumes of " contraction " for every three volumes of gas-air mixture taken.

$$CH_4+2O_2=CO_2+2H_2O$$
$$2H_2+O_2=2H_2O$$

Thus the hydrogen is found by taking two-thirds of the total contraction from which twice the volume of carbon dioxide found has been deducted.

The explosion is preferably repeated with a fresh portion of the residual gas. The results, which are the most inaccurate part of the analysis, since only a portion of the gas is used, should agree to ± 1 per cent. The errors most likely to occur are due to the incomplete removal of carbon monoxide from the residual gases and absorption of carbon dioxide resulting from the explosion before the total contraction has been measured. The former leads to low results for the methane and nitrogen,

---

[1] For the use of phosphorus in place of pyrogallol, see **128*b*.**

while the hydrogen comes too high. The latter leads to the reverse. Care is to be taken to renew all the absorbents regularly or serious errors will occur; carbon dioxide may be left to be absorbed by the pyrogallol, the latter may give off carbon monoxide, olefines may effect the explosion results and oxygen may render the cuprous chloride solution useless. The results from the explosion method may be checked by combustion methods, and the nitrogen may in a similar way be determined as a residue from one operation. (See **135***a*, **135***b*.)

42*a*. *Minor Constituents—Ammonia.* Probably the only minor constituent which it will be desired to estimate in the retort-house gas is ammonia. In any case at least 1 cubic foot of gas will be required, and a suitable aspirator to draw this through absorbents is necessary. A tank containing 2 or 3 cubic feet of water fitted to syphon off at constant head will serve, or a suction pump on a supply of water at constant pressure may be arranged. The sampling tube of silica is inclined downwards and fitted as described. (See **36***b*.) The condensed matter, which forms as the gas is drawn through, drains into a small bulb or tube with filter pad of cotton, or glass-wool. The gas is next drawn through one or more absorption vessels containing suitable reagents. For ammonia a dilute solution of sulphuric acid is used. If the aspirator is of known capacity it is used as a measure of the gas passed. Otherwise a test-meter, protected by a guard tube of oxide of iron, is necessary. The suction is then attached to the outlet of the test-meter. Gas is drawn through at the rate of about 1 cubic foot per hour till sufficient has passed. The absorption vessels may then be transferred to the laboratory. In the case of ammonia estimation the filter bulb is washed out into a distilling flask followed by the contents of the absorption vessels. The solution is then rendered alkaline and distilled into excess of standard acid as described later. (See **93***d*.)

Hydrogen sulphide can be dealt with in the same way, using ammoniacal zinc chloride as reagent. (See **114***b*.) Naphthalene is absorbed in acetic or picric acid (see **81***b*), but in this case the filter bulb is rinsed down with a few drops of acetic acid, and the rinsings added to the main bulk.

REFERENCES

V. B. Lewes. Carbonisation of Coal, 1912 and Cantor Lectures. *Gas World*, 1911, **55**, 665, 708, 738, 770.

H. G. Colman. Lecture on Carbonisation. *Gas World*, 1910, **53**, 736.

G. M. Gill. Carbonisation in Horizontal Retorts. *Trans. Inst. Gas Eng.*, 1921, 471.

C. Drury. Dessau Vertical Retorts. *Trans. Inst. Gas Eng.*, 1911, 102.

J. G. Newbigging. Glover-West Vertical Retorts. *Trans. Inst. Gas Eng.*, 1911, 129.

Gas Invest. Comm. of Inst. Gas Eng.—4th Report. Steaming Vertical Retorts. *Trans. Inst. Gas Eng.*, 1920, 260.

Fuel Research Board. Report on Steaming Vertical Retorts, 1920–21.

Harger. Carbonisation. *J.S.C.I.*, 1914, 389.

A. Short. Carbonisation—nitrogen and sulphur distribution. *J.S.C.I.*, 1907, 581.

W. B. Davidson. Experiments at Birmingham. *Trans. Inst. Gas Eng.*, 1910, 269.

W. B. Davidson. Vertical and Horizontal Retorts. *Gas World*, 1912, 278, 459.

Constam and Kolbe. Tests of English Coal. *Gas World*, 1909, 51, 330.

J. W. Cobb. William Young Mem. Lecture. 1914.

Cobb and Hollings. Influence of red-hot Coke and Thermal Studies of Carbonisation. *Gas World*, 1914, **60**, 872.

Tervet. Liberation of Ammonia and effect of atmosphere. *J.S.C.I.*, 1883, 445.

O. Simmersbach. Nitrogen distribution. *Gas World*, 1915. Cok. Sect., Mar. 6, 1918.

A. C. Monkhouse. Liberation of Nitrogen and Sulphur. *Trans. Inst. Gas Eng.*, 1921, 543. *Gas World*, 1922.

H. J. Hodsman. Stability of Ammonia and effect of Oxygen (Thau's experiments). *Gas World*, 1922. Cok. Sect., p. 10.

S. F. Dufton and J. W. Cobb. High-temperature reactions of Benzene and Toluene. *Trans. Inst. Gas Eng.*, 1920, 137.

Hempel. Gas Analysis.

CHAPTER IV

COKE

The coke made in gasworks varies very largely both as result of the coal used and of the method and conditions of carbonisation. The most suitable coals from the gas-making point of view are not those which produce the best coke, hence a compromise has to be effected. In a gasworks the yield and quality of the gas are the most important considerations, and there is a tendency to neglect the quality of the coke which after all forms a substantial portion of the revenue. Attempts made in recent years to provide a free-burning but smokeless fuel for the domestic grate have shown that the residual volatile matter is not all-important in this respect, and that it may be possible in the future to manufacture such a fuel without necessarily sacrificing high temperature products. The essential qualities desired in coke for the general uses to which it is put are, freedom from dust and small breeze, a size graded to suit the particular purpose, a calorific value of not less than, say, 12,500 B.Th.U. per lb., a low ash and sulphur content and, more important still, a suitable texture. Unfortunately we have at present little or no means of estimating the rate at which different types of coke will burn under natural draught conditions, and the factors which constitute the property of " free-burning " are not known. Certainly texture has a great deal to do with it. Coke with a structure made up of an infinite number of small pores surrounded by very hard division walls seems to possess the property to a very large extent. Possibly also the ash may play an important catalytic rôle, and militate to some extent at least for its other very obvious disadvantages. The distribution of the ash is important. With badly picked coal large lumps of slate and stone corresponding to the maximum size that the coal-breaker will pass are visible in the coke and are very detrimental from the selling point of view, although in reality the total quantity of ash may not be large. The composition and properties of the ash are of great consequence when the coke is used for large furnace work.

The volatile matter in coke is probably of little real consequence, and its complete extraction in the form of gas is preferable if economically possible; always providing that the texture of the coke is left in a finely divided and yet firm structure.

Coke is somewhat hygroscopic. When wetted it can retain a very large amount of water in its pores. It is therefore very advisable to exercise care in the quenching of coke. Results of producer and generator working may be completely upset by the charging of coke which is saturated with water. Not only is the fire damped and severe strain brought upon the furnace, but brickwork on which steam condenses has a tendency to rot.

There is little need to point out and emphasize the importance of regular size in dealing with coke as a fuel. A little elaboration of screening and breaking plants in this country would be amply repaid.

Specific Gravity. The true specific gravity of coke is that of the coke substance, and is obtained by crushing the coke and determining the specific gravity of the powder. The coke in bulk has an apparent specific gravity which is considerably less owing to the number of pores it contains. The determination of the two specific gravities will therefore provide an index of the porosity, but does not indicate the size of the individual pore. As a criterion of the texture the result is therefore incomplete.

45*a. Method for Specific Gravity of Coke Substance.* The coke is crushed down until it passes a 60-mesh screen. About 3 grams are weighed out exactly into a 50 c.c. specific gravity bottle of which the weight empty and completely full of water at 15° C. is known. About 20 c.c. of distilled water are added, and the bottle immersed up to the neck in a beaker of water. To the neck of the bottle is attached a glass tube with the end drawn out so as to enter the neck of the bottle. The other end is then connected to a suction and the beaker of water raised to boiling-point. After an hour's treatment the flask is disconnected, cooled, and filled with freshly boiled water at 15° C. The stopper is slipped in and the excess of water removed. The flask is then wiped dry and weighed. If W is the weight of coke taken ; W_1 the weight of bottle full of water ; and W_2 the weight when finally weighed with coke powder, then the specific gravity is given by :—

$$Sp.\ gr. = \frac{W}{W + W_1 - W_2}$$

It is advisable to check the specific gravity bottle after heating in this way as the volume is liable to alter.

45*b. Use of Other Liquids.* A method which is very much quicker and avoids heating is to use a liquid of superior wetting power in place of the water. A clean petroleum oil, or xylene of known specific gravity, may be used. Even in the case of coal the former has so little effect in the cold as a solvent that it gives fairly accurate results. It is only necessary to introduce the weighed quantity of substance into the bottle, add the liquid, and tap the bottle repeatedly to eliminate bubbles. Gentle warming may be used for very light powders. The specific gravity is calculated as before ; and is reduced to the basis—water=1—by multiplying the result by the specific gravity of the liquid used.

45*c. Apparent Specific Gravity.* The simplest method is to take advantage of the fact that the thrust on a solid suspended in water is equal to the weight of fluid displaced, e.g. the weight of an equal volume of water. The solid lump is weighed in air in the usual way, suspended by a fine thread from the beam of the balance. A wooden bridge is then placed across the pan and on it is placed a beaker of distilled water at 15° C. The solid is then immersed in the water so that it is able to swing with the balance arm while totally immersed. The weight immersed is then taken. The weight in air divided by the difference of the weight in air and in water gives the specific gravity. Adherent bubbles of air on the surface may be removed with a wet feather or brush. In the case of most cokes it will be found that the apparent specific gravity is less than unity and the coke floats. In this case a sinker must be attached to the coke lump. If W_1 is the weight of coke in air; W_2 the weight of the sinker alone in water; W_3 the weight of sinker and coke both immersed in water; then the specific gravity of the coke is given by :—

$$\frac{W_1}{W_1+W_2-W_3}$$

To prevent penetration of water into the pores the lump may be "painted" over with cellulose acetate solution and allowed to dry before the experiment.

46*a*. *Specific Gravity of a number of Lumps.* The apparent specific gravity of a number of small lumps may be taken by using a volumenometer, consisting of a wide tube, or jar, covered with a ground-glass conical top leading to a centrally placed outlet tube and tap. To an opening at the base of the jar is attached a flexible tube connecting the jar to the lower end of the measuring tube of a Hempel burette. By raising the burette water flows into the jar and completely fills it. The reading of the level of water in the burette is then taken. The burette is then lowered until the water has fallen in the jar below the ground glass-top. The latter is removed and the weighed pieces of coke inserted. The top of the jar is then replaced and water allowed to flow from the burette until the jar is again completely full. The level of the water in the burette is again read, when by difference with the former reading the volume of water equal to the volume of coke taken is found. (See also **63***b*.)

46*b*. *Porosity.* The difference between the real and apparent specific gravity divided by the real specific gravity and multiplied by 100 expresses the porosity. By dividing the porosity by the apparent specific gravity the total volume of pores in c.c. per 100 grams of coke is given. The size of the pores is also a matter of importance, but the only method of obtaining an idea of this seems to be to compare the structure of different cokes microscopically.

Hardness of Coke. The definition of hardness in respect of coke is a matter of some difficulty. The property that is really required is the strength of the division walls between the pores. The size of coke heaps in stock often brings a considerable crushing strain on the coke at the base. During transport coke has to sustain a good deal of abrasion. The crushing strength may be obtained in a machine similar to that in use for blast furnace coke, but probably an abrasion test such as that suggested by Hewson is more useful.

46*c*. *Hewson's Method.* The coke is crushed with a hammer on an iron plate to a size varying from one-inch to half-inch diameter. The small is sieved out with a 2-mesh screen. The lumps are then dried at 100° C. and 28 lb. weighed out, placed in a drum 26 inches diameter and 16 inches deep. The drum is mounted to revolve. Twelve cast-iron balls $1\frac{1}{4}$ inches diameter are added on top of the coke and the drum revolved at uniform rate of about 1,000 rev. per hour for one hour. The coke is then withdrawn and sieved through a screen with 8-mesh per lineal inch. The remainder is weighed back and the large calculated as a percentage on the weight taken. This is called the hardness number.

47*a*. *Sampling Coke.* Coke is one of the most difficult solids to sample. Sampling is carried out in the same way as in the case of coal. Separate moisture samples are almost always necessary in view of the difficulty of reducing coke to powder. The reduction is best carried out by using a steel hammer on a steel plate in the first instance. Grinding by hand or by power is inadvisable, owing to the chance of introducing particles of iron which will influence the composition of the ash. The final reduction to a fine powder is conveniently made in a " diamond " steel mortar and plunger, such as is used in metallurgical work. The broken coke is placed in the mortar and the plunger slipped in on top. A hard and sharp blow with the hammer on the plunger will reduce the coke to fine powder. If the composition of the ash is required and not the total quantity, sampling may be carried out in wedgwood ware, as impurities so introduced will not be important.

47*b*. *Screening Test.* It is necessary to use a considerable bulk, say 10 cwt., which if possible consists of a number of units of transport—a bogey or telpher or truck load. The weight of the whole and of each fraction which passes through and rests on $\frac{1}{2}$-, $\frac{3}{4}$-, and 1-inch mesh-screens is obtained. If each size is reduced and sampled down and then mixed in the proportions found, a sample is obtained which is more likely to be representative than that taken in any other way. The different sizes of coke show a considerable difference in composition, which varies in the first place with the maximum size of the coal breaker in use.

47*c*. *Moisture.* The special sample is broken down quickly on an iron plate with a hammer until of such a size that it would, if screened, pass through a 2-mesh screen. The actual operation of screening is to be avoided. The broken down sample is mixed and 200–500 grams are immediately weighed out, dried at 100° C., and the whole cooled in a desiccator and weighed. Loss represents moisture and occluded gases. Dried coke is slightly hygroscopic.

47*d*. *Volatile Matter.* The determination is carried out as in the case of coal. (See **14***c*.) When the volatile matter is very low and it is feared that the air in the crucible may be left to oxidise the coke, a drop or two of alcohol may be added to the crucible before heating, or the crucible with coke may be imbedded in one of larger size filled with charcoal.

47*e*. *Calorific Value.* A bomb calorimeter is used as in the case of coal. Dry coke powder will not adhere when compressed to form a pellet, and if the powder is used in the determination it will be found that there is a tendency for the top layer to protect the rest of the powder from combustion. To avoid this a substance of known calorific value is mixed with the coke dust so that a pellet may be made. For this purpose benzoic acid, which may be obtained pure, and which possesses approximately the same calorific value as coke, is best. Two grams of coke and 0·2 gram of benzoic acid are weighed out, transferred to an agate mortar and ground together till a homogeneous mixture is obtained. This is then formed into pellets, as in the case of coal. From 1·1 to 1·2 grams of the pellet are weighed out and used in the same way as pellets of coal. A deduction of one-eleventh of the weight of mixture represents the benzoic acid taken, and this weight multiplied by the calorific value (6330 cal. per gram) gives the number of heat units which must be deducted on this account from the number of calories liberated, leaving the balance, subject to the usual corrections, as due to the coke. (See **26***a.*)

Sulphur. The presence of sulphur in coke forms a serious objection. The use of coke in many cases depends on the freedom of the products of combustion from soot and tar which might interfere with the articles being manufactured, or might vitiate the atmosphere around open coke fires. Although the products of combustion may be otherwise clean, any large proportion of sulphur compounds is usually just as detrimental as smoke. According to the conditions the sulphur may be evolved as hydrogen sulphide, sulphur dioxide or sulphur trioxide. If calcium or barium figure largely in the composition of the ash a considerable proportion of the sulphur may be retained as sulphate, and this reduces the amount in the volatile products. Hence the total sulphur can hardly be used as a means of comparison of different cokes unless the sulphur retained by the ash is also considered. Lime is sometimes purposely added to the coal before carbonisation for the purpose of reducing the sulphur evolved on combustion of the coke (" Liming Process "), but naturally in this case the total ash is seriously increased. By excessive steaming during carbonisation the sulphur in the coke may also be reduced, but it does not seem possible to completely extract all the sulphur in this way until the carbon has been completely gasified.

48*a. Total Sulphur in Coke.* The estimation is carried out as described for coal. (See **23***a*, **23***b*, **24***a.*)

Sulphur in Ash. (See **51***a.*)

48*b. Nitrogen.* The nitrogen left in coke has practically no value, as even when gasified in the presence of steam the recovery is not economical. Although an appreciable amount of the nitrogen may be evolved as ammonia, the concentration is very low. The estimation is chiefly required for the purpose of obtaining by difference from the nitrogen in the coal that which has been expelled during carbonisation.

The determination is carried out by the Kjeldahl or Dumas methods, as in the case of coal. (See **24***b*, **25***a.*) Sometimes a residue of black specks of graphitic carbon are observed after the oxidation, but this does not seem to affect the result.

Arsenic. Gas coke is often used in connection with the preparation of foodstuffs either for direct heating or drying of materials. The estimation of arsenic is therefore sometimes required.

48*c. Total Arsenic.* The method recommended by the Royal Commission on Arsenical Poisoning (1903) consists in igniting from 2 to 5 grams of the dry powdered coke as in in the lime method of determining the total sulphur in coal. (See **24***a.*) The residue is dissolved in dilute hydrochloric acid and filtered. The filtrate is reduced with an aqueous solution of sulphur dioxide, saturated with hydrogen sulphide and allowed to stand in a closed conical flask with the excess of hydrogen sulphide for a day or two. The precipitate of arsenious sulphide is filtered off, extracted with warm dilute ammonia and the solution evaporated to dryness. The residue is dissolved in a conc. solution of ammonium carbonate and the ammonia evaporated off.

The solution of about 20 c.c. is reduced again by warming with aqueous sulphur dioxide and then estimated as in Marsh's method, or Gutzeit's test.

By estimating the arsenic left in the ash on combustion the volatile arsenic may be obtained by difference.

49*a*. *Volatile Arsenic.* An alternative method consists in burning 10 grams of the fuel in a combustion tube in a current of oxygen. The outlet end of the tube is drawn out and turned down to dip into acid contained in an absorption vessel. When the combustion is complete the drawn-out end is cut off and carefully rinsed down with a little dilute acid into the absorption vessel. The whole is made up to 50 c.c., and 25 c.c. are dealt with in one of the following ways :—

49*b*. *Marsh's Method.* A standard apparatus is used such as that illustrated. (Fig. 12.) In the calcium chloride tube is placed a roll of lead acetate paper, followed by a wad of cotton-wool. Next is filled in granulated calcium chloride and the tube is closed by another wad of cotton-wool. In the flask is placed 20 grams of arsenic-free zinc. Pure acid is filled into the cup and added to the zinc, so that a flame at the end of the heated tube is about $\frac{1}{4}$-inch long. The tubes should be similar and heated 1 inch of the length. A piece of copper gauze wrapped round the heated part of the tube will distribute the heat evenly. With good materials no mirror should result in 30 minutes. The hydrochloric acid used, unless proved free from arsenic, is treated with sufficient bromine to colour it strongly yellow. Excess of sulphur dioxide is added and the whole allowed to stand 12 hours. The solution is then boiled until one-fifth is volatilised. Standard mirrors are then prepared by adding to the hydrochloric acid two or more c.c. of a solution of arsenious oxide containing 0·001 mg. of As_2O_3 per c.c. The full mirror should be obtained in 20 minutes. It is removed and a second tube inserted to prove that the deposition has been completed. A set of standards are prepared in this way. The mirror portion of the tube is sealed off while full of hydrogen. The test is carried out in the same way. A preliminary blank test is always necessary, and the test solution is then added. To prove that the mirror obtained is arsenic, the tube is cut off, the hydrogen expelled with air, and the ends of the tube sealed off. By careful warming the mirror will disappear, to be replaced by minute crystals of arsenious oxide.

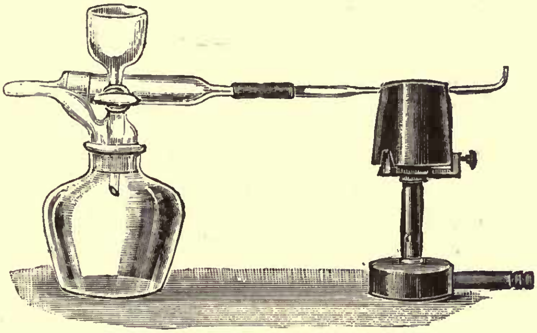


Fig. 12.—Apparatus for Estimation of Arsenic (marsh)

The arsenic may also be driven off by electrolytic generation of hydrogen instead of by the use of zinc and hydrochloric acid.

49*c*. *Gutzeit's Test.* The official British Pharmacopœia method of estimating arsenic consists in introducing a suitable amount of the arsenical solution into a glass bottle of about 120 c.c. fitted with rubber cork and a straight delivery tube, 20 cm. long, with an internal diameter of 5 mm. The lower end of the tube is constricted to about 1 mm. and a hole blown in the side above the constriction. The upper end is widened slightly to a diameter of 8 mm. A strip of lead paper is placed in the tube so that the top of it is not less than 2 cm. below the top of the tube. A piece of mercuric chloride paper (filter paper soaked in a saturated aqueous solution of mercuric chloride and dried) is placed to cover the top of the tube and secured round the side by a rubber ring. Ten grams of arsenic-free zinc are placed in the arsenical solution in the bottle, which contains a considerable excess of hydrochloric acid. The cork and tube are immediately fixed in position so that the end of the tube is clear of the surface of the liquid. The action is allowed to proceed for 30 to 40 minutes out of sunlight. The stain produced on the mercuric chloride paper is compared with stains produced in a similar way from known amounts of arsenic. The "standard" stain is that produced from the solution obtained by adding to 50 c.c. of hot water 10 c.c. of hydrochloric acid and 1 c.c. of fresh arsenic solution containing 0·00001 gram As. The hydrochloric acid used contains 1 per cent. of a solution of stannous chloride, the latter prepared by dissolving 20 grams of tin in 60 c.c. of hydrochloric acid and 100 c.c. of water. This is diluted with an equal volume of hydrochloric acid, boiled, filtered, and made up to the original mark.

Phosphorus. The presence of phosphorus in gas coke is often undesirable when it is used for some metallurgical work. As a rule it is higher than in coke-oven coke, as the coal used is not selected with this impurity in view. All the phosphorus appears in the ash. The estimation is made as given below (**51***b*).

Ash. So far as is known at the present time the ash is an inert constituent which is undesirable from every point of view. Not only is the weight of material to be handled increased by the ash content, but the obstruction it causes in use, and its fluxing powers on refractory materials, becomes an accumulative disadvantage as the proportion increases. The estimation is made in the same manner as for coal. It is important that in the burning off, the coke should not be raised immediately to a high temperature, or the time of complete combustion will be prolonged.

Composition of Ash. The composition of ash is chiefly of importance in respect to the behaviour of the ash at the temperatures reached in the furnaces. In this respect it is to be remembered that the ash as obtained by ignition is oxidised, while under practical conditions the ash is liberated in a reduced state. This is of great importance in respect to the iron, which is not a fluxing agent in the ferric state, but forms low melting silicates when in the ferrous state. Sometimes, in practice, metallic buttons have been found in the clinker. The relation of composition to melting-point is a somewhat intricate subject, and at present it would seem easier to determine the melting-point experimentally.

50*a*. *Complete Analysis.* An analysis of the constituents of ash may be made in the manner described for silicates and refractory materials. (See **69***d*.)

If only the total iron is required, 1 gram may be fused with sodium carbonate and determined volumetrically, as described for the estimation of iron in iron ores. (See **109***c*.)

51*a*. *Sulphur in Ash.* One gram of the finely powdered ash is fused with sodium carbonate as for a complete analysis. (See **69***d.*) The solution of the melt is repeatedly evaporated with hydrochloric acid, and filtered to remove silica. The iron is next removed by addition of hydrogen peroxide and ammonia to the hot solution, and the sulphur precipitated in the filtrate by addition of barium chloride and hydrochloric acid. (See **23***a.*) The sulphur may also be obtained in solution by digestion of the ash with conc. nitric acid and a little potassium chlorate. The bulk of the nitric acid is driven off by evaporation with hydrochloric acid, and the sulphur precipitated with barium chloride. This method is apt, in some cases, to give low results.

51*b*. *Phosphorus.* Two or three grams of the ash are fused in a platinum crucible with about eight times the weight of sodium carbonate as in silicate analysis. The melt is dissolved in dilute sulphuric acid, which is taken down to dryness and baked to remove silica in the usual way. Alternatively the ash may be digested with conc. hydrochloric acid, evaporated to dryness, taken up with dilute hydrochloric acid and filtered. In either case the filtrate is nearly neutralised with ammonia and evaporated down to about 50 c.c. Ammonia is added till a precipitate forms which is permanent, and about 3 c.c. of conc. nitric acid, and 15 c.c. of ammonium nitrate solution (320 grams per litre) are added, so that the solution has between 5 and 10 per cent of ammonium nitrate. A thermometer is placed in the liquid, which is heated to 70° C. and then poured rapidly into 20 c.c. of fresh ammonium molybdate solution (34·34 grams of $(NH_4)_6\,Mo_7O_{24}.\ 4\,H_2O$ in one litre). The solution is agitated briskly for 10 minutes and allowed to stand in a warm place for about 30 minutes. The solution is decanted off through a filter and the precipitate washed by decantation and on the filter with cold 2 per cent. nitric acid. The filtrate obtained should not show any yellow precipitate on standing overnight with a further addition of ammonium molybdate, and is then rejected. The beaker in which the precipitate was formed is placed under the filter and the precipitate dissolved into it with about 4 c.c. of conc. ammonia. The filter is washed once with hot water, the whole of the filtrate passed through it again and the filter is finally washed several times with hot water. The solution containing the dissolved precipitate is raised to boiling-point and 10 c.c. of hydrochloric acid and 10 c.c. of a 4 per cent. solution of lead acetate are added. Immediately the whole is poured into a mixture of 50 c.c. of ammonium acetate and 10 grams of ammonium chloride also at boiling temperature. The molybdenum present in the phospho-molybdate is thus precipitated as lead molybdate and is filtered off, washed with hot water and dried. The bulk of the precipitate is transferred to a tared porcelain crucible, the filter paper burnt and added, and the whole ignited, cooled, and weighed. The phosphorus is equivalent to the weight found multiplied by 0·007.

$$P \rightarrow (NH_4)_3PO_4.\,12MoO_3 \rightarrow 12\;PbMoO_4$$

The ammonium phospho-molybdate may also be redissolved in ammonia as above, made acid with hydrochloric acid and the phosphorus precipitated from the hot solution with magnesia mixture (55 grams of cryst. magnesium chloride with 70 grams of ammonium chloride and 200 c.c. conc. ammonia made up to 1 litre), followed by 3 per cent. ammonia. The precipitate should be crystalline in character and allowed to stand with frequent stirring for some time. It may then be filtered off, dried, and ignited as pyrophosphate, $Mg_2P_2O_7$.

The ammonium phospho-molybdate precipitate may also be weighed directly after filtering off through a Gooch crucible and asbestos fibre and drying at 100–105° C. The residue then contains 1·63 per cent. of phosphorus.

The ammonium phospho-molybdate precipitate may also be titrated with alkali, in which case the washing is finished with a 2 per cent. solution of potassium nitrate until the washings are neutral. The residue is thrown into 30 c.c. distilled water and excess of standard caustic soda added. When the yellow precipitate has been dissolved the excess of caustic soda is titrated back with standard nitric acid, using phenolphthalein as indicator. The nitric acid and caustic soda are standardised under the conditions in use by adding a further known amount of the alkali and again titrating back the excess.

$$P \rightarrow (NH_4)_3PO_4 . 12\,MoO_3 \rightarrow 23\,NaOH.$$

Arsenic, if present, is precipitated with the phospho-molybdate, while titanium may also influence the results.

Fusion of Coke Ash. The ash not being a pure substance has no definite melting-point, but on heating gradually passes from a solid to a viscous mass, which ultimately forms a mobile liquid. In comparing the behaviour of ash at high temperatures it is necessary to observe the fusion range between the first softening point and complete liquation. Cokes with low softening ashes are not always to be preferred if the fusion range is large, as they may form a tough viscous mass arching far above the fire-bars.

52*a*. *Furnace for Fusion Range.* The maximum temperature likely to be required in the examination of coal ash is about 1,550° C. This temperature can be reached with coal gas and air under pressure. Special furnaces, such as those employed for determining the refractoriness of firebrick, may be used, but are expensive. In a gasworks where silica brick can be obtained a furnace may readily be built up. A layer of insulating brick is laid down first, on which flat silica bricks are placed to form the furnace floor. Silica bricks form the sides. At one end of the oblong furnace thus formed is cut an opening, into which the burner is inserted just above the level of the furnace floor. In the centre of the interior is placed a small silica muffle, say, 2¼ by 4 inches long ; which is supported by small square silica blocks 2 inches from the floor. The flame will then play underneath the muffle and up and over the sides and end. At the opposite end, facing the open end of the muffle, and at the same height, is cut a sighting hole, by which the test-pieces may be seen and through which a pyrometer may be sighted. Over the burner end of the muffle, reaching as far as the burner wall, and covering about half the muffle, is placed a silica or firebrick " split " to form an " arch " and direct the flame along to the front end of the muffle. The waste-gas opening is then placed over the " arch." The roof is built of silica bricks laid transversely across from wall to wall. There is no need to use any cement unless the bricks used do not fit well. The furnace may then be covered with loose insulating brick. The arrangement can be dismantled or altered with great ease.

Some difficulty may possibly be found in getting a suitable burner. The burner illustrated (Fig. 13), is easily made up and will give, with good gas supply and air at about 1 lb. per sq. in. pressure, temperatures up to 1,500° C. It consists of a $1\frac{1}{4}$-inch Keith injector body to which is added, at the burner end, a barrel nipple to form a tube. At the other end a T-piece is screwed. The air passes in by the right-angle opening and the gas into the straight opening of the "T" through a $\frac{3}{16}$-inch jet which terminates opposite the compressed air inlet. Wire gauze is pushed well down the burner tube to prevent the flame striking back. The injector air forms a secondary supply. In this way a good mixture of gas and air issues from the burner and is pre-heated to a certain extent by the hot burner tube. Adequate mixing of the gas and air is essential for small furnaces, as the time allowed for combustion to take place in the furnace is very small.

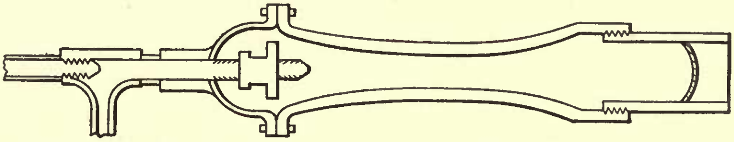


FIG. 13. KEITH INJECTOR BURNER.

53*a*. *Method of Determining the Fusion Range.* The ash is finely ground and should pass a 100-mesh screen. Fieldner and colleagues recommend completing the oxidation of the ash by combustion in oxygen after grinding to pass a 200-mesh. The ash is made into a paste with a small amount of 10 per cent. dextrin solution and compressed or moulded into triangular pyramids about $\frac{1}{4}$ inch wide at the base and $\frac{3}{4}$ inch high. The pyramids are mounted by pressing into a silica slab, made in the same way from ground silica and dextrin solution, which is of such a size as to fit into the furnace muffle. The slab and cones are dried slowly and finally burnt off at a low red heat in a muffle. It is best to take at least two cones of each ash. The slab is placed in the muffle and the furnace-top bricks placed in position. The temperature is quickly raised to 800° C. with the use of excess of gas. The temperature is then raised at about 10° C. per minute and the cones carefully watched. The temperatures are noted at which there is the first sign of softening and at which the ash is fluid enough to flow. An intermediate stage can often be observed when the pyramid has become a more or less spherical lump. To obtain the highest temperature it will be necessary to adjust the gas and air to nearly the neutral point, but the atmosphere up to this point is maintained with a distinct excess of gas. If preferred, granulated retort carbon may be placed around the test-piece in the muffle.

REFERENCES

W. C. ANDERSON (O. SIMMERSBACH). Chemistry of Coke, 1904.

E. R. SUTCLIFFE and E. C. EVANS. Combustibility of Coke. *J.S.C.I.*, 1922, 196T.

FUEL RESEARCH BOARD. Report on Low Temperature Carbonisation, 1920–21.

A. E. FINDLEY. Sampling Coke for Ash Determination. *J.S.C.I.*,1919, 93T.

W. W. SCOTT. Standard Methods of Chemical Analysis, 1917.

J. W. MELLOR. Treatise on Quantitative Analysis. 1913.

G. W. HEWSON. Hardness of Coke. *J.S.C.I.*, 1918, 61T.

COCHRANE (and JONES). Hardness of Coke. *J.S.C.I.*, 1918, 304A.

W. C. ANDERSON. Porosity of Coke. *J.S.C.I.*, 1896, 20.

LLOYD and YEAGER. Volatile Matter. *J. Ind. Eng. Chem.*, 1922, **14**, 220.

BRITISH PHARMACOPŒIA. Arsenic in Coke—Gutzeit's Test.

SMITH and R. L. JENKS. Arsenic in Coal and Coke. *J.S.C.I.*, 1901, 437.

PLATTEN, McGOWAN and FLORIS. Arsenic in Coal and Coke. *J.S.C.I.*, 1905, 265.

F. IBBOTSON. (Determination of Phosphorus.) Chemical Analysis of Steel Works Materials. 1920.

J. T. DUNN. Coal Ash Analysis and Fusion Point. *J.S.C.I.*, 1918, 15T.

PALMENBERG. Coal Ash. *J.S.C.I.*, 1913, 1144.

FIELDNER. Coal Ash. *J.S.C.I.*, 1915, 704.

FIELDNER and Colleagues. Fusibility of Coal Ash. U.S.A. Bureau of Mines, *Bull.*, 129, 1918.

BURGWIN. Coal Ash. *J. Ind. Eng. Chem.*, 1914, **6**, 694.

CHAPTER V

MAINTENANCE OF HEATS

THE importance of maintaining a sufficient and uniform temperature in the settings is obvious. The temperature to be aimed at in the combustion flues will depend on such considerations as the weight of coal carbonised, thickness of retort, and the properties of the refractory materials. In general, it will be some 200° to 250° C. above the maximum temperature reached inside the retort, i.e. in the neighbourhood of 1,300° C. It is necessary to assume a softening point under load of the usual refractory materials of about 1,400° C. Although such a temperature may be sustained without damage for a short time, the accumulative effect of flue dust and load will render such a temperature dangerous. It will be seen that considerable care will be necessary with a working temperature of over 1,300° C., to avoid local heating forcing the temperature too high.

Heat transference through refractory material is slow under the best of circumstances. The quantity of heat transmitted depends on the difference of temperature between the inside and outside of the retort walls, and therefore the greater quantity of heat required to be supplied to the retort per hour the greater must be this difference in temperature. It is evident that if the heat transmitted with a certain temperature difference is not utilised or dissipated by the carbonising coal the temperature will gradually rise first on the inside and then on the outside of the retort. As carbonisation proceeds and the evolution of gas carrying heat away falls off, the temperature conditions rise. Overspent charges may cause an abnormal temperature in the flues. The maximum working temperature that can be allowed therefore depends on the nature and variation of the coal as well as the weight of charge and the time given for carbonisation.

Fortunately the heat capacity of the setting is sufficiently large to tide over small fluctuations, but it is a matter of practical observation that should the reserve of heat once become exhausted the temperature falls very rapidly. To restore the conditions the quantity of heat supplied by the producer has to be increased. The adjustment necessary to effect this can only be of a temporary character, and to avoid risk of ultimate overheating, has to be carefully made. The time occupied in restoring the conditions tends to lengthen; meanwhile the results of carbonisation are poor.

The maintenance of heat is therefore dependent on (1) the type of coal, (2) the throughput of coal, (3) the working of the producer, and (4) the regulation of the setting. There is also the effect of the atmosphere. Not only do atmospheric conditions influence the draught regulation but exert a considerable effect on the heat lost by conduction and convection from the external surfaces of the setting. If a retort house is not sufficiently protected, a wind from a certain direction may cause uneven distribution of heat.

Temperature Control. To maintain even and consistent control over settings the temperature has to be estimated frequently in a large number of flues. Owing to the number, installations of fixed pyrometers are hardly possible, so that the pyrometer has to be carried round and adjusted in position in each case. This procedure requires more time than can usually be given as a matter of routine, so that control, in most cases, is a combined system of direct vision coupled with daily pyrometric determinations.

56*a. Estimation by Direct Vision.* Temperatures from 800° C. to 1,500° C. can be judged with an accuracy of about ±50° C. by those accustomed to do so. At times the accuracy becomes greater, but at other times the human judgment is very erratic. Temperatures appear less than they really are on a bright sunny day and higher during the night-time. Continual observation over a long period tends to throw the impression higher than the temperature really is. The continual viewing of combustion flues is a strain on eyesight, and may cause trouble to those who possess eyes with larger pupils than normal.

56*b. Extinction Pyrometers.* Certain forms of pyrometers operate by the movement of a coloured glass or quartz wedge across the field of vision, and the position of the wedge at the moment of extinction gives an index of the temperature of the surface under observation. These instruments are easily carried about and used. When the operator has acquired the knack an accuracy of about 30° C. can be obtained, but this accuracy varies with different operators.

56*c. Radiation Pyrometers.* Pyrometers, such as the Féry instrument, are more complicated but give direct readings of an accuracy of ±10° C., and an instrument of this type is necessary for the purpose of obtaining accurate and reliable readings. The pyrometer may be used for any internal surface and at any distance from it so long as the field of vision is correspondingly increased. The area of the hot surface must not be less than the aperture shows to be necessary to cover the image of the thermo-couple. Consequently it is sometimes difficult to read the maximum temperature of a flue when it is located far away from the observer. Care must be taken not to include nostril-holes in the field of vision. The field of view also must not be obscured by steam or vapour such as often rises from the open end of a retort mouthpiece. In such cases the readings will be low.

56*d. Optical Pyrometers.* Pyrometers of the Wanner type are also very reliable and accurate, but the accumulator which has to be carried about to supply the current for the small electric lamp, against which the intensity of the radiation is compared, is a great stumbling-block to its use. The illumination has also to be standardised periodically with a pentane flame and the voltage adjusted.

Control of the Producer. In gasworks are to be found all types of gas generator, from the direct-fired furnace to the external producer. In all cases the function is to convert the solid fuel to a gaseous form so that it may be applied to the heating of the setting. The gasification agents are steam and air. The energy required to raise the temperature of the fuel to the point at which it is capable of gasification is supplied by the partial combustion of the fuel. To control this process it is necessary to know the composition of the fuel, the amount of fuel gasified, the composition of the gas, and the temperature of the fire. The composition of coke has already been dealt with. The amount gasified is often hard to arrive at, as it is usual to fill the producer with hot coke straight from the retort. Although in this way heat is saved by the fact that the coke when charged is nearly at the requisite temperature, yet it is far too large in size, and the quantity used can be only roughly guessed from the weight of coal charged. The producer has to be filled at stated intervals, which may or may not be frequent enough.

With a given fuel and furnace, the rate of combustion is dependent on the draught and temperature conditions. As the draught is reduced so is the temperature reduced, but to maintain the same quality of gas the depth of fuel bed must be increased. A reduction of the depth of fuel bed must be accompanied by a reduction in the size of fuel if sufficient contact between air and fuel is to be maintained.

The amount of producer gas will be increased by giving more draught, but either the temperature will rise to a point when an excessive amount of clinker is formed and the furnace lining suffers, or time contact becomes too small, and the inferior quality of gas produced soon diminishes the amount of heat sent forward. For this reason producers do not respond readily when attempts are made to force them beyond a certain capacity. As a rule, the capacity is at a maximum when the quality of gas is at a maximum, and poor gas results in poor heats. If the heats can only be maintained by a rush of poor gas, it is obvious that the producer design is faulty and the process inefficient.

It was formerly the custom to regulate the admittance of primary air by slot openings in the furnace door or under the grate of the producer, but the liability of the draught to become too sharp, and the damaging effect of sudden rushes of gas going forward when the doors were open, has led to the entire opening of the slots, or even the doors themselves, and the regulation of the producer by the producer gas dampers, or, if such cannot be operated, by the waste gas dampers. Under this system the coke can be gasified evenly and at a temperature sufficiently low to prevent any great clinker trouble. While the system presents great advantages, it suffers from the defect that comparatively large quantities of unburnt fuel are found in the ashes. Probably if the fuel used was evenly sized, and not larger than, say, 1 inch diameter, the trouble in this respect would disappear.

The theory and practice of producer gas plants are dealt with elsewhere; it is sufficient to note the following points to which attention has to be given :—

(1) The quality of gas is maintained above a certain minimum depending on the producer.
(2) The temperature of the fire is maintained at as low a temperature as is consistent with (1).
(3) The fuel bed is even and kept to its designed level.
(4) Excessive rushes of air through the fire at clinkering, or other times, are prevented.
(5) The producer is tight and the lid sealed with flue-dust or sand.

Producer Gas. Carbon dioxide is always present in producer gas and is, to a large extent, a measure of the efficiency. The amount may rise from 3 to 5 per cent., or over, according to the conditions of the fire. Oxygen is rarely present. Carbon monoxide is the chief constituent, ranging up to 30 per cent. with " dry " producers. There is usually from 5 to 12 per cent. of hydrogen in " dry " producers, resulting from the decomposition of water in the fuel as charged or the water placed on or below the fire-bars to keep the grate cool. With the introduction of steam the hydrogen content rises and, if the temperature is not maintained, the carbon dioxide also. Small amounts of methane are usually present, resulting from the residual volatile matter in the coke ; sometimes, possibly by the catalytic effect of lime in the ash. The proportion of methane can hardly be controlled, but is important as adding materially to the calorific value of the gas. Exceedingly good results can be obtained from producer gas containing 20 per cent. carbon monoxide, 12 per cent. hydrogen, and 2 per cent. of methane. As a rule, the total combustibles will amount to about 35 per cent., and the calorific value per cubic foot will be about 115 to 120 B.Th.U. gross. Owing to the absence of hydrocarbons other than methane the calorific value can be calculated accurately from the analysis by multiplying the percentage of each constituent by its calorific value, adding the results together and dividing by 100. (See Table X.)

58*a*. *Sampling of Producer Gas.* Very often no arrangements will have been made for sampling the gas. A circular hole may be cut through to the duct leading to the setting. This may be lined near the top by an iron tube closed by a loose plug. A silica sampling tube may then be introduced right into the flue by removing the plug. A sample can be taken in the way described for gas under vacuum. (See **37***a*, **38***b*.)

In the case of producer gas, a rubber aspirator may be used in place of glass if it is held vertically so that the valve drops back on to its seat after each squeeze. The valve is cleaned periodically with a little benzol.

58*b*. *Analysis of Producer Gas.* The analysis is made with a Hempel apparatus, as already described. (See **40***a*.) For control work an estimation of the carbon dioxide, oxygen and carbon monoxide may be made in an Orsat apparatus into which the sample may be directly drawn. The residual methane and hydrogen can, if required, be determined by methods of combustion or explosion. (See **40***a*, **61***b*.)

Clinker. The composition of the ashes and clinker is a factor to be considered. Whether it is better to use a high fire temperature, completely burning the fuel and forming clinker, or whether it is better to keep the fire comparatively cool and recover coke from the ashes, is a matter for individual consideration. The most efficient way of working necessitates the formation of clinker, but efficiency in this respect may give place to the advantage of having to deal with unfused ashes.

The future may see some attempt made to control the composition of the ashes, and addition of fluxes to give suitable low melting ashes and easily flowing clinker. Probably the greatest trouble to-day occurs when the clinker arches over the fire-bars in a tough and viscous mass. Arches formed in this way can often be brought down easily by addition of lime or alteration in the type of coke used.

59*a*. *Sampling of Clinker.* The sampling of clinker and ashes is even more difficult to accomplish than that of coke. To obtain a representative sample it is necessary to break down the whole " draw " to about a ½-inch size before attempting to cone or quarter. Sometimes it is necessary to hand-pick the whole into three " fractions "—clinker, coke lumps, and smalls. The three fractions are then weighed and sampled separately.

59*b*. *Analysis of Clinker.* Usually the moisture and carbon content only are required. The moisture is taken on 10 grams of the coarse sample dried at 100° C. The loss on ignition of 1 or 2 grams of the dried and ground sample is taken to represent coke. A complete analysis is carried out on 1 gram of the ignited material, as in the case of silicates. (See **69***d*.) The carbon may be estimated by combustion. (See **22**.)

Combustion of Producer Gas. The combustion of the gas in the flues is a matter to which considerable attention may be given. The object is to completely burn the gas with a minimum quantity of air over the entire length of the combustion flue. To attain this consideration has to be given to several factors.

Mixing of Gas and Air. It is easier to secure adequate mixing of producer gas and secondary air than of coal gas and air, owing to the volumes in the former case being approximately equal. Unless proper mixing is effected the length of the flue, to secure complete combustion, has to be indefinitely prolonged.

Turbulence of Flow. The combustion of the gas raises the products to a very high temperature. The transference of the heat so present to the setting is another matter. It is obviously possible to burn gas down a straight, open flue without imparting any considerable proportion of the heat to the brickwork at the sides of the flue. A layer of gas on the surface of the brickwork forms a good non-conducting film—a phenomenon analogous to that experienced in problems of cooling and condensation. Unless the flue is packed with refractory material, such as is used in surface combustion, the flow of the burning gas should be made as turbulent as possible, for example, by imparting a whirling motion. In this way the non-conducting gas film is torn away and the heat of the burning gas imparted to the flue walls by direct contact as well as by the radiation from the flame.

Proportioning Air to Gas. The proportion of air to gas admitted has a relation not only to the efficiency of the heating process, but to the distribution of the temperature along the surface. Excess of air gives a short, sharp flame, which leads to local high temperatures at the producer end of the flue. Excess of gas increases the length of flame and combustion may not be completed until the chimney flue is reached. The maximum efficiency is obtained when the proportions are equivalent, but it may sometimes be necessary to sacrifice some efficiency in this respect if the length of the heating surface is unduly large. Very rarely, if ever, is it advisable to work with a large excess of air, although when the mixing cannot be effectively accomplished such a measure may be necessary.

Speed of the Gases. The velocity at which the gases are drawn through the setting must have relation to the length of travel and limits within which the gas must be burnt. It is quite possible to draw the burning mixture at such a rate that there is insufficient time for combustion to become complete within the setting. The gases may then be so rapidly cooled in the regenerator or waste gas flues as to show the presence of both carbon monoxide and oxygen in the chimney gas.

Control. Control of the combustion is regulated by draught gauges, pyrometer readings, and by analysis of the producer and waste gas.

Draught and Flue Dust. The most disturbing influence in the control of the heats is the deposition of dust from the producer in the flues. Not only does the dust slag the refractory material, and provide, in this way, a large proportion of the deterioration of the setting, but it will soon block the flue passages and reduce the damper openings. The effect is usually to reduce the proportion of air admitted, as the producer gas is often under a slight pressure, due to its sensible heat. Chiefly for this reason, fresh regulation of dampers is necessary from time to time. Much care is necessary to keep deposits of dust within limits. So harmful a part does the flue-dust play, and so great is the trouble caused by it, that possibly greater economy would be attained, in the long run, by sacrificing a portion of the sensible heat of the producer gas, in order to reduce its temperature sufficiently to clean it.

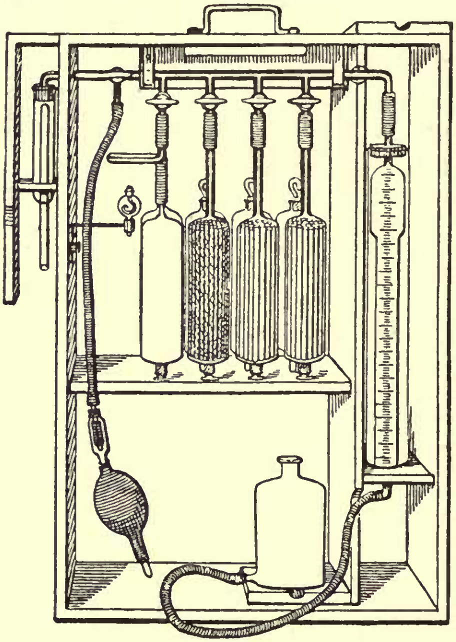


FIG. 14.—ORSAT-LUNGE GAS ANALYSIS APPARATUS.

60*a*. *Waste Gas Sampling.* Sampling places are provided at a point as near as possible to the end of the combustion flue, either before or immediately after the gases enter the regenerator; and also at the end of the regenerator and at the base of the chimney. Regenerators can never be relied upon to be perfectly tight. Serious errors may therefore be introduced if reliance is placed on the waste gas sampled in and after the regenerator alone. The samples taken at the entrance and exit provide an indication of the amount of short circuiting which is taking place, but the former is also used for the control of the setting. Serious leakage may result in both oxygen and carbon monoxide being found at the outlet. The sampling is accomplished by insertion of a silica tube through the aperture provided, to which is attached the " T " tube. To this is attached the aspirator and sample tube. (Cf. Fig. 8.) An Orsat apparatus may take the place of the sample tube. It is important to note the position of sampling, the state of the producer, the draught, and other factors which may influence the results.

61*a*. *Analysis by Orsat Apparatus.* The Orsat apparatus is used extensively owing to its portability. It consists of a measuring tube surrounded by a water jacket, to which is fused or attached a length of capillary tubing bent over horizontally and provided with four side tubes and gas taps and terminating in a three-way cock. To the taps of the side tube are attached the absorption pipettes. All the rubber connections are made with thick-walled, small-bore rubber tubing, and wired on. The absorption side of the "U"-shaped pipettes are often filled with beads or glass tubes to provide surface, which remains wetted with reagent when the gas displaces the absorbing liquid. In this case great care is required to prevent bubbles of gas remaining trapped in the packing material. If glass tubes are used, they are arranged so that no tube terminates over, or nearly over, the outlet by which the liquid passes to the outer limb. Otherwise there is a risk that gas may pass more rapidly down the inside of the glass tube than the outside and may pass over with the liquid and be lost. A great improvement has been made in the introduction of a spiral gas washing pipette such as that illustrated (Fig. 15). This particular form is cast in a spiral form. The gas passes down an inner tube, bubbles up around the spiral and issues again at the top. By the time the gas has been passed through in this way the absorption is complete.

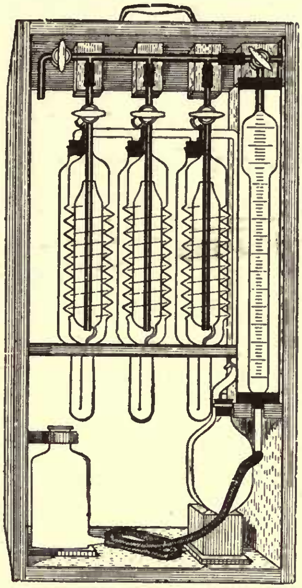


FIG. 15.—SPIRAL FORM OF ORSAT PIPETTE.

The reagents in the pipettes are protected from the atmosphere by attacking small balloons to the neck of the outer limb, so confining the "atmosphere" with which the reagent is in contact.

61*b*. *Method of Analysis.* The pipettes are filled with the same reagents as described for other gas analysis (see **127**), one with caustic potash, one with pyrogallol, and two with cuprous chloride, and are used in that order.

The gas sample may be drawn directly into the tube, allowed a minute or two to cool, and the levelling bottle brought to compress the gas, so that its volume is exactly 100 c.c. The tube of the levelling-bottle is then nipped tightly and the three-way cock opened for a minute to the atmosphere. There should then be exactly 100 c.c. enclosed. This is passed successively two or three times into each of the reagent pipettes and back to the measuring tube; the absorption being noted in each case. Care is required to maintain an even temperature throughout the analysis and to bring the reagent back to some constant mark at the head of each pipette. The liquid used in the burette is made distinctly acid and can be coloured with methyl orange.

The later forms of Orsat apparatus (Orsat-Lunge), such as that illustrated (Fig. 14), are fitted with a small silica tube containing a platinum spiral, which may be used to complete the analysis.

REFERENCES

T. Brooke. Modern Retort Settings. 1918.

W. N. Booth. William Young Mem. Lecture : Efficiency and Maintenance of Retorts. *Gas World*, 1921, **75**, 210.

Burgess and Le Chatelier. Measurement of High Temperature. 1911.

E. Griffiths. Methods of Measuring Temperature. 1918.

W. A. Bone. Coal and its Scientific Uses. (*Producers and Producer Gas.*) 1918.

N. Friend. Combustion. 1922.

Bone and Wheeler. Combustion. *J. Chem. Soc.*, 1902, **81**, 535.

H. B. Dixon. Combustion. *J. Chem. Soc.*, 1886, T**49**, 94.

H. B. Dixon. Combustion of Hydrogen. *J. Chem. Soc.*, 1910, **97**, 661.

C. W. Edwards. Use of Metal Sampling Tubes. *Gas World*, 1922, Cok. Sect., April 1st.

CHAPTER VI

REFRACTORY AND INSULATING MATERIALS

It has been felt for some years that the variation in the quality and size of refractory materials is far greater than necessary. Both the Ceramic Society and the Institution of Gas Engineers, now supported by the Society of British Gas Industries, have appointed Committees for research and co-operation between manufacturers and users. In the past, however, the gas industry has betrayed remarkably little interest in the work of examination and improvement of materials which are a very heavy item in the expenses of gas manufacture. The methods of examination and our knowledge of the behaviour of materials under load are far from perfect, and it is difficult to see how improvement will result until every user examines the properties of his materials and compares their behaviour in practice.

Most of the tests do not require apparatus beyond the means of ordinary laboratories ; most of them may be made sufficiently accurate for comparative purposes at very little cost of time and trouble.

The principal properties which may be examined are size, specific gravity, porosity, contraction or expansion, refractoriness, conductivity, specific heat, and chemical composition.

Size. The importance of uniformity in size has recently been dealt with by G. M. Gill. Examination is merely a matter of measurement. A variation of $\pm 1\frac{1}{2}$ to ± 2 per cent. is allowed in the Institution of Gas Engineers' specification according to the class of material.

63*a. Sampling.* Entire portions of the materials are selected in an haphazard manner. Should the portions be too large for the required tests, two transverse sections are cut from side to side and end to end and used for testing in this form.

Apparent and Real Specific Gravity, and Porosity. These determinations will indicate the texture of a brick. A high porosity will enable a firebrick to stand abrupt changes in temperature, but entails a low crushing strength. As a rule the latter is far above that required, so that it may largely be disregarded. The porosity for retort materials, according to the specification of the Institution of Gas Engineers, should be between 18 and 30 per cent.

63*b. Method.* The sample is cut into small cubes which are dried at 100° C. for 2 hours and weighed. One or more pieces are then placed in a vacuum desiccator and soaked in water, paraffin, or other liquid of known specific gravity for 12 hours at least, under reduced pressure. The saturated sample is then weighed suspended in the liquid ; and after the excess of liquid has been removed from the surface it is weighed suspended in air, while still saturated with liquid. If W is the weight taken dry, W_1 the weight of the saturated piece in air, and W_2 its weight suspended in liquid of specific gravity S, then the

$$\text{Apparent Specific Gravity} = \frac{W}{W_1 - W_2} \times S$$

$$\text{Real Specific Gravity} = \frac{W}{W - W_2} \times S$$

$$\text{Porosity} = \frac{100\,(W_1 - W)}{W_1 - W_2}$$

The methods described in the case of coke (see **45, 46**) may also be used. A volatile liquid like paraffin or xylene will penetrate the pores of the brick quicker and for this reason is preferable to water, which may in fact partially hydrate the material. C. W. Washburn recommends soaking the piece in hot vaseline under reduced pressure. Paraffin wax may be used.

Contraction and Expansion. When a refractory material is heated two classes of alteration in volume are distinguished. There is the difference in volume before and after the heating—in each case measured cold—described by Mellor as the "after expansion or contraction," and the alteration in volume which takes place between the cold and hot states of the material. This latter alteration is reversible and denoted by "reversible expansion or contraction." These alterations in volume affect one another sometimes so far as to cause a reversal of the alteration. The after expansion or contraction should not exceed, according to the English specification: for retort materials, 1·25 per cent; for firebricks, No. 1 grade, 1·0 per cent.; and for No. 2 grade, 1·25 per cent.; for silica and siliceous materials, 0·75 per cent.

64*a*. *Method.* The test-pieces, 4½ inches long and 4½ inches wide, are cut straight across the sample. The opposite ends are ground parallel on a grinding wheel and the length measured by means of a vernier gauge reading to 0·1 mm. Several measurements are taken and the places marked in some way on the brick. The piece is then supported loosely in a gas-fired furnace in a neutral or slightly oxidising atmosphere and heated for 2 hours at a temperature of 1,410° C. for retort materials and firebricks, and of 1,350° C. for silica materials. After cooling the piece is again measured. It is preferable to make the determinations in duplicate on pieces cut in opposite directions. The result is given as a percentage linear contraction or expansion.

64*b*. *Method for Reversible Contraction or Expansion.* This is expressed as the change which occurs when unit length is heated 1° C. It may be measured by fixing two platinum "sight" wires upright on one side a short distance from each end of the test piece. The piece is placed in a cold furnace, levelled horizontally and the distance between the sighting wires measured by a cathetometer through two holes in the furnace door. The temperature is then raised and readings of the cathetometer taken at the desired temperatures.

Refractoriness. The softening, melting, and fusing points of refractory materials are indefinite and may cover a considerable range of temperature. It is better, therefore, to state a temperature range in which the material "softens," "melts," and "liquates." The range is influenced by the atmosphere in which the material is exposed to high temperatures. A reducing atmosphere transforms the ferric oxide present into a ferrous state, when it easily combines to form low-melting silicates. The load or weight of superincumbent mass also reduces the fusion range considerably, especially over a period of time. For these reasons the conditions under which the refractoriness is determined should bear some relation to the purposes to which the material is to be put. To determine the effect of load, a whole brick or section is taken and supported in the furnace in such a manner that a regulated load may be brought to bear by means of a balanced arm. J. W. Mellor has described a special arrangement.

The normal refractoriness, according to the specification of the Institution of Gas Engineers, should not be less than the following : The material should not show signs of failure at cone 28 (1,630° C.) for retort materials ; at cone 30 (1,670° C.) for grade 1 firebricks ; cone 26 (1,580° C.) for grade 2 ; cone 32 (1,710° C.) for silica materials of 92 per cent. or over of SiO_2 ; cone 29 (1,650° C.) for siliceous materials containing between 80 per cent. and 90 per cent. of SiO_2.

65*a*. *Method for Normal Fusion Range.* The behaviour of the material shaped into small pyramids is observed when heated in a furnace of the Hirsch type or a gas-fired furnace of the Deville or Méker types. A furnace packed with retort carbon is described by F. J. Bywater. A loose brick furnace may be built up in the manner already described for determining the fusion range of coal ash, but to stand the higher temperatures the furnace is lined inside with carborundum $\frac{1}{2}$-inch splits or with magnesite powder made into a paste with 10 per cent. dextrin and burnt off. The furnace is more clumsy, but very much cheaper. To obtain temperatures up to 1,800° C., the gas-air burner described is reinforced by a burner taking a gas-oxygen supply. When the highest temperature on gas-air mixture has been reached the oxygen-gas burner is brought into use and the air supply reduced. The test block is always protected from direct impingement of the flame by a refractory muffle or crucible inside of which it is placed. When oxygen is used it is a matter of some difficulty to prevent local heating, and it is a good plan to provide a retort carbon packing so as to distribute the flame. The test cones are made by grinding chips of suitable shape to form pyramids, say, $\frac{1}{2}$ inch diameter at the base and $1\frac{1}{2}$ inches high. Cones made by breaking the brick down and remoulding it may be used, but unless very great care is exercised in retaining the size of grain and the proportion of coarse and fine matter that occurs in the original brick the results will not be the same. Several cones of each brick are used, mounted in a refractory base of magnesia, or other high refractory, made by moulding the powder with dextrin and burning off.

The temperature is increased by about 50° C. every five minutes until the cones bend, begin to lose their shape and finally liquate, the temperature ranges being noted.

The temperature is most conveniently measured by a Féry or Wanner pyrometer in conjunction with Seger cones placed around the test-pieces. Seger cones may be used independently, but probably in this case a preliminary run will be required in order that Seger cones may be selected to cover a small temperature range, including that of the test-piece. Some care is necessary in the use of Seger cones in a reducing atmosphere, as it is possible for the interior of the cone to " run " while the exterior shell bound with a carbon skeleton is left to deceive the operator.

66*a*. *Conductivity*. The conductivity of firebricks can be conveniently compared as described by Dougill, Hodsman, and Cobb, whose apparatus is illustrated.[1] (Fig. 16.) A furnace is built of firebrick, of which the test-piece forms the roof. On this roof is placed a copper calorimeter nearly the size of the test-piece and containing an inner compartment with the base common to the rest of the apparatus. The size of the base of the inner vessel must be accurately measured and may be, say, 4 inches by 2 inches, or 8 sq. in. in area. Each compartment has an outlet at the top, the outer one being connected to a reflux condenser and the inner to a condenser arranged vertically to deliver the condensate to a measuring cylinder. The temperature of the lower and upper sides of the brick below the calorimeter is indicated by pyrometers inserted in shallow grooves cut in the brick, so as to allow the heads to lie flush with the surface in the centre of the brick. The calorimeter is evenly bedded down on to the brick by dipping the under surface in a fireclay mud and slipping on to the brick. Both inner and outer compartments of the calorimeter are partly filled with a liquid, say water, of known latent heat. The under side of the brick is then heated by a gas burner adjusted to give a uniform heating. For lower-temperature work an iron plate may be inserted below the test-brick so as to equalise the temperature. When the conditions have become stabilised, the liquid boiled from the inner compartment is measured over an interval of time, during which the temperatures above and below the brick are noted. The coefficient of conductivity K is given by

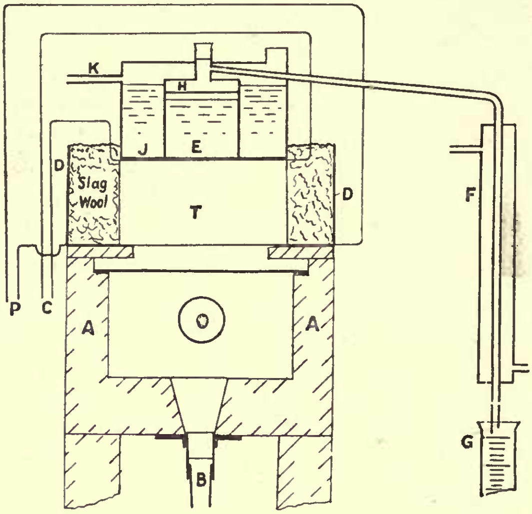


FIG. 16.—APPARATUS FOR DETERMINATION OF CONDUCTIVITY OF FIREBRICK.

$$\frac{Qd}{a(\theta_2-\theta_1)t}$$

where Q is the quantity of heat, i.e. the c.c. of liquid collected multiplied by the latent heat of vaporisation, d is the thickness of the test-brick in cm., a is the area of the base of the inner compartment, θ_1 and θ_2 the temperatures °C. above and below the test-piece respectively, while t is the time in seconds to collect the liquid vaporised.

The conductivity can in this way be measured between considerable limits.

Another method which may be convenient is described under insulating materials. (See **74***a*.)

---

[1] Reproduced by permission of the Society of Chemical Industry.

67*a*. *Specific Heat.* The specific heat of a material can be most easily determined by the method of mixtures. The sample is heated to a known temperature and rapidly transferred to a polished copper calorimeter, or " thermos " flask, containing a known amount of water. The temperature of the water is then noted, as in the usual calorimetric way, and a correction applied for loss by radiation. The water equivalent is determined by using a substance of known specific heat in the same way. A convenient method is to place a weighed quantity of the clean broken material in a silica tube arranged horizontally in a furnace which has a slot in one side to enable the tube to be rapidly tilted to a high angle. The temperature is raised to that desired and maintained for 15 minutes, as measured by a pyrometer inserted down the inside of the tube from the furnace end. The tube is then tilted and the contents shot into a calorimeter which may be rolled up on wheels and which is as rapidly removed from the neighbourhood of the furnace. Stirring is then commenced and temperature readings are taken at half-minute intervals. The corrected rise in temperature of the water is obtained as in the case of the method of determining the calorific value of coal. (See **26***a*.) If T is this corrected temperature, t the temperature of the water before the solid was placed in it, t_1 the temperature to which the material was raised, m its mass, and M the weight of water and water equivalent, then the specific heat is given by :

$$C=\frac{M(T-t)}{m(t_1-T)}$$

67*b*. *Abrasion.* The power to resist abrasion is of importance in the case of retort material where the movement of hard coke leads to wear and tear. Tests are purely comparative and are made with a sand-blast or with a grinding machine running at set speed, against which the test-pieces are thrust with regulated pressure. The loss of weight gives an index to the relative abrasion.

Spalling. The tendency of bricks to break or peel off under alternate rapid heating and cooling is very difficult to measure. Examination is usually of a qualitative character only. Test conditions are as a rule very much more severe than in practice. In the latter case the material is part of a structure and usually heated only on one side. Under test conditions the material is heated at the same time on all sides and much more rapidly. Bricks placed in flues of working settings and left for a few days, removed and quenched, always show bad effects.

67*c*. *Spalling Test.* The following method after Nesbitt and Bell is used by W. Emery and L. Bradshaw. The bricks are dried at 110° C. and weighed. They are then placed in a muffle heated to 700° C. and kept there for half an hour, when they are taken out. One end is immediately immersed to a depth of 4 inches in $1\frac{1}{2}$ gallons of water at 15° C. for 20 seconds. After being allowed to dry in the air for one minute, the bricks are replaced in the muffle and the whole operation repeated eight times. Finally they are dried at 110° C. and after any easily detachable pieces have been removed with the fingers the bricks are again weighed. The percentage loss of weight is calculated as a comparative figure.

Crushing Strength. Examination in this direction is not usually necessary. The Weber machine and method of operation is described by J. W. Mellor.

Microscopic Examination. If a miscroscope is available much information can be secured by an examination of a thin section under transmitted light. The difficulty of obtaining a thin section of soft materials, such as silica brick, by mounting in Canada balsam and grinding down on a glass slide as in petrological work, is very great. In this case a comparatively thick specimen may be treated with balsam on the surface and polished. It is then examined under reflected light. The size and distribution of the quartz grains and other minerals may be noted.

Flue Dust. The effect of flue dust in fluxing refractory materials of almost any description is so great that any test of resistant power in this direction may well be omitted, and attention turned to the problem of eliminating or reducing the amount of dust carried forward. It is obviously somewhat futile to select a refractory material with very high refractory properties, in order to expose it to flue dust which will reduce the melting-point below the limits of inferior brick.

Chemical Composition. Methods of so-called "rational" analysis have largely given way to exact chemical analysis. The properties of binary and ternary mixtures of known chemical composition have been investigated to a very large extent, but the effect of comparatively small amounts of various substances such as are invariably found in practice are usually the deciding factor in the behaviour of the material in practice. The chief constituents are silica and alumina. From a squatting temperature of about 2,000° C. for pure alumina, the squatting temperature for mixtures of pure alumina and silica falls rapidly to about 1,600° C., corresponding to the eutectic mixture containing 10 per cent. of alumina, and then rises abruptly to 1,670° C. for pure silica. Suitable fireclays contain at least 20 per cent. (preferably 30 per cent.) of alumina. Addition of silica is not advisable. On the other hand, in the case of "silica" materials, there should not be more than 2 or 3 per cent. of alumina present. The remaining constituents can to a certain extent be regarded as adding either to the proportion of alumina or of silica, and considerably alter the eutectic point. In this respect it has to be remembered that refractory materials are not homogeneous ; the mass has not been completely fused, and may be said to consist of individual grains of one constituent, usually silica, surrounded by more or less definite compounds of other constituents. Hence the analysis of the average sample may be said to represent a state which will not occur until the material has been liquated. The chief object of a chemical analysis is not so much to determine the composition and probable temperature of complete liquation, but whether there is present sufficient of the low-melting constituents which can be regarded as fluxes, to gradually attack and bring the silica grains into a state of liquation at a temperature below that required in practice. The process is one of solution, and obviously the effect of load on the material will be to shorten the time for solution. Chemical analysis is therefore particularly helpful when the squatting temperature under load has not been determined.

Silica, besides being present in separate grains, also results, with alumina, from the dehydration of the alumino and silico acids constituting the true clay substance. Aluminium silicates containing alkali or alkali earth bases such as soda, lime, potash, form easily melting compounds which attack and, if present in sufficient quantity, will ultimately flux the main portion of the material. Such compounds may be purposely introduced to bind the material together, but this proportion has to be strictly limited and the amount added evenly distributed. Iron is one of the most dangerous constituents, as although ferric oxide may not be in itself harmful, ferrous iron passes with extreme ease into low-melting and mobile silicates, and under the conditions of use, reducing atmospheres are the rule. Any large proportion of lime, soda, or potash is to be avoided, and even titanium is now viewed with suspicion. Typical analyses are shown below :

	Firebrick	Silica Brick
Loss on Ignition	0·15	0·22
Silica, SiO_2	64·35	93·80
Alumina, Al_2O_3	30·62	2·45
Titanic Oxide, TiO_2	1·15	0·41
Ferric Oxide, Fe_2O_3	2·60	0·63
Magnesia, MgO	0·35	0·08
Lime, CaO	0·43	2·36
Potash, K_2O	0·37	0·18
Soda, Na_2O	0·23	0·16

69*a* *Sampling.* It is very difficult to avoid contamination in sampling down a material containing particles of such varying hardness as are found in refractory materials to a sufficient degree of fineness, and every precaution has to be taken to avoid contamination, at least by such substances as iron and alkali, which may, even in small amount, materially affect the result. Two sections are cut transversely across the piece in each direction and are broken to small pieces by tapping with a porcelain pestle in a porcelain mortar. No attempt is made at this stage to break the hard grains unless they are very large indeed, when a diamond steel mortar may be used, as in the case of coke. (See **47***a*.) A magnet may then be passed over the broken powder to remove particles of iron. The powder is sifted through a 10-mesh screen and any large particles left are individually broken down and added to the main bulk. The whole is ground down in a porcelain mortar and passed through a 40-mesh screen before the sample is reduced by coning and quartering. Finally, an agate mortar placed on a sheet of black glazed paper is used till the material has been reduced to an impalpable powder.

69*b*. *Moisture.* Refractory materials are hygroscopic and the moisture varies with the atmospheric conditions. The ground sample is dried at 105–110° C. immediately before use and kept in well-stoppered bottles. The actual loss in moisture is hardly worth recording.

69*c*. *Loss on Ignition.* One gram of the dried sample is heated in a covered platinum crucible over a No. 4 Méker burner at full heat for about 30 minutes, the lid being removed after the first few minutes. After cooling and weighing a further heating is advisable to ascertain if the weight is constant.

69*d*. *Analysis* (*after Hillebrand*). One gram of the dried material, or the residue from the ignition, is weighed in a platinum crucible and mixed with about six times the weight of pure sodium carbonate. It is gently fritted over a burner for 15 minutes. The full heat of a No. 4 Méker is then given for a further 15 minutes, or the fusion may be completed in the oxidising flame of a blast-bunsen. The melt, which should be quiescent and only slightly turbid, is detached by rapid chilling in cold water, or may be spread in a thin cake round the sides of the crucible by a circular motion. The melt is transferred to a tall beaker, covered with water, and hydrochoric acid (sp. gr.—1·1) added in excess to dissolve the melt. The whole is transferred to a porcelain dish and evaporated on a water bath till dry. The residue is moistened with conc. hydrochloric acid, warmed, covered with water, and again heated. It is well mixed with a glass rod and decanted on to a filter. If the residue is lumpy it is broken down with a glass rod in presence of further acid, warmed, and finally the whole is brought on to the filter. The residue is washed with hot dilute acid, followed by hot water till free from chloride. The filtrate is evaporated down in the same basin to dryness and taken up with water and conc. acid as before. It is filtered through a second filter paper and washed. The two residues are ignited at a strong red heat over a large Méker or blast flame for 20 minutes, cooled, and weighed. The residue is moistened with 2 or 3 drops of sulphuric acid (1:1) and about 5 c.c. of hydrofluoric acid. The crucible is gently warmed with the lid on at first and then further heated to expel the silicon tetrafluoride and hydrofluoric acid. After cautious heating the crucible is brought to red heat for five minutes, cooled, and weighed. The difference in the weight, plus the correction to be made for the silica carried forward in the filtrate, gives the total silica.

The filtrate from the silica may be dealt with in either of two ways: by the basic acetate precipitation of alumina, iron and titanium, followed by a second precipitation with ammonia in presence of ammonia salts, or a double precipitation with ammonia may be made. The former is preferable in the presence of any considerable amount of manganese.

(*a*) To the filtrate previously concentrated to about 100 c.c., is added sodium carbonate till the iron is on the verge of being precipitated. About 10 c.c. of syrupy ammonium acetate are added (prepared by taking the solid acetate and adding 0.88 ammonia till the mixture smells equally of ammonia and acetic acid). Addition of filter paper pulp aids in the collection of the precipitate and quickens the filtration. The whole is poured into about 400 c.c. of boiling water and is kept at boiling-point for 5 minutes. The precipitate is allowed to settle, and filtered through a large filter. The residue is washed with water containing a very little ammonium acetate, re-dissolved in hydrochloric acid and re-precipitated by ammonia as in the method described below. Losses of iron and alumina in the first filtrate may be recovered by evaporation to dryness, taking up with water and digestion on the water bath for a short time. The solution is filtered, washed with the filtrate from the second precipitation containing ammonia which has been evaporated to a small bulk. The final washing is made with hot water and the filtrate and residue added to the main filtrate and residue.

(*b*) The precipitation by ammonia is made in the presence of sufficient ammonium salts to keep magnesium in solution. Either 2 to 3 grams of pure ammonium chloride, or the equivalent of a solution of ammonia and hydrochloric acid, is added to the filtrate from the silica which should occupy about 400 c.c. The whole is raised to boiling-point and excess of ammonia added. The precipitate is filtered, washed once or twice with hot water containing a little ammonium nitrate, re-dissolved in a slight excess of hydrochloric acid in the beaker previously used, and again precipitated with ammonia in the same way. The precipitate is then dealt with as below. The loss of iron and alumina in the filtrates can be recovered by evaporating them to a small bulk, adding a few drops of ammonia, filtering, and washing as before.

The residue from the determination of silica, the main precipitate obtained by the basic acetate or ammonia precipitation, and the precipitate recovered from the filtrates from these separations, are combined in the platinum crucible containing the first-named. After slowly burning off the filter papers, the residue is ignited at full red heat for 15 minutes, cooled, and weighed. To the residue is added 6 to 7 grams of sodium or potassium pyrosulphate. The crucible is gradually heated and the heating continued, adding more pyrosulphate if necessary until the whole has dissolved. The melt is transferred to a porcelain dish and dissolved by warming gently with dilute sulphuric acid. The solution is evaporated down on the water bath and then heated on a hot plate till fumes are evolved. On cooling, water is added, and the dish placed on the water bath. The residue of silica is filtered off and treated as in the separation of silica above. The amount so found is added to that already obtained. Any residue is fused with pyrosulphate and dissolved and added to the main filtrate in which the iron and titanium are determined. The recovery of this silica should not be necessary except in very accurate work.

The solution in a conical flask, and containing about 2 per cent. of free acid by volume, is brought to the boiling-point. Hydrogen sulphide is passed in to reduce the iron, the precipitated sulphur is filtered off and the hot solution again saturated with hydrogen sulphide. The reduction being complete the excess of hydrogen sulphide is driven off by boiling in presence of carbon dioxide. When lead acetate paper shows no discoloration the solution is titrated with N/10 or N/50 permanganate.

The titanium is estimated in the solution from the iron determination colorimetrically. The solution is evaporated, if necessary, to about 100 c.c., and sufficient hydrogen peroxide added to develop the whole of the colour (about 20 c.c.). The solution is then diluted to 150–200 c.c., according to the depth of colour, 50 c.c. placed in a Nessler glass and matched against a standard solution in a similar glass. The temperature of the solutions should be about the same. The presence of alkali sulphates and ferric salts interfere. The first is corrected for by sulphates introduced into the standard solution, while the latter is compensated in a similar way by adding sufficient iron to give the solutions about the same concentration in ferric iron.

The standard solution is prepared by fusing 1 gram of pure titanic oxide with 10 grams of sodium or potassium bisulphate. The melt is extracted with water, made up with water and approximately 10 c.c. of conc. sulphuric acid in the cold to 1 litre. The strength may be checked by precipitating portions with ammonia, filtering, igniting, and weighing. One c.c. contains about 0·001 gram of TiO_2.

By deducting the sum of the weights of the ferric oxide, titanic oxide, and silica impurity, found from the total weight of the ammonia or basic acetate precipitate, the amount of alumina is obtained.

Manganese may be precipitated in the filtrate from the alumina and iron after freeing it from traces of alumina and iron that have passed through. To the filtrate is added a few c.c. of ammonia, and hydrogen sulphide is passed in to saturate. The whole is left to stand for some time. The precipitate is collected, washed with water containing ammonium chloride and sulphide. It is then re-dissolved with dilute hydrochloric acid saturated with hydrogen sulphide. After evaporation of the solution with a few drops of sodium carbonate solution to expel ammonia, hydrochloric acid and a drop of sulphurous acid is added to decompose carbonate and dissolve the precipitate. The manganese is then re-precipitated at boiling heat by sodium carbonate, filtered, washed, and dried. The precipitate is turned out on to a tared crucible, the filter paper burned separately in a coil of platinum wire, and the ash is added to the porcelain crucible. The crucible is ignited at red heat and the residue weighed as Mn_3O_4. The manganese may also be thrown down by addition of 1 c.c. liquid bromine in the presence of slight excess of ammonia.

The filtrate from the separation of manganese is raised to boiling-point and excess of ammonium oxalate added to throw out the lime. After vigorous stirring and digestion in a hot place for an hour or so, the solution is filtered, the precipitate washed with a minimum quantity of warm water and re-dissolved in the original beaker with dilute hydrochloric acid. The lime is again re-precipitated with ammonia and ammonium oxalate as before. The precipitate is transferred wet to a platinum crucible, the paper charred off slowly and the residue finally ignited at full red heat for 10 minutes with the lid on. The crucible containing the calcium oxide, CaO, is weighed as soon as cool.

The magnesia is next determined in the combined filtrate by adding a decided excess of sodium ammonium phosphate and raising to boiling-point. Five or six c.c. of strong ammonia are added, and the solution allowed to stand, with occasional vigorous stirring, for some hours. The solution is filtered, washed once or twice with cold water, re-dissolved in a minimum quantity of dilute hydrochloric acid, raised to boiling-point, a few c.c. of phosphate solution added, followed by a similar quantity of strong ammonia solution. With vigorous stirring over a few hours the precipitate becomes granular, and may be collected in a Gooch crucible, dried, ignited, and weighed, or it may be filtered through filter paper, transferred to a platinum crucible, charred slowly and burnt off at low heat till carbon has disappeared. The residue is then exposed to full red heat, cooled, and weighed as $Mg_2P_2O_7$.

Alkalies. The determination is both important and difficult. It is strongly advisable to estimate both soda and potash.

72*a. The Lawrence-Smith Method.* A quantity of 0·5 gram of the dried sample, reduced to as fine a powder as possible, is weighed out and intimately mixed in an agate mortar with 0·5 gram of pure ammonium chloride, and about 2 grams of pure precipitated calcium carbonate. The whole is brushed into a platinum crucible, covered with another gram of the carbonate, and gently fritted over a small flame with the lid on till all ammonia fume has passed away. The crucible is then heated at a low red heat for nearly an hour. After cooling, the sintered mass is moistened and tipped out into an evaporating dish. The crucible is washed out and the mass crushed and digested with boiling water for 30 minutes. The residue, which is discarded, should be completely soluble in hydrochloric acid and show no trace of unattacked mineral. The calcium in the filtrate is precipitated by adding a few c.c. of ammonia and ammonium carbonate, filtered and washed once. The precipitate is re-dissolved into the original vessel and again precipitated hot in the same way. The precipitate is filtered off and the filtrate passed into the main filtrate. The residue is rejected. The combined filtrates are evaporated down to dryness in a platinum basin and ammonium salts driven off by cautiously heating to a dull red heat, or by repeated treatment with fuming nitric acid. On cooling the residue is taken up with a few c.c. of water and the last traces of calcium thrown out with a drop or two of ammonia and ammonium oxalate. The solution is filtered and washed with water containing a little ammonium oxalate. The filtrate is caught in a tared platinum basin, evaporated, and gently ignited. The residue is moistened with water and hydrochloric acid, dried, gently ignited, cooled, and weighed. The residue is digested with water and any residue collected ignited and weighed. The weight is deducted from the weight of the mixed chlorides already obtained.

The solution of the chlorides is concentrated, if necessary, to about 50 c.c. in a porcelain dish, and excess of chlor-platinic acid solution added. When heated on the water bath any precipitate should re-dissolve. The solution is evaporated down till it solidifies on cooling. It is then covered with 80 per cent. alcohol, the larger crystals of the residue crushed as far as possible, and the whole filtered by decantation through a very small filter, and washed with alcohol. The dish and filter are then dried a few minutes, the total precipitate transferred to a weighed platinum crucible, using a little hot water if necessary, and dried with the lid on at 100° C. The temperature is finally raised to 130–135° C. for a few minutes, cooled, and weighed.

This gives the weight of K_2PtCl_6 equivalent to 2KCl. The corresponding amount of chloride deducted from the total weight of mixed chlorides gives the sodium chloride by difference. The chlorides are calculated into and reported as oxides Na_2O; K_2O.

A blank test is necessary.

Insulating Materials. The reduction of heat losses by using compositions and bricks to cover hot surfaces is an important means of economy. As a rule the materials are of a low crushing strength and will not support any material weight. The low conductivity is often ascribed to a high porosity, but the probability is that it is not so much the total volume of pores that is concerned, as their size. Materials with a high total porosity combined with a minimum size of pore seem to give the best results.

The materials may be examined in the same way as given for refractory material. Determinations of the real and apparent specific gravity, the crushing strength and composition are important factors, but the conductivity is naturally the essential point. The method of Darling, as modified by J. S. F. Gard, is most suitable.

74*a. Method—Conductivity.* In the case of pipe-covering, the method consists of supporting a 3 foot length of 6-inch pipe, closed with hemispherical ends, in the centre of a room free from draughts.[1] (Fig. 17.) The pipe is slung so that it is at least 3 feet from the floor and walls. A series of thermo-couples are arranged so as to measure the temperature over the interior of the pipe, at chosen places in the thickness of lagging and on the surface of the lagging. These may be connected to a central switchboard and indicator. The atmospheric temperature of the room is also taken by means of thermometers at different places. Inside the pipe is placed an electrical resistance heating element, which is supported centrally and along the length of pipe. The element may consist of nichrome wire wound on a porcelain core. The current passed through it is measured by an accurate watt-meter. In running the test, the current necessary to obtain the required temperature is selected by trial and adjusted to maintain a constant temperature inside. Half-hourly readings of the watt-meter are made. The current used is equivalent to the heat loss (watts × 0·057 = B.Th.U. per minute) through the walls and lagging, and the amount can be calculated per square foot of surface per hour for a standard thickness and difference in temperature. It is convenient to first estimate in this way the heat loss from the bare pipe and then to cover it with, say, 2 inches of lagging and repeat the test.

The method can easily be adapted to measure the conductivity of brick. The test bricks are built into a rectangular furnace on a well-insulated base, as illustrated. (Fig. 18.) The thermo-couples and heating element are distributed as before, and the test carried out in the same way. The nichrome wire can be used up to about 1,000° C. For higher temperatures still the resistance may be made of "Cutter Hammer bars."

REFERENCES

J. W. Mellor. Hot and Cold Sizes: After Contraction. *Trans. Inst. Gas Eng.*, 1917, 115.

E. Coppée. Contraction and Expansion. *J. Iron and Steel Inst.*, 1913, **88**, 32.

D. A. Jones. After Contraction. *Gas Journal*, 1921, **156**, 498.

F. J. Bywater. Refractoriness—Furnace, etc. *Trans. Inst. Gas Eng.*, 1908, 273.

J. W. Mellor and B. J. Moore. Refractoriness under Load. *Trans. Inst. Gas Eng.*, 1918, 71.

J. W. Mellor, Moore, and Emery. Refractoriness. *Trans. Cer. Soc.*, 1916, **15**, 117; 1917, **16**, 360.

L. Bradshaw and W. Emery. Formation of Graphitic Carbon on Cones. *Trans. Inst. Gas Eng.*, 1921, 337.

J. W. Mellor, Emery, and Scott. Corrosive Action of Flue Dust. *Trans. Inst. Gas Eng.*, 1919, 179.

Dougill, Hodsman, and Cobb. Conductivity. *J.S.C.I.*, 1915, 465.

A. T. Green. Conductivity. *Gas World*, 1922, **76**, 554.

---

[1] The photographs—Figs. 17 and 18—supplied by J. S. F. Gard.

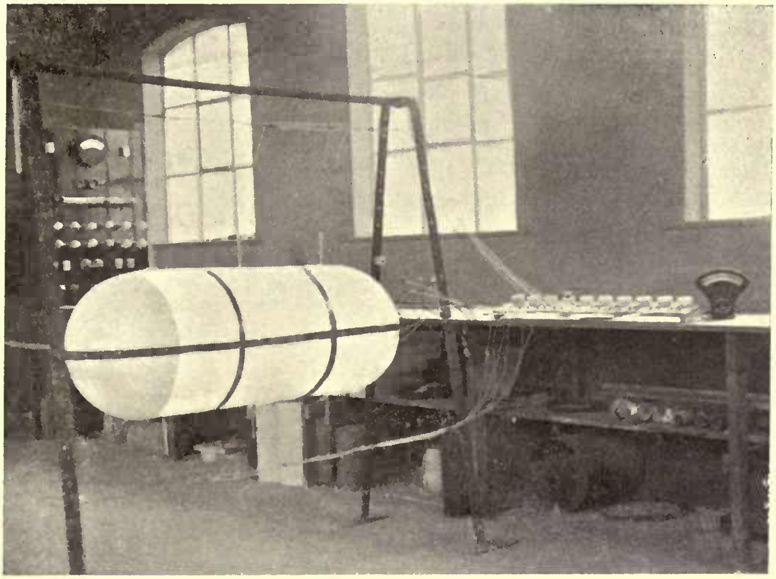


FIG. 17.—METHOD OF DETERMINING CONDUCTIVITY OF INSULATING MATERIAL.

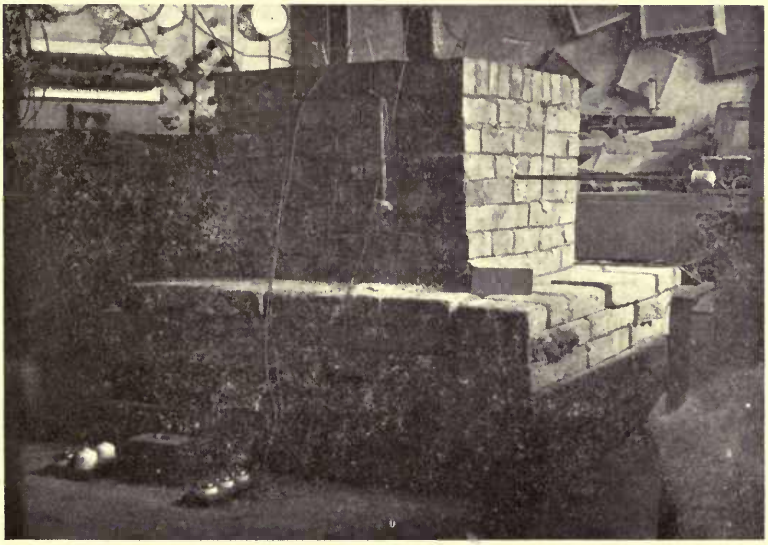


FIG. 18.—METHOD OF DETERMINING CONDUCTIVITY OF INSULATING BRICK.

J. W. Mellor and Committee. Weber Crushing Machine. *Trans. Cer. Soc.*, 1918 ; *Trans. Inst. Gas Eng.*, 1918, 29A.

Refractories Standardization Com. Cer. Soc.—Report. *Trans. Inst. Gas Eng.*, 1918, 1A.

W. Emery and J. W. Mellor. Crushing Strength. *Trans. Inst. Gas Eng.*, 1919, 378.

W. Emery and L. Bradshaw. Spalling Tests. *Trans. Inst. Gas Eng.*, 1920, 98.

W. F. Hillebrand. Analysis Silicate and Carbonate Rocks. U.S.A. Geol. Survey, *Bull.*, 422, 1910.

J. W. Mellor. Treatise on Quantitive Inorganic Analysis. 1913.

CHAPTER VII

TAR

As the temperature of the gases and vapours leaving the retort falls the gas becomes super-saturated in respect of the higher boiling constituents, and they are precipitated as minute globules in the form of tar fog. The gas in passing along the mains meets with surfaces and the globules coalesce to form the liquid tar. Very little is known as to the conditions under which the complex aggregation of hydrocarbons can exist in the vapour state or are carried in suspension in the form of fog. Many of them are not chemically inert, and if additional time, at high temperature, was given the composition of the tar might be altered. Two or more substances which in the liquid state are immiscible, such as benzene and water, can exist together as vapour, according to their vapour pressures, as if they were separate. The only factor to be considered is the temperature. At any temperature the amount of each required to saturate the gas would be known. But the vapour pressure of a substance such as benzene is affected by the presence of another similar substance such as toluene or naphthalene, and therefore the amount of benzene which can exist as vapour in the gas is dependent on the presence of other hydrocarbons. It is less than the amount which could be contained if other hydrocarbons were absent. Owing to the large number of such hydrocarbons, it is impossible, with our present knowledge, to calculate the relative amounts which may exist as vapour in crude coal gas. Other substances, such as ammonia, carbon dioxide, hydrogen sulphide, enter into chemical combination in the presence of water, and are removed in solution, according to the amount of steam condensed and according to their relative solubilities and concentrations.

If a volume of gas was gradually cooled in a single chamber, a condition of equilibrium would be reached ; the composition of the tar and gas would be definite for each temperature provided sufficient time was given. But if the tar was gradually and continuously removed from the system as it was formed a different relationship would be found. In practice, the tar is removed from the gas in stages, and it is easily seen that a sudden chilling of the gas below the saturation point of most of the vapours present will result in gas of different hydrocarbon content than if the gas be cooled gradually. For this reason it is found that tar from water-cooled condensers, operating at the same range of temperature as air-cooled condensers, is of different composition from tar collected from the latter, while the gas at the exit of the former is found deficient in benzene compared with that from the latter.

The lowest temperature attained by the gas does not determine the amount of benzene, say, left in the gas as vapour, since the tar has been separated at various temperatures. Hence, if the average cold tar is circulated through the gas, benzene passes from gas to tar till a final equilibrium is reached depending on the temperature. Previous to the war, in the days of candle-power gas, it was preferable to retain as much of the benzol in the gas as possible. Although benzol has a high calorific value, it does not add so much proportionately to the thermal value as it can add to the candle-power. It is now common to remove it by circulating wash-oil or to reduce it by more drastic cooling.

The temperature gradient of cooling is important, and many difficulties can be avoided by its control. Temperature control starts from the retort mouthpiece onwards. The temperature of the gas leaving the retort is influenced by the volume of gas passing, but rises rapidly with partial stoppage of the ascension pipe, a hanging charge in vertical retorts, or from slow penetration of heat into the charge. The fall of temperature along the collecting main is important in view of the possible deposition of ammonium chloride in the solid state. Although soluble in water, ammonium chloride may deposit, while the gas is at a temperature of over 100° C., before any steam has condensed. It is advisable to encourage the temperature to drop as quickly as possible to below 100° C. It is true that the circulation of tar or liquor will prevent trouble from deposits, but the quality of the washing agent will not be improved by exposure to such temperatures. Tar especially will be depreciated if oxygen is present in the gas.

Provided that sufficient cooling power is available, the temperature at the inlet of the water-cooled condensers may be kept as near 100° C. as possible, so that in the sudden chilling which will result naphthalene may be thrown out as far as possible. The cooling water may even be sent in the same direction through the plant as the gas stream, so that the coldest water will meet the hot gas. Naturally, the efficiency of the condensers will be impaired by this method of working. On the other hand, if benzol washing is in use it is desirable to leave as much benzol to go forward as possible, and as the naphthalene can also be removed by the oil washing, the duration of condensation may be prolonged. Water-cooled condensers may be made to help in the general economy of gas manufacture by using the hot water at the outlet for boiler supply or other necessary purposes. A feed-water supply, at a temperature of, say, 140° F., represents a distinct saving, and up-to-date condenser systems working on counter-current principle will give water at the outlet very nearly as high in temperature as the gas at the inlet.

The temperature of the gas at the inlet of the exhausters is usually reduced to about 70° F. Temperatures over this lead to trouble with the maintenance of even exhausting, and, probably, to an undue amount of tar falling in the scrubbers. In summer the temperature may well be low, but in winter it is preferably kept as high as possible for the benefit of the purifiers. In any case, a considerable amount of light tar will be deposited in the scrubbing system. Usually the gas will rise a few degrees in temperature in passing through the exhausters.

78*a*. *Temperature Indications.* Some definite system of indicating and registering the temperature of the gas at different points of the condensing system is clearly advisable. The common practice of installing a few dial thermometers at odd places is misleading. If ordinary thermometers are installed the bulbs are let into the gas stream about one-third of the diameter of the main. The bulb is best insulated from contact with any metal work, and if a metal protection case is fitted this should also be insulated from the metal of the main so that heat will not be conducted away from the immediate vicinity of the thermometer. It is advisable to use only thermometers of which the glass has been well annealed, as, even at comparatively low temperatures, false readings will otherwise be given after a period of use. "Plug" thermometers inserted in a case let into a pocket in the main are quite useless. The best type is a well-made straight thermometer with the scale engraved on the stem.

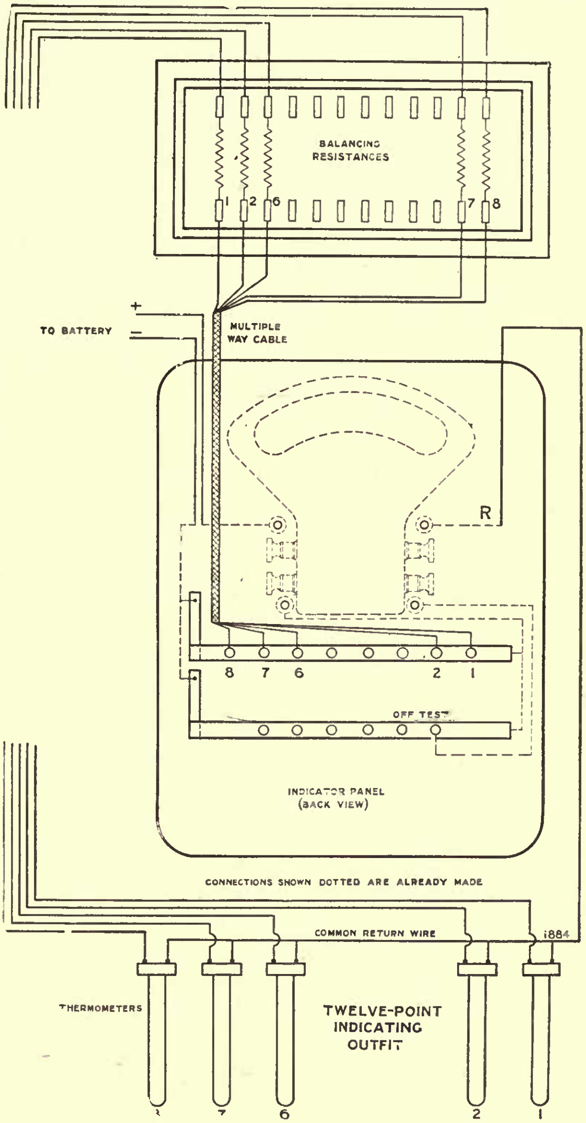


Fig. 19.—Showing Connections of Platinum Resistance Thermometers.

One of the best systems, which is possibly as cheap as any in the long run, is an installation of electrical resistance thermometers. In this type, a platinum wire is wound round and imbedded in a porcelain rod and covered up with a lead or metal tube. As the temperature rises the resistance of the platinum wire increases, and provides an index of the temperature. The resistance is measured by a "Wheatstone Bridge" system, the necessary current being supplied by a small accumulator. The indicator is direct reading. A set of thermometers of any number, none of which are placed at a distance of more than 50 yards or so from a central point at which the indicator is placed, may be coupled to one switchboard. A cable is led from each thermometer head to the board and a common return wire may be used to complete the circuit (Fig. 19).

The cable on long distances becomes the expensive item, but the upkeep is practically restricted to the expense of maintaining the accumulator. Recording instruments can be added if desired. Such an installation avoids the necessity of going round at stated intervals to read thermometers, and the thermometer heads may be placed without regard to their accessibility. Fig. 20 shows a 50-point outfit by the Cambridge and Paul Scientific Instrument Company, Ltd.

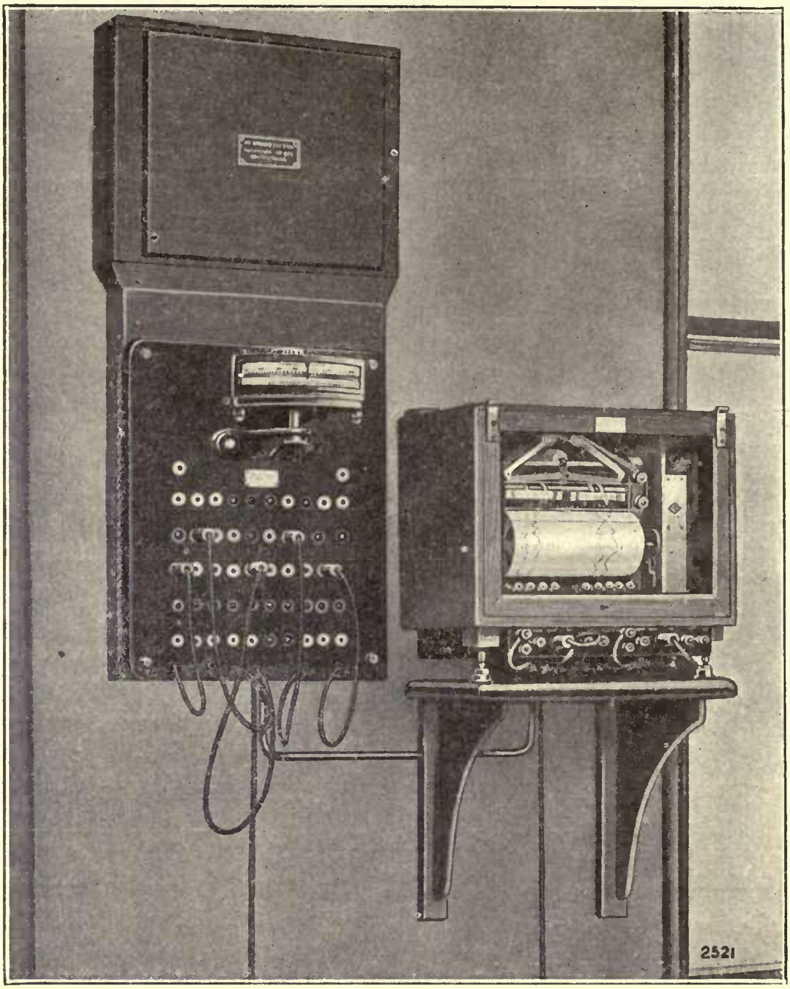


Fig. 20.—A 50-point Resistance Thermometer Installation.

Individual mercury thermometers of recording types are expensive, but are used for registering temperature at special points, such as at the meters. The records may be averaged by placing down the average for each hour, as seen by inspection, adding and dividing to obtain the average, say, for 24 hours. Otherwise the temperature readings are made at specified intervals, say, every 3 hours.

Tar Fog. In condensation, where contact is not intimate, the small globules of tar may be carried very considerable distances without deposition. Under static conditions slow coalescence occurs and drops become sufficiently large to separate as liquid. The rate at which the deposition occurs can be encouraged electrostatically, or by forcing the gas through small interstices or dividing it by a fine spray of liquid. Tar fog is particularly detrimental if carried as far as the purifiers, and it is a great hindrance to the extraction of ammonia.

81*a*. *Method of Estimation of Tar Fog.* One method consists in allowing the gas to pass through a standard-sized jet, so as to impinge on a piece of white test-paper for a certain duration of time. The colour of the jet is then compared against a set of standard colours. Special forms of "tar cameras" have been devised for the purpose.

Different descriptions of tars give different stains. Water gas and creosote oil give yellow to brown stains, not unlike that shown by a trace of hydrogen sulphide on lead acetate paper.

The estimation may also be made by filtering the gas through cotton- or glass-wool and obtaining the increase in weight. The chief difficulty is to prevent moisture (which is intimately connected with the formation of tar fog) from condensing and adding to the figure obtained. Skirrow and Clayton place a wide tube, sealed at one end and with a hole in the side $\frac{1}{3}$-inch from the end, into the gas main, with the hole facing the direction from which the gas is flowing. A plug of cotton-wool lies in the tube behind the hole and is in that part of the tube which is in the main. It therefore attains the same temperature. Gas is then allowed to pass through the tube and is measured. The tube is removed when sufficient gas has passed, and is wiped clean. The tarry cotton-wool is extracted with carbon-disulphide in a Soxhlet extractor. The carbon-disulphide is evaporated off at a low temperature, and dry coal gas passed through the flask to remove the last traces before the residue is weighed. The result is low, owing to loss of the free carbon and of the more volatile portion of the tar.

According to Feld, a weighed U-tube, with cotton-wool, may be used instead, through which dry gas of the same hydro-carbon content as the test gas, but free from tar fog, has been passed to saturate the cotton-wool and tube with vapours before weighing. This is then connected to the gas supply and a measured volume used. After the absorption dry gas is again passed through till the weight is constant. The difference in weight then gives the tar fog.

In the case of a heavy tar content, it is sufficiently accurate to scrub a measured volume of the gas in a tared absorption bottle containing a nearly saturated solution of salt, which is immersed in a vessel of water 2° or 3° C. above the temperature of the gas in the main.

81*b*. *Naphthalene in Crude Gas.* ("*Metro.*") It is important to check the content of naphthalene in the gas at various points. The naphthalene is absorbed in acetic acid and subsequently precipitated by excess of picric acid. In presence of more than, say, 10 grains of ammonia per 100 cubic feet, this is first removed by a wash-bottle containing a concentrated solution of oxalic acid, which is kept at about 80° C. during the test. This is followed by two absorption vessels, each containing 180 c.c. of 30 per cent. acetic acid, and finally a guard tube, with picric acid solution, before the gas is measured. The inlet connecting tube to the first bottle may be washed down into the bulk if necessary. When the required amount of gas has been passed the solution is washed out and the naphthalene precipitated by addition of excess of picric acid solution. The picrate is then filtered, washed, decomposed with hot water, and the acid released titrated with N/10 caustic soda, as described later. (See **143***a*.)

Absorption of Oxygen by Tar. An extremely high pitch content in tar is due to partial oxidation. Cold liquid tar will absorb several per cent. of its weight of oxygen quite readily. Part of the oxygen combines with the hydrogen of the tar constituents and forms water, part remains in combination to be eliminated later as water on distillation. The elimination of hydrogen in this way leaves the carbon content of the tar more concentrated and raises the amount of pitch present. Oxidation is greatly accelerated by rise of temperature. The oxygen content of the gas is therefore to be kept low, and air required for revivification of oxide at the purifiers is not admitted until after the tar has been removed from the gas.

Owing to the difficulty of detecting small leaks of air into gas under vacuum, more air gains admittance in this way than is commonly supposed. To check leakage of this sort samples of gas may be taken simultaneously at different points of the condensing system, when the content of nitrogen will indicate if the gas is gathering air as it passes through. A suitable sampling arrangement has already been described. (See **37***a*, **38***b*.) The method also leads to the discovery of plugs inadvertently missing, or of cocks left open.

Even when the crude tar is dispatched to external tar distillers a complete analysis from time to time is very advisable, as it provides not only an index of the quality of the tar, but incidentally provides very valuable information as to the conditions of carbonisation.

82*a*. *Sampling Tar.* It is comparatively easy to sample tar, provided that no information in respect to the quantity of liquor contained is required. But usually this is one of the purposes of the sampling. Sampling from a seal-pot is impossible. The sample has to be withdrawn from a running stream or tapped off before the seal-pot. If the flow is a continuous one, and a sample under the particular conditions obtaining at the time only is required, a large bucket is inserted in the stream or under a branch sampling pipe, so as to receive, if only for a few moments, the whole of the tar stream. The bucket of tar is withdrawn and the contents mixed by vigorous stirring. A pot is then dipped in while the stirring is continued, and emptied into another receptacle. This is repeated several times so as to take about one quarter of the contents. If the portion so selected is still too large, it is stirred and reduced in the same way.

Where the composition of the tar varies from time to time, and an average sample is required, the operations detailed above are repeated at intervals, each bucket being "quartered"; the "quarters" mixed and the reducing continued as necessary.

Sampling from bulk is best avoided, whenever possible, as a large volume cannot be stirred. Liquor in storage wells gives especial trouble as it floats about in large masses, sometimes at considerable depths below the surface. Where sampling has to be carried out under these conditions a syphon pump may be used to withdraw a considerable amount from each of many equidistant depths, say 12 inches apart. The portions so collected are then quartered as before. A " dipping tube " may also be used. This consists of a 1-inch diameter tube, with a valve at the lower end, which can be operated from the opposite end to close the tube. The tube, with the valve open, is lowered very gradually to the bottom of the tank ; the valve is then closed and the tube withdrawn and emptied into a bucket. This is repeated several times at different places until an adequate sample has been obtained. The method is sometimes liable to considerable error, as liquor will rush into the tube much quicker than tar, and the relative proportions depend to a certain extent on whether tar or liquor " wets " the surface first.

The same considerations apply to the sampling of small tanks, such as railway tanks, but the matter is more complicated by the boundary surfaces. The illustrations will convey an idea of the problem. Fig. 21A is the result of pouring tar into a vessel containing water ; Fig. 21B shows what happens when liquor is poured on to tar. It is obvious that samples by dipping will not be representative in either case. It is always better to sample tar as it is being run off or pumped into tanks. In a case where a large quantity of liquor has separated, as often happens during transport, the separated liquor is dipped to ascertain the depth, and the amount is calculated from the shape of the tank by drawing the latter on squared paper, allowing for the curvature of the surface due to the surface tension of the liquor. For dipping, a soft wood dipping rod is used, which is well soaked with paraffin. The tar will then adhere and mark a fairly clear division.

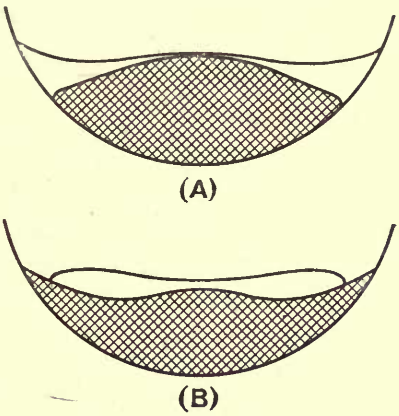


Fig. 21.—Showing Boundary Surfaces of Liquor and Tar.

83*a*. *Estimation of Water in Tar*. The sample on standing may show a considerable separation of liquor, in which case the latter is removed and measured. The total weight of the sample being known, this liquor is returned as " Separated Liquor " per cent. on the sample as received. The remainder of the sample is vigorously stirred for at least 5 minutes and a quantity of not less than 250 c.c. poured off into a distillation retort. The container is then weighed back to ascertain the weight of tar taken. Glass flasks and glass retorts are often used, and the tar is distilled with an equal volume of benzene or other hydrocarbon to increase the volume of distillate and carry the water over at a lower temperature ; but it is certainly preferable and far less dangerous to use a metal vessel which is not tapered or constricted in any way between the level of the tar and the lid of the vessel. The portion of the vessel above the tar should contain a volume of air space equal to the space occupied by the tar. Colman's still or the modification of the author is suitable. Both are constructed of steel with welded joints. Carbon deposits can be easily removed by placing the retort body on a coke brazier when the necessity arises. In Colman's still (Fig. 22*a*) the ring burner is adjusted just below the level of the tar at the start, so that top distillation is given while the water is present. As distillation proceeds the ring is lowered and a burner at the bottom also lighted. To prevent overheating in the vapour space it has been suggested that a steam jacket, containing a little water, could be placed round the outside of the upper part of the still.

In the second modification the burner is placed underneath, near the elevated end of the still, so that at the start only a small layer of tar is heated, and as distillation proceeds the burner is shifted towards the lower end. An asbestos cover is placed over the top of the still to hang down. It is kept from touching the sides by a little packing. This affords protection from draughts, while the products of combustion circulate between the cover and the retort body. Local heating is thereby avoided.

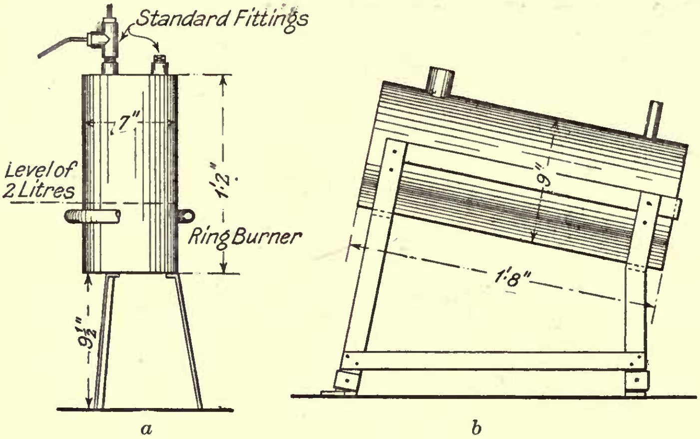


Fig. 22.—Laboratory Tar Stills.

In distilling heavy tars containing water it is important to avoid local heating, as something akin to an explosion may occur. The flame from the burner is only sufficiently aerated to prevent it from being luminous and depositing soot.

For accurate work air is removed from the retort by an inert gas.

The tar having been introduced, the water and naphtha are distilled off through a small splash bulb and efficient condenser. The distillate is collected in a dry, tared conical flask. The distillation is continued for some time after the "crackling" has ceased, when the tar settles down to quiet distillation. At about 180° C. the water will usually have all passed off. A few c.c. more of distillate are collected and examined for traces of water.

The weight of distillate is then ascertained, the water separated and weighed, and the naphtha poured back into the cooled residue in the retort. A good specimen of coal tar should not contain over 5 per cent. of water.

84*a*. *Specific Gravity*. Tar is usually bought and sold by weight, but is handled and stored on the works in gallons. The specific gravity is therefore of importance, and will be required not only of the tar as sampled, but also of the dehydrated tar. It is usually determined by means of hydrometers, which give sufficiently accurate readings if the temperature is adjusted. The tar must be well mixed. Hydrometers of the long stem type are used, giving a difference in the readings of the upper and lower marks of 0·1 units. The dehydrated tar should, strictly speaking, contain the naphtha which is returned after the distillation, but frequently the specific gravity of the residue left in the retort without the naphtha is given.

The specific gravity may also be obtained by use of the Westphal balance or by weighing in a small pipette—provided with ground-glass stoppers at each end—into which the tar can be sucked to the graduation. Horizontal retort tar has a specific gravity of about 1·20 ; vertical retort tar 1·15 (dehydrated).

85*a*. *Proximate Analysis.* As nearly as possible, 1 gram of dehydrated tar is weighed exactly into a platinum crucible covered with a lid and cautiously heated until the volatile matter has been driven off. It is then maintained at a full heat for 5 minutes, cooled, and weighed. The coke is burnt off and the ash weighed.

85*b*. *Calorific Value.* A bomb calorimeter is employed, as in the case of coal or coke. (See **26***a*.) About 0·8 gram of tar is exactly weighed into the crucible in which has been placed 1 or 2 grams of kieselguhr or precipitated silica. If the weight taken is not too large, the combustion will be complete. Allowance is made for the inert matter used by adding a correction to the water equivalent.

85*c*. *Sulphur.* The total sulphur may be determined in the bomb washings (see **23***a*), or as in the Eschka method (see **23***b*), weighing the tar into a tall crucible of narrow diameter, covering with magnesia or lime, and inverting into a dish. The crucible is then packed round with magnesia or lime. The crucible is very cautiously heated at first from the top downwards.

85*d*. *Ammonia and Chlorine.* About 20 grams of tar are washed with water by decantation until the washings are shown to be free from ammonia. The washings are made up to 250 c.c., of which, say, 50 c.c. are taken for the ammonia determination (see **93***d*) and 100 c.c. for the chlorine (see **95***a*).

85*e*. *Free Carbon.* A filter paper is washed with benzene (toluene or xylene may be used) followed by alcohol and dried in a water oven and weighed. About 5 grams of the well-mixed and dehydrated tar are accurately weighed out and mixed with about 200 c.c. of benzene, or other solvent, in a conical flask. The whole is boiled for 2 hours under a reflux condenser and is then filtered hot through the prepared filter paper. The residue is washed with hot benzene till clean. Particles of carbon in the flask are chased on to the filter with a glass rod having a small cork at the end. The washing is finished by using hot alcohol and the filter paper and carbon are dried and weighed. The filter paper, with the precipitated carbon, may be placed in a Soxhlet extraction apparatus and extracted with carbon-disulphide after the benzene, instead of alcohol. In this case, a piece of cotton-wool will have been weighed with the filter paper, and is used to close the aperture of the filter paper cone, the edges of which are turned over. If the tar is placed directly in a " thimble " and extracted, the results are inaccurate ; the free carbon should be precipitated first by an excess of benzene. The free carbon ranges from 5–8 per cent. in vertical retort tars, up to 15 per cent. in horizontal retort tars.

Separation of Pitch and Tar Oils by Precipitation. Ab-der-Halden has pointed out that the pitch constituents are thrown down when petroleum oil is added to a solution of tar. It is necessary, however, that the tar should be dissolved in a tar oil—say, benzene—and the free carbon precipitated before the petroleum oil is added. In fact, it appears that it is largely the free carbon which keeps the pitch in liquid form.

A method of examination which has much to recommend it consists in dissolving the tar in benzene, removing and estimating the free carbon as detailed above. The pitch oils are then separated from the tar oils by adding an equal volume of petroleum ether. On warming slightly the pitch coagulates. The liquid products can then be decanted, and the pitch washed with a mixture of equal volumes of petroleum ether and benzene, pressed, dried, and weighed. The ether and benzene may be removed from the tar oils by evaporation and the residual tar oil examined.

86*a. Primary Distillation.* Since the presence of water influences the temperature at which tar compounds will distil, the assay of tar by distillation is carried out on the dehydrated tar, prepared as already described, to which the naphtha has been returned. Between 3 and 4 litres is a convenient quantity, and is poured into the retort from a container, which is then weighed back to ascertain the weight of tar taken. The tare weight of the retort should also be known, so that any residue left from pouring off the pitch can be allowed for.

Little trouble will be experienced in distilling the tar from which the water has already been removed. The rate is maintained at about 15 to 20 c.c. per minute. A straight-through 24-inch Liebig condenser will be needed, and this is furnished with a T-piece on the water inlet at the base, so that the condenser can be entirely drained off from water when the naphtha has been removed. The distillates are collected in tared conical flasks to the following temperatures taken with the thermometer bulb in the vapour :—

Naphtha . . .	0–180° C.
Light oil . . .	180–230° C.
Creosote oil . . .	230–280° C.
Anthracene oil . .	280–350° C.

The receiving flasks are changed without interrupting the distillation. As soon as the naphtha fraction has come over the condenser is drained so as to allow the distillate to enter the flask at about 40° C. Trouble with stoppages in the condenser will not occur unless the distillation is interrupted. The remarks already made as to the necessity of using a voluminous flame and avoiding local heating are very important.

When the distillation is finished the flasks are weighed. The specific gravity of each fraction is then obtained at a few degrees above the temperature at which each is liquid. The results can be calculated in per cent. by weight and in gallons per ton. The pitch from the retort is run off as soon as it has cooled sufficiently into tared metal pans previously rubbed over with chalk. The pans are allowed to cool and are weighed. The retort itself is then checked for residue. The total loss on distillation should not exceed 0·5 to 1 per cent.

Examination of Primary Products. A further examination of the distillation products is necessary to appreciate the value and composition of the tar.

87*a*. *Naphtha. Fractionation.* The naphtha obtained is separated from water, dried by adding a lump or two of calcium chloride, and filtered through a clean funnel containing a small plug of cotton-wool. A volume of not less than 100 c.c. is distilled through a 12-bulb Young, or other efficient fractionating column, at a rate of 7 c.c. per minute, till the thermometer on the column outlet shows 180° C. The distillation is then stopped. Without interrupting the distillation, the volume of distillate is noted at each 10° C. rise in temperature, starting from the " drop point," say, when 0·5 c.c. have passed over. The residue may be counted as light oil and the distillate as crude benzol. The latter may be further examined for its content of benzene, etc., by the methods described later. (See **139**.)

Distillation Range. It is common practice to determine the distillation range (boiling-point) of naphtha and other products without fractionation. Sometimes a distillation flask is used and sometimes a glass retort. The former gives more consistent results, and is preferable; but to avoid confusion, the apparatus used should be named in reports.

87*b*. (a) *Flask Method.* One hundred c.c. is distilled in a 250 c.c. flask, with thermometer in the vapour space just below the level of the outlet tube. A rate of 7 c.c. per minute is maintained. The apparatus shown (Fig. 23) is convenient. The condenser is of the double surface type, a tube through which water flows being held centrally. There is less likelihood of naphthalene stoppages with this form.

87*c*. (b) *Retort Method.* A special form of glass retort is used, holding about 280 c.c. There is a contracted " sump " at the base, so that the distillation may be carried to the last few c.c. A thermometer with a small round bulb is used, and is placed to stand vertically in the liquid $\frac{3}{8}$-inch from the bottom of the sump. It is always immersed. The graduations on the stem start sufficiently high to bring the range from 60° C. upwards outside the retort. Distillation is carried out at the rate of 7 c.c. per minute, and the volume of distillate noted for each 10° C. rise without interruption of the distillation. Where accurate work is demanded, the thermometer readings are corrected for barometric pressure, in addition to the usual correction to the National Physical Laboratory standard. (See **140***a*.) The drop-point is also noted, and may be conveniently taken when 0·5 c.c. have collected, as the temperature corresponding to the first drop coming over is uncertain.

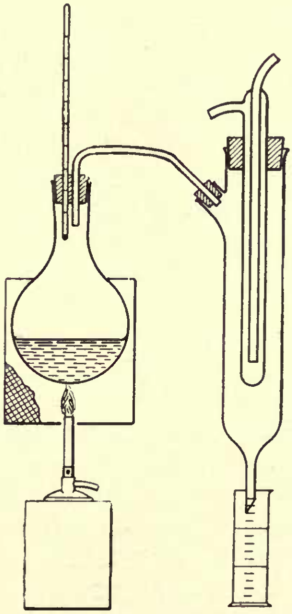


Fig. 23.—Apparatus for Determination of Boiling-point Range.

88*a. Tar Acids and Bases.* The distillate from the above is kept sufficiently warm to keep the whole liquid. It is shaken gently with three or four successive quantities of about 15 c.c. of 15 per cent. caustic soda solution (sp. gr.=1·2)-until the washing liquid is free from phenol when acidified. The combined washings from the separating funnel are placed in an evaporating basin and digested on the water bath till traces of oil have disappeared and the smell is clean. Alternatively the solution is shaken with 60 c.c. of petroleum ether in a separating funnel and the ether layer removed. The ethereal solution is washed with a few c.c. of soda solution. The washings are added to the main phenate solution. The whole is then gently warmed to remove residual ether vapour.

The pure solution of phenate (and cresylates) is cooled in a measuring cylinder diluted with water so as to measure 30 c.c. and acidified with sulphuric acid (sp. gr.= 1·3). The acidification is performed with a continuous stream of cold water running down the outside of the cylinder. The crude tar acids which separate are then measured in the cylinder and returned as per cent. by volume. If required, the tar acids may be collected and 100 c.c. distilled, with or without fractionation, to determine the approximate composition. Whereas the carbolic acid used to be the only tar acid of commercial value, the cresylic acids now are of almost equal value.

The residual oil left from the alkali washing may afterwards be washed in a similar way with dilute sulphuric acid (sp. gr.=1·3) in quantities of 10 c.c. at a time, till the last wash on neutralising with conc. caustic soda gives no appreciable odour of pyridine. The combined washings are made alkaline in a measuring cylinder with conc. caustic soda and the volume of separated pyridine oils measured.

Light Oil. The light oil fraction may be examined in much the same way as the naphtha. In addition, the amount of separated naphthalene, the total naphthalene content, and the crystallising-point may be required.

88*b. Separated Naphthalene.* The value of an attempt to estimate separable naphthalene salts is doubtful. Even if the salt so separated could be freed from adherent oil and weighed without loss, the tendency of tar oils to hold naphthalene in super-saturated solution makes it almost impossible to get two determinations even approximately the same. Naphthalene continues to separate for some time after the first deposition, and separates to a greater extent after the tar acids are removed. The usual method is to maintain the oil at 15° C. for several hours with occasional agitation. The solid is then filtered off with the aid of a vacuum pump through a Büchner funnel in fine filter cloth. The residue is pressed for 12 hours between filter paper and the resultant cake weighed.

88*c. Total Naphthalene.* The picric acid method gives, as a rule, somewhat high results, but is the most accurate method known. The fraction of oil distilling between 200° C. and 300° C. is weighed in a beaker. It is then mixed and warmed till all is in solution. About 0·5 gram is accurately weighed out into a small beaker and a few drops of glacial acetic acid is added. The mixture is poured drop by drop into a beaker containing 500 c.c. of a nearly saturated solution of picric acid. The whole is stirred and the small beaker washed out with a few more drops of glacial acetic acid. The whole is allowed to stand for an hour or so, and is then filtered, washed with the picric acid solution till free from acetic acid, and then once with water which has been used to rinse round the beaker. The precipitate and filter paper are transferred to the original beaker, which need not have been completely cleared of precipitate so long as it is free from acetic acid. About 250 c.c. of water is added, and the solution warmed to decompose the picrate. The free picric acid is then titrated with N/10 caustic soda, using phenolphthalein as indicator. Naphthalene picrate is easily decomposed in air, and the precipitate should therefore not be left uncovered while washing. (See also **143***a*, **144***a*.)

One molecule of naphthalene combines with one molecule of picric acid, which is a monobasic acid. Therefore 128 parts of naphthalene are equivalent to 40 parts of caustic soda.

The amount of naphthalene found is calculated on the total 200–300° C. fraction, and then represents the amount on the oil taken for distillation. From this volume and its specific gravity the amount can be calculated on the tar.

89*a*. *Crystallising Point.* The point at which solid begins to separate can be conveniently determined in an apparatus consisting of a test-tube of about 5 inches long, fitted into a slightly larger one about 7 inches long. The space between forms an air-jacket. A thermometer reading to 0·2° C. is placed in the inner tube along with a stirrer of bent copper wire. The thermometer bulb comes about 2 inches below the water-line when the whole is placed in a beaker of water which forms the cooling vessel. The oil is dried over calcium chloride and placed in the inner tube to fill the latter two-thirds full. It should be two or three degrees above the crystallising point when placed inside. Cold water, or a mixture of ice and water, is placed in the outer beaker, so that the tubes are gradually cooled. The thermometer is observed without stirring until it ceases to fall. The oil is then stirred vigorously, when the thermometer reading will rise. The highest temperature reached is taken as the crystallising-point.

Creosote Oil. The examination is made by the methods already given for the other fractions. The distillation range between 200 and 300° C., the content of tar acids, the naphthalene content and crystallising-point are the most important determinations.

89*b*. *Anthracene Oil.* The examination is made as already described for other fractions, except that the distillation is carried up to 350° C. The anthracene may be determined as follows :—

The anthracene oil is allowed to crystallise at 60° F. for 24 hours, and is then filtered through fine linen cloth. The residue is pressed as dry as possible by hand and is then left between filter paper overnight. The crude cake is weighed, ground-up, and a portion taken for analysis by the Luck-Hochst method. One gram is weighed out into a 350–400 c.c. round-bottom flask and 45 c.c. of glacial acetic acid is added. The flask is connected to a plain vertical condenser tube about 75 cm. long. The flask is heated to simmering-point and a mixture of 15 grams of chromic acid crystals in 10 c.c. glacial acetic acid and 10 c.c. of water is gradually added over a period of 2 hours. Care should be taken that no vapour escapes the condenser tube. After standing, say, 12 hours, the flask is rinsed out with 400 c.c. water into a beaker. After settling the anthraquinone is filtered off and washed, first with cold water and then with water made slightly alkaline and used hot, till the filtrate is clear on acidifying. The washing is then finished with pure hot water till free from alkali. The residue is transferred to a small porcelain dish, using a little water, and dried at 100° C. Ten grams of fuming sulphuric acid (sp. gr.$=1{\cdot}88$) are added, and the dish heated to 100° C. for 10 minutes on the water bath. After standing in a damp place to dilute, about 200 c.c. of cold water are carefully added. The anthraquinone is filtered off and washed as before. The residue is transferred to a tared porcelain dish and dried at 100° C. to constant weight. The anthraquinone is then volatilised by gently heating the dish over a naked flame and the residue is weighed back.

The difference of the weights gives the anthraquinone, $C_{14}H_8O_2$, corresponding to the anthracene, $C_{14}H_{10}$ in the crude salt taken.,

It may be mentioned that a " unit " of anthracene is $\frac{1}{100}$ cwt., or 508 grams of pure anthracene. The " A " quality of commercial anthracene contains 40–45 per cent. pure anthracene and the " B " quality 25–40 per cent.

Pitch. The quality of the pitch is determined by the specific gravity, melting-point range, and ash content.

90*a*. *Specific Gravity.* The sample is ground up as fine as possible, or if it softens too easily it may be melted and cooled slowly, so as to preclude the possibility of any air bubbles remaining in the pitch. The ground-up pitch is melted in an iron dish and cooled till viscous. It is then moulded to form a lump, suspended by a very fine thread to the arm of the balance and weighed. It is afterwards weighed in water, when the specific gravity may be calculated. (See **45***a*, **46***b*.)

90*b*. *Melting-, Twisting-, and Softening-Points.* A piece of the sample of pitch is moulded to form a block 2 inches by ½ inch square, and is suspended in water over a porcelain dish by means of a wire thrust into it while the wire is hot. The water is heated at a constant rate of 2° C. per minute, and as the softening-point is approached it is taken out for an instant and an attempt made to twist it. The point at which the pitch gives at once to the fingers, without appreciable force being applied, is taken as the twisting-point. The heating is then continued, and when the pitch, as suspended, begins to lose its shape, the temperature is read as the softening-point. When the pitch drops off the wire as a fluid mass the melting-point is reached.

Spielmann and Petrie suggest a method which consists of suspending a block of the pitch 1½ inches long by ½ inch square by a wire in such a way as to form an " L." The lower arm of the " L " is formed by the block of pitch. As this is heated and the pitch softens the block falls over, and ultimately comes into line with the vertical arm. The temperature at this point is taken as the softening-point.

90*c*. *Volatile Matter and Ash.* One gram of the finely powdered sample is weighed out into a platinum crucible, covered with the lid and gently heated over a Bunsen in a draught-cupboard until the main bulk of volatile matter has been removed. It is advisable not to allow the gas evolved to catch fire, or dense clouds of soot will be formed. The crucible is finally heated over the full force of a Méker burner for 5 minutes, removed, cooled, and weighed. Loss is the volatile matter. The coke is burnt to ash and the crucible again cooled and weighed to obtain the weight of ash.

REFERENCES

Steere. Tar Camera. *Gas Journal*, 1922, **157**, 36.

Dougill. Condensation. *Gas World*, 1918, **68**, 269.

G. T. Purves. Fractional Condensation. *J.S.C.I.*, 1915, 329.

W. G. Whitman and J. L. Keats. Absorption and Heat Transfer. *J. Ind. and Eng. Chem.*, 1922, **14**, 186.

Skirrow and Clayton. Tar Fog. *Gas Journal*, 1907, **98**, 660.

A. Edwards. Estimation of Tar Fog. *J.S.C.I.*, 1918, 35T.

Ab-der-Halden. Precipitation of Tar Oils. *Gas Journal*, 1913, **123**, 46.

J. M. Weiss. Analysis of Coal Tar Products. *J. Ind. Eng. Chem.*, 1918, **10**, 732, 817 ; 911.

J. C. Mann. Temp. of Deposition of Naphthalene Apparatus. *J.S.C.I.*, 1910, 732.

P. E. Spielmann and G. C. Petrie. Softening-Point of Pitch. *J.S.C.I.*, 1919, 68T.

H. G. Colman and Yeoman. Analysis Crude Benzol, etc. *J.S.C.I.*, 1919, 57T, 136T, 152T.

W. J. Jones. Freezing-Point Method. *J.S.C.I.*, 1919, 128T.

G. Lunge. Coal Tar and Ammonia. 1916.

G. Malalesta. Coal Tars and Derivatives. 1920.

S. E. Whitehead. Benzol, Recovery, etc. 1920.

P. E. Spielmann and E. G. Wheeler. Analysis Benzol, etc. *J.S.C.I.*, 1916, 396.

P. E. Spielmann and Butler Jones. Carbon-Disulphide in Benzol, etc. *J.S.C.I.*, 1919, 185T.

Brégéat. Cresols for Benzol Recovery. *Gas Journal*, 1920, **149**, 364 ; 432.

CHAPTER VIII

AMMONIA

The recovery of ammonia is dependent in the first place on the conditions of carbonisation. Although it appears to be possible under certain conditions to obtain as ammonia practically the whole of the nitrogen combined in the coal, it is very rarely that more than 20 per cent. is actually recovered and worked up to sulphate of ammonia. The bulk of the nitrogen remains in the coke, from which it is apparently impossible to entirely remove it without complete gasification. Conceivably the nitrogen is liberated from the coal in the form of basic compounds similar to, and largely consisting of, ammonia, but secondary reactions reduce the amount in this form by the formation of cyanogen compounds and free nitrogen. Low temperatures during carbonisation are not conducive to a high evolution of ammonia, nor is ammonia present to any great extent in that portion of the gas which is liberated on the cooler side of the plastic zone. On the other hand, exposure of the gas to hot coke or radiant heat leads to excessive loss by the decomposition of the ammonia. Steaming the charge, and dilution of the gas with water vapour and hydrogen increase the amount recoverable.

Of the ammonia passing as such to the foul main, a considerable portion of that combining with hydrochloric acid is lost in pitch deposits. Further loss occurs in the use of liquor for flushing mains, and generally speaking in all cases where liquor is handled or exposed to the atmosphere. It is not safe to rely on the odour of ammonia as a criterion of loss taking place, as the ammonia vapour is readily absorbed by the moist and usually slightly acid surroundings of a gasworks, and so the odour rapidly disappears. It is often difficult to trace or become aware of loss from leaking pipes, tanks, and wells, when these are placed, as they usually are, underground. It is often advisable to have draining pits at intervals along important pipe lines so that the drainage may be periodically examined for ammonia.

Loss occurs in the gas passing from the scrubbing system. The total loss in ammonia from all causes, which occurs between the retort house and the sulphate plant, is usually very much higher than the loss entailed in working up the liquor to sulphate. Unfortunately it has not been customary to instal any means of measuring the liquor made, and seldom is it possible to arrive at the amount of liquor and consequently of ammonia which actually arrives at the sulphate plant. The matter is also somewhat complicated by the fact that a certain proportion of the liquor remains in the tar, and before this is separated and returned for sulphate manufacture it has suffered considerable losses. It is certainly most advisable that the liquor used at the sulphate plant should be known accurately from day to day, and if possible the amount of " virgin liquor " made, and the amount of water used at the scrubbers.

The ammonia in the gas at the retort house can be determined as follows :—

93*a*. *Ammonia in Crude Gas.* The apparatus already described (see **38***b*) for sampling gases under reduced pressure is used. The hot gas drawn downwards through a glass sampling tube, passes directly through an absorption vessel containing dilute sulphuric acid, before reaching the aspirator bottles. The gas is drawn through at a convenient rate, say, about 1 cubic foot for an hour, and the gas so passed is calculated from the amount of water which passes from the first to the second bottle. The volume, as usual, is corrected to 60° F. and 30 inches. The sampling tube is removed and swilled down into the absorption vessel. The contents of the latter are transferred to a boiling flask through a funnel and a plug of cotton-wool which will retain the thick tar. The funnel and bottle are washed out with cold water. The ammonia is then determined by distillation into standard acid as detailed later. (See **93***d*.)

Virgin Liquor. As the gas is cooled, fixed salts are deposited which are subsequently dissolved in condensed steam. Below about 80° C. ammonium sulphide and carbonate are formed in solution. The liquor so formed is known as the " virgin liquor." The ammonia content of this varies according to the temperature of separation from the gas, and the concentration of the ammonia and steam in the gas. Naturally if the liquor is run off from the foul main at a high temperature it will contain very little ammonia, and it is often advisable to collect and circulate this liquor through the scrubbers to increase the strength. Excessive steaming will result in a very large amount of weak liquor. The strength of the liquor from the foul main and condensers is determined from time to time and compared with the scrubber liquors.

93*b*. *Crude Liquor.* The sampling is made as in the case of tar (see **82***a*) and the sample will usually include a considerable amount of tar, some of which may float on the surface. The whole is allowed to stand and the separated liquor taken for analysis.

93*c*. *Specific Gravity.* The specific gravity may be required in order to arrive at the weight of liquor. The determination is of no use whatever as a guide to the content of ammonia. The use of hydrometers is quite reliable provided tar is absent.

93*d*. *Ammonia.* It is customary to distinguish between the ammonia which is volatile on distillation—ammonia in the form of carbonate and sulphide—and the portion of the ammonia which cannot be driven off unless the equivalent amount of alkali is added. The former is termed " free " and the latter " fixed." The estimation is carried out by placing 25 c.c. of the liquor in a 750 c.c. boiling flask containing about 250 c.c. of water. A small piece of zinc or porous pot is added to prevent bumping, and the free ammonia driven off by distillation into 50 c.c. of normal sulphuric acid. A splash bulb is necessary at the head of the flask and a short condenser is advisable. The apparatus shown (Fig. 24) is convenient for all such determinations of ammonia by distillation. When about 150 c.c. have passed over, the apparatus is disconnected and the adapter rinsed into the acid. The excess of acid is then titrated back with normal alkali, using methyl orange as indicator. Methyl red may be used, provided carbon dioxide is expelled by boiling the distillate for a few minutes. The distillation may then be continued into fresh standard acid after adding about 50 c.c. of 10/N alkali to the residue of the flask. The fixed ammonia evolved is distilled into 10 c.c. or more of normal sulphuric acid, and the excess titrated back as before. If only the total ammonia is required the caustic soda is added at once to the crude liquor and the ammonia distilled into 50 c.c. of normal acid.

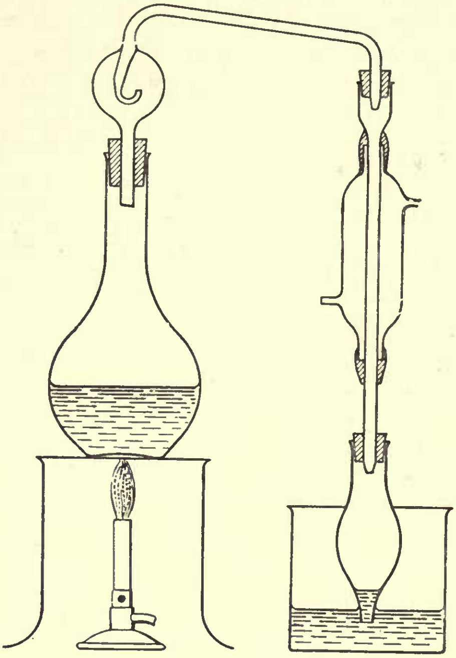


Fig. 24.—Apparatus for Estimation of Ammonia.

The method does not distinguish exactly between the ammonia combined as a salt of mineral acids, such as chloride, and that present in weaker combination, such as carbonate, since chloride and sulphate are to some extent decomposed on boiling impure solutions.

It is still common to express the content of ammonia in terms of "oz. strength," an expression which has now lost its utility. This represents the number of ounces of sulphuric acid which will be exactly neutralised by the ammonia in one gallon of the liquor. A liquor of standard strength is "10 oz." and contains 1,518 grains of ammonia, equivalent to 0·8421 lbs. of sulphate of ammonia per gallon. For ordinary use it is more convenient to use the percentage weight/volume; in which case "10 oz. liquor" contains 2·1658 grams of ammonia per 100 c.c.

94*a*. *Carbonate.* It is desirable, for the sake of the quality of the gas, that as much of the carbon dioxide should appear in the liquor as possible. The estimation is made by dropping 25 c.c. of the liquor gradually from a pipette into excess of clear ammoniacal calcium chloride in a conical flask. The reagent may be prepared by adding ammonia to 10 grams of calcium chloride till the precipitate is just dissolved. The solution is passed through a filter paper immediately before use, and made up to about 100 c.c. A portion of 25 c.c. diluted to 300–400 c.c. with fresh distilled water will be sufficient. The flask containing the precipitated calcium carbonate is closed with a cork and short length of capillary tube to provide an outlet, and heated on the water bath for an hour or so with occasional shaking. The precipitate is filtered and washed with boiling water. The residue is placed in the funnel above the original flask. The filter paper is pierced and the bulk of the precipitate is washed through. An excess, say, 50 c.c., of standard normal hydrochloric acid is run in, over and through the filter paper. The paper is washed with hot water into the flask and the excess of acid titrated back with normal alkali, using methyl orange as indicator.

$$(NH_4)_2CO_3+CaCl_2=CaCO_3+2NH_4Cl$$
$$CaCO_3+2\,HCl=CaCl_2+CO_2+H_2O.$$

95*a*. *Chloride.* A portion of 25 c.c. or so of the liquor is diluted and heated to remove volatile ammonia. Hydrogen peroxide,[1] say, 25 c.c. of 10 vol., are added, and the boiling continued. A few drops of potassium chromate are added to the boiling solution, followed by a slight excess of sodium carbonate. After filtration and cooling the filtrate is made up to 250 c.c. and a portion is withdrawn, neutralised with dilute nitric acid, and titrated with standard neutral silver nitrate solution.

In the case of very dirty liquor the following method may be preferred: The liquor is evaporated to dryness on water bath, taken up with water and filtered. The filtrate is mixed with ferrous sulphate to keep the solution reduced, and copper sulphate is added to precipitate thiocyanate. The latter is removed and washed with a little warm water. To the filtrate is added nitric acid, followed by excess of silver nitrate. The solution is heated to boiling-point, filtered, and the residue washed with hot water. The bulk of the residue is digested with conc. nitric acid to decompose any thiosulphate. The residue is taken up with water, filtered through the same filter paper, and the whole dried. The filter paper is incinerated separately to the bulk of the residue, the ash is added to the latter in a tared crucible, moistened with a drop of nitric acid, followed by a drop of hydrochloric acid, and heated to about 350° C. for a few minutes, or until the silver chloride just shows signs of fusion at the edges, then cooled, and weighed as silver chloride, $AgCl$.

$$NH_4Cl+AgNO_3=AgCl+NH_4NO_3.$$

95*b*. *Sulphide.* A portion of, say, 25 c.c., of the liquor is added to excess of ammoniacal zinc chloride, diluted to about 100 c.c. with warm water. The precipitate of zinc sulphide is decomposed with iodine as described later. (See **114***b*.)

95*c*. *Sulphate.* A known quantity, say, 200 c.c., of the liquor is evaporated nearly to dryness. One or two c.c. of conc. hydrochloric acid are added to decompose thiosulphate and the evaporation continued. The residue is extracted with water and the sulphate precipitated as barium sulphate. (See **23***a*.)

95*d*. *Total Sulphur.* A known quantity, say, 10 c.c., is dropped into 25 c.c. of fuming nitric acid in a conical flask with agitation. The solution is gently warmed in a fume chamber till clear, and is then evaporated down to dryness on the water bath with a few c.c. of hydrochloric acid. The residue is diluted with water and the sulphate precipitated as barium sulphate.

Complete Analysis. For the estimation of cyanogen compounds, thiosulphate, thiocarbonate, etc., see the Alkali, etc., Inspector's Reports, 1903; 1909; 1917; 1918; 1919.

95*e*. *Pyridine.* Pyridine appears as an impurity in sulphate of ammonia, and leads to a good deal of nuisance when the salt is completely neutralised. In many cases the amount of pyridine in the liquor may prove worth while recovering. The

---

[1] Proved to be free from chloride.

estimation in presence of ammonia provides some difficulty. A critical review of various methods appears in the Alkali, etc., Inspector's Report for 1919. Ladd's method is modified and adapted to the estimation in liquor as follows: The ammoniacal liquor is made acid and distilled through a small acid trap to remove hydrogen sulphide and volatile impurities, and the acid in the trap after boiling is returned to the residue. Or, if it is preferred, the liquor may be distilled with excess of a saturated solution of lead nitrate, as in Feld's method for estimation of cyanide. The liquor freed from sulphide is placed in a distilling flask, diluted to about 250 c.c., neutralised with soda and an excess of one or two c.c. of a 25 per cent. soda solution added, followed by 1 to 1½ grams of sodium citrate. The solution is distilled for 35 to 40 minutes into another distilling flask containing 50 c.c. of hypobromite solution in 150 c.c. of water, the whole being kept cool.

The hypobromite solution contains 79·5 grams of bromine and 100 grams of caustic soda per litre. The ammonia distilled over with the pyridine is destroyed :—

$$2NH_3+3NaBrO=N_2+3NaBr+3H_2O.$$

The hypobromite solution is then distilled in its turn until 100 c.c. of distillate have been collected in a receiver containing 25 c.c. of N/10 nitric acid. The nitric acid solution is then titrated with N/10 caustic soda, using first methyl orange as indicator, and then continuing with phenolphthalein. The methyl orange end-point is subtracted from the phenolphthalein end-point and the difference is multiplied by 0·0079 to give the amount of pyridine bases in grams of pyridine. The end-points are difficult to judge, and the presence of carbon dioxide in the caustic soda affects the results. The solutions are therefore standardised to both end-points before use. The difference may amount to 0·5 c.c. and is added as a "correction" to the difference of the titres.

Prideaux finds that nitric acid is the best standard acid for the purpose, and in titrating ammonia in presence of pyridine α-naphtholphthalein gives the best results as indicator; while congo red is the most suitable for pyridine alone.

Gas Scrubbing. When gas containing ammonia is allowed to remain in contact with water an equilibrium is established between the ammonia in the gas and that passing into solution. This equilibrium is dependent, the pressure being constant, on the temperature and the concentration of ammonia in the crude gas. No matter how long the gas and water remain in contact, once equilibrium is established, no further alteration in the distribution will occur. Even at 0° C. the vapour pressure of ammonia is appreciable, and therefore it is impossible by mere contact of a mass of gas and a mass of water to remove ammonia completely from the gas, or to obtain a sufficiently concentrated solution of ammonia in water. If the gas is brought into contact with only a small portion of the water till an equilibrium is established and the solution is then removed and replaced by a fresh quantity of water, a second equilibrium will be established, which will diminish the concentration of the ammonia in the gas below that possible in the first case. By repeated treatment with successive quantities of water the ammonia in the gas will be reduced to an infinitely small amount. It will be obvious, however, that the solutions will become weaker in each successive case, and in the last case will contain practically no ammonia. But by bringing the last portion of solution into contact with more of the original gas, where the concentration of ammonia is at its maximum, the liquor will increase in strength. In practice this is achieved by the counter-current system of working. The washing apparatus will consist of a number of compartments each containing a portion of the water. Equilibrium is established in each compartment successively, and the gas and resulting liquor is passed from one compartment to another, the flow being in opposite directions. Thus the nearly clean gas is washed by nearly clean water, while the liquor of nearly maximum strength meets in the final compartment crude gas of the maximum content of ammonia. To obtain equilibrium in each compartment in reasonable time good contact must be made. The more intimate the contact the less the time required, and the more rapid may be the stream of gas passed through. The ultimate strength of the liquor must depend on the concentration of ammonia in the gas in the first place, and on the temperature of the gas and water in the second. Modern mechanical washers are constructed to give good contact, and the size of the apparatus can therefore be greatly reduced. Care must be taken, however, not to reduce the number of compartments. Short circuiting, by which gas from one compartment can gain access to another without establishing an equilibrium in the intermediate compartments, will obviously produce inefficient working. In tower scrubbers, gravity flow is substituted for mechanical pressure, and reliance is placed on a distributing device for splitting the water into a fine state of division as it falls downwards against the gas stream. The contact is usually poor, and therefore the cross-sectional area must be great to secure the necessary time contact. Strictly speaking, the height should merely function in a similar way to the number of compartments in a mechanical washer, but owing to poor contact equilibrium is spread over a considerable distance, and the height, as well as the diameter, is used to give additional time for contact.

The solution of ammonia in water gives rise to a considerable evolution of heat ($NH_3, Aq = 8{,}430$ cal.: Thomsen), and while in exposed tower scrubbers, where radiation losses are great, the increase in temperature may not be noticed, it may be sufficient to seriously influence the efficiency of mechanical washers operating under full load.

One of the greatest troubles of ammonia scrubbing lies in the deposition of tar in the scrubber. Contact is lost and a comparatively small deposition may place several compartments out of commission.

The scrubbing system is generally required to remove from 110 to 150 grains of ammonia per 100 cubic feet of gas with an efficiency of about 99 per cent. ; in other words, not more than one grain per 100 cubic feet is allowed to pass the scrubbers. The liquor obtained should be of such strength that when mixed with the " virgin " liquor the whole will give a strength suitable for working up at the sulphate plant, say, 1·8 per cent. w/v. Hence the strength of the scrubber liquor depends, to some extent at least, on the amount of virgin liquor made.

The presence of hydrogen sulphide and carbon dioxide reduces the solubility of ammonia in water, but it is very desirable to reduce the amount of carbon dioxide in the gas. A considerable reduction may be effected, if scrubbing capacity is available, by re-circulating the ammoniacal liquor through the first scrubber so that the full equivalent of carbon dioxide may be absorbed. Solutions of sulphides are decomposed by carbon dioxide so that the hydrogen sulphide is thrown forward and replaced by carbon dioxide. The possibilities of liquid purification are very great, but so far have been wrecked by the extreme ease with which loss of ammonia occurs in the handling of the liquor. Carbon disulphide is another impurity which can be removed to a considerable extent as thiocarbonate in the presence of ammonium sulphide.

Control of Scrubbing. Information as to the temperatures prevailing in different parts of the system are required. The thermometer arrangements described in the last chapter may be extended to cover the scrubbing system. Generally speaking the lower the temperature the better, but it may be necessary in winter time to allow the gas to pass in at not less than 60° F., and to heat the water used to the same temperature so that the purifiers may not be unduly starved.

98*a*. *Ammonia in the Gas.* It will be necessary to keep a constant watch on the ammonia passing away, particularly if the condensing system allows the gas to pass to the scrubbers at varying temperature, and if the make of gas is subject to large fluctuations. The estimation may be carried out by passing the gas direct by as short a connection as possible to an absorption vessel containing, say, 50 c.c. of normal sulphuric acid. The rate should not exceed about 1 cubic foot per hour. After passing the acid the gas is purified by a tube containing oxide of iron and is then measured. The excess of acid in the solution so obtained is afterwards titrated direct with normal caustic soda, using methyl orange as indicator. In the case of a very dirty solution it is distilled with excess of caustic soda into standard acid as already described. Turmeric paper, prepared by soaking absorbent paper in an alcoholic solution of turmeric root, is also used as an indicator for checking the ammonia in the outlet gas. The colour will perceptibly redden with gas containing one grain of ammonia per 100 cubic feet.

98*b*. *Carbon Dioxide.* The gas may be analysed volumetrically and the carbon dioxide determined by absorption, or if a more accurate method is required the gas may be passed through an absorption vessel containing ammoniacal calcium chloride. A guard tube with a portion of the same solution will be required. The gas is afterwards measured in the usual way. The liquid after the absorption is treated as in the determination of carbonate in liquor. (See **94***a*.)

Hydrogen sulphide and sulphur compounds may be estimated as described later. (See **114***b*, **116***b*.)

98*c*. *Ammonia in Scrubber Liquors.* As there is seldom any quantity of "fixed" ammonia salts present in scrubber liquor, the ammonia may be estimated with fair accuracy by direct titration, or by adding a known excess of acid and titrating back to find the excess, using methyl orange as indicator. The use of hydrometers is to be deprecated, as the results are quite unreliable. Reference has already been made to the estimation of other compounds in ammoniacal liquors.

Sulphate Plant. The manufacture of sulphate of ammonia from the ammoniacal liquor is a process complete in itself, and should be regarded as a distinct manufacture of which complete figures of costs and efficiencies are necessarily to be kept. The raw materials are the ammoniacal liquor, sulphuric acid, lime, and steam. All of these are measured or weighed and an efficiency balance may be obtained weekly with fair accuracy. The efficiency of both the ammonia and acid used on the equivalent obtained as sulphate is easily kept over 95 per cent.

The analysis of ammoniacal liquor has been dealt with. The actual lime equivalent of the liquor may be obtained as follows:—

99a. *Lime Equivalent of Liquor.* An average sample of the lime is broken to the size of peas. Of this 70 grams are placed in a covered dish and slaked with 750 c.c. of boiling water. The whole is then washed into a litre flask and made up to one litre. Of this 50 c.c. is boiled with 25 c.c. or more of the crude liquor until no more ammonia is evolved. This is allowed to cool, and the excess of lime titrated back with normal hydrochloric acid using phenolphthalein as indicator.

$$2HCl + CaO = CaCl_2 + H_2O.$$

The acid used gives the excess of lime, and by deducting this from the amount taken, as estimated by direct titration of a fresh 50 c.c. of solution of the milk of lime, the theoretical quantity of the lime required will be found. In practice about 5–10 per cent. extra will be found sufficient.

99b. *Lime.* The chief impurity in the lime as received will be calcium carbonate, or unburnt limestone, or possibly silica. An accurate determination of carbon dioxide may be made in a calcimeter, that of S. H. Collins being most suitable. Or a volumenometer may be used. A small weighed amount is placed in a small tube with a piece of aluminium foil or wire about 0·08 gram. This is connected by capillary tubing to a gas-measuring vessel. A few c.c. of pure dilute hydrochloric acid is run in, and as the reaction proceeds the tube is warmed. The hydrogen from the aluminium carries over the last traces of carbon dioxide. The evolved gas collected in the measuring burette is cooled to room temperature, measured, transferred to a potash bulb, and the carbon dioxide absorbed. The residual gas is measured and the volume of absorbed gas corresponding to the carbon dioxide is corrected to N.T.P.; 1 c.c. of carbon dioxide at 0° C. and 760 mm. weighs 1·976 mg.

A rapid volumetric method of analysis, which gives sufficiently accurate results for most purposes, consists in slaking the lime and making up a litre solution as described above. Of this 25 c.c. is warmed to boiling-point and titrated with normal hydrochloric acid, using phenolphthalein as indicator. The titration must not be made too rapidly and the solution should be well agitated. The titre gives the equivalent of the free calcium oxide. A further 25 c.c. is run slowly into excess of standard acid in a conical flask boiled for 2 or 3 minutes, and the excess of acid titrated back with normal caustic soda and phenolphthalein. This will give the lime present, both as oxide and carbonate, whence by deduction the lime as carbonate can be obtained.

Sulphuric Acid. The third raw material, sulphuric acid, requires checking for strength and purity. Sampling is effected by dipping glass tubes in the acid, closing the top of the tube and withdrawing the tube full of acid. The samples are preserved in stoppered bottles.

100*a*. *Specific Gravity.* The strength can be determined by the specific gravity for all ordinary purposes. Accurate hydrometers are used and the temperature is adjusted carefully to 15° C. Reference to tables will give the corresponding percentage of sulphuric acid, H_2SO_4. The usual strength of acid employed contains about 78 per cent. of sulphuric acid, sp. gr. 1·71 (142° Tw.)

If required, a direct estimation may be made by titration or by precipitation with barium chloride. In both cases the acid in combination with the iron will be included. Lead sulphate should be removed after dilution. The dilution is made by placing 25 c.c. of the sample in 100 c.c. of water in a litre flask, which is cooled and made up to the mark. Of this 25 c.c. are taken and again made up to 1 litre, a portion of which is used for analysis.

100*b*. *Iron.* The iron impurity is very detrimental, as it contaminates the mother-liquor, and when a certain concentration of iron is reached the latter is thrown out into the salt. The estimation is made in the diluted acid by warming 50 c.c. or more with a few drops of hydrogen peroxide. An excess of ammonia is added, the precipitate is filtered off, re-dissolved in very dilute sulphuric acid, reduced, and titrated with permanganate. (See **109***c*.)

100*c*. *Lead.* Considerable amounts of lead sulphate are sometimes present, both in solution and as a sludge. That in solution may be thrown out by diluting 1 volume of the strong acid with an equal volume of water, adding 5 volumes of 90 per cent. alcohol,[1] allowing to stand, and filtering off the lead sulphate. It may be washed with a mixture of alcohol and water, dried, and weighed.

100*d*. *Arsenic.* Traces of arsenic in non-arsenical acid may be detected and estimated as in the method given for arsenic in coke. (See **49***b*, **49***c*.) The arsenic in pyrites acid may be found by diluting 250 c.c. of the strong acid of known sp. gr. with an equal volume of water. The whole is warmed to about 90° C. and hydrogen sulphide passed in until the precipitation is complete. The arsenious sulphide is filtered off and washed with water containing hydrogen sulphide. The filtrate is concentrated and again treated with hydrogen sulphide. The precipitate, if any, is added to the main bulk. The whole of the wet precipitate is transferred to a large beaker and digested with solid ammonium carbonate. The liquid is poured through a filter into a 500 c.c. graduated flask, and the residue again treated with fresh ammonium carbonate. The residue is finally transferred to the filter and washed with hot ammonium carbonate solution. The solution is cooled and made up to the mark. Of this 25 c.c. are taken and 50 c.c. of hydrogen peroxide added. The whole is brought to the boil for a few minutes. It is acidified with hydrochloric acid and 2 grams of potassium iodide added. The free iodine is removed with a few drops of sulphurous acid and the excess of sulphurous acid boiled off. A crystal of potassium iodide will show if the reduction is complete. If it is not, the reduction must be repeated. The solution is then cooled and made nearly neutral with caustic soda. Two to three grams of pure sodium bicarbonate (a distinct excess) are added and the arsenious salt titrated with N/10 iodine and starch indicator.

$$As_2O_3+2I_2+2\,Na_2O=As_2O_5+4\,NaI.$$

---

[1] Preferably, absolute alcohol. A rebate on the duty can be claimed if certain conditions are fulfilled.

101*a*. *Nitrous Acid.* The presence of nitrous acid renders the acid very corrosive towards lead. It may usually be detected by warming about 500 c.c. of the acid in a large flask, when a distinct red colour develops, or by addition of a solution of ferrous sulphate, when a brown ring is formed. If present in appreciable quantity it may be estimated by running the acid from a burette into a conical flask containing 10 c.c. of N/10 permanganate, diluted to about 250 c.c., and kept warm. When the colour is discharged the acid used is noted.

$$5\ N_2O_3+4\ KMnO_4+6\ H_2SO_4=2\ K_2SO_4+4\ MnSO_4+6\ H_2O+5\ N_2O_5.$$

Control. It is not intended here to discuss different types of plant or methods of working them, but merely to indicate the chief means of chemical control. It is extremely important that the liquor used should be measured fairly accurately from day to day and its content of ammonia estimated in average samples obtained. The volume may be accurately measured with a calibrated tank, a weir system, or a "Rotameter." The strength and quantity of acid used is also to be carefully noted, and the stocks of mother-liquor and sulphate balanced at every opportunity. It must be remembered that acid kept in stock becomes gradually weaker, and allowance has to be made for this. In addition to the raw materials already mentioned, the amount of steam and water are worthy of attention, as they form an appreciable part of the cost.

101*b*. *Spent Liquor.* The spent liquor is preferably sampled continuously. Several excellent sampling devices are on the market. The ammonia in the spent liquor is estimated by distilling 250 c.c. with excess of caustic soda into 50 c.c. of N/10 sulphuric acid. The excess of acid is afterwards titrated back in the manner described for ammonia in liquor. (See **93***d*.) P. Parrish considers the economical limit of ammonia allowed in the spent liquor to be 0·015 per cent., but usually 0·010 per cent. is considered the desirable upper limit.

101*c*. *Excess of Lime.* A drop or two of phenolphthalein is added to 100 c.c. of the spent liquor. If there is a colouration showing alkalinity, the whole is titrated with N/10 hydrochloric acid. If alkalinity is not shown, insufficient lime has been used, and the deficiency may be gauged by adding a known excess of lime and titrating back. The alkalinity can be expressed in grams of calcium oxide, CaO, per 100 c.c.

The quantity of spent liquor effluent is in excess of the crude liquor used owing to condensation of steam and addition of milk of lime. The excess is usually about 40–50 per cent.

101*d*. *Waste Gases.* Ammonia is liable to pass into the waste gases if the saturator bath is too weak or the distribution of the gases entering the saturator is defective. It is convenient to have a catch-box containing acid after the saturator. Turmeric paper may be used to indicate ammonia in the waste gases. For longer tests an aspirator and absorption vessel containing sulphuric acid is used as in estimating ammonia in coal gas under vacuum. (See **42***a*.) Carbon dioxide and hydrogen sulphide may also be estimated by methods of gas analysis, but it is to be remembered that the amounts per cubic foot will be considerably higher in waste gases than in coal gas. The results will be given per cubic foot of the waste gas, excluding steam. The volume and composition of the waste gas passing can be calculated roughly from the composition of the liquor and the amount used per hour. Linder found that the composition in one case was

$$CO_2=86{\cdot}5 \text{ per cent.}; \quad H_2S=12{\cdot}6 \text{ per cent.}; \quad HCN=0{\cdot}9 \text{ per cent.}$$

Saturator-Liquor and Mother-Liquor. The saturator contents are usually kept at about 3 per cent. acidity reckoned as sulphuric acid. The control is frequently exercised by taking the specific gravity of the hot liquor as obtained by dipping the saturator with a Twaddell hydrometer, but a titration is much to be preferred. The strength in the former case is about 56° Tw. when the salt is falling. It is not possible to keep the contents of the saturator neutral, as ammonium sulphate suffers decomposition at boiling temperature.

Practically all the impurities accumulate in the mother-liquor until a certain concentration is reached, when they are thrown out with the salt. By a periodical cleansing of the mother-liquor a very pure salt can be maintained. The chief impurities are iron and arsenic, both of which may be estimated by methods already given.

The presence of tar and particularly paraffin is very detrimental. Not only is the salt contaminated, but the crystallization becomes intermittent and the grain of crystal is very small. Very considerable trouble was experienced on an occasion when paraffin wax was found floating on the cooled mother-liquor. The salt was only thrown down at intervals and the ejector operated unevenly, giving sudden bursts of considerable violence.

Ammonium Sulphate. Considerable attention has recently been focussed on the production of a pure neutral and dry salt. The varieties formerly produced, containing small amounts of free acid, caked so that the salt could not be distributed with mechanical drills. The bags used to pack the salt also rotted quickly. Recently salt has been produced of a purity comparing favourably with that of a laboratory reagent. The appearance has also been improved by an increase in the size of the crystal grain, which in the case of the "Metro" salt consists of little spindles about ¼ inch in length. The salt is almost universally sold on analysis, and the determination of ammonia and of impurities must necessarily be very accurate in method and manipulation. Most of the salt manufactured now contains over 25 per cent. NH_3.

102*a*. *Sampling.* The sampling does not present any great difficulty, except that care must be taken to crush the smallest lumps before reducing the sample to less than 10 pounds. The salt is affected by the humidity of the atmosphere, and samples are kept in stoppered or sealed vessels. The final reduction is performed on a thick glass plate, the granules being carefully crushed and mixed with a spatula.

102*b*. *Moisture.* The moisture is usually determined by the loss on drying 10 grams of the salt at 100° C., but if free acid is present, moisture is retained at this temperature. In this case the salt may be weighed into a small U-tube. To the outlet is attached a weighed calcium chloride drying tube which has been previously saturated with dry gas containing ammonia. The U-tube with the salt is suspended in a beaker containing a mixture of glycerine and water and warmed to 105° C. The dry gas containing ammonia is passed through for about 30 minutes. The calcium chloride tube is then detached and weighed. It is replaced and the process repeated for a further 15 minutes, when there should be very little further gain in weight. The U-tube and salt can also be weighed back. This will gain in weight owing to absorption of ammonia, and will lose in weight by loss in moisture. Knowing the content of free acid the allowance may be made for the former, and the gain in weight of the calcium chloride tube checked by the total loss thus calculated.

103*a*. *Free Acid.* Ten grams of the sulphate are weighed out and placed with about 150 c.c. of water in a 500 c.c. graduated flask. A few drops of methyl orange are added and the acidity titrated (without heating) with N/10 caustic soda. It is important that the same end-point be taken as that chosen in making up the standard solution. The final yellow is perhaps more definite than intermediate shades. Unfortunately methyl red, which gives a sharper end-point, cannot be used as an indicator in this case.[1] Traces of carbonate and sulphur acids other than sulphate are present which affect this indicator. If the solution be boiled, to drive off carbon dioxide, thiosulphate decomposes, free sulphur is formed and the acidity increases. If the salt is alkaline, the alkalinity is estimated in a corresponding manner.

103*b*. *Ammonia.* The neutralised solution from the determination of the free acid is made up to 500 c.c. and 50 c.c. taken for distillation in the apparatus already described. (Fig. 24.) About 300 c.c. of water are added, followed by excess of caustic soda solution, say, 5 c.c. of a 10 per cent. solution. About 200 c.c. of distillate are collected in 50 c.c. of normal sulphuric acid, and the excess of the latter titrated back with normal caustic soda. Methyl red may be used in place of methyl orange as indicator if the solution is boiled for a minute or two before titration. The end-point is much more distinct than in the case of methyl orange. From the difference in the titre of the normal acid before and after distillation the sulphuric acid equivalent of the ammonia present is found.

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

103*c*. *Blair's Method.* A quicker method consists in taking a portion of 25 c.c. of the carefully neutralised solution, made up as described above, and placing it in a conical flask. About 100 c.c. of water are added and the solution boiled for 3 or 4 minutes to expel carbon dioxide. About 10 c.c. of a neutral solution of formaldehyde is added. This reagent is prepared by adding one part of a 40 per cent. solution to two parts of water. A few drops of phenolphthalein are added and then N/10 caustic soda is run in until there is just a pink tinge. The solution turns acid and requires neutralisation before use. After addition of the formaldehyde, boiling is continued for five minutes. The hot solution is then titrated with normal caustic soda, using phenolphthalein as indicator, till a permanent pink colour is obtained. The formaldehyde decomposes ammonium salts liberating free acid, so that the acid equivalent of the ammonia is determined.

$$2\,(NH_4)_2SO_4+6\,CH_2O+4\,NaOH=(CH_2)_6N_4+10\,H_2O+2\,Na_2SO_4.$$

---

[1] L. Wallis—Private communication.

104*a*. *Insoluble Matter.* Twenty-five grams, say, of the sample are dissolved in 150 c.c. of cold water and filtered through a tared Gooch filter crucible. The residue is washed with cold water till free from sulphate, and the crucible is dried at 100° C. and weighed.

Minor Impurities. Small amounts of iron and lead, as sulphate, ferrocyanide and sulphocyanide, may be present. Traces of carbonate, sulphite, and thiosulphate and free sulphur are also common, while traces of arsenic often occur. Small particles of pitchy nature resulting from the decomposition of tarry matter are sometimes present.

Coloration in acid salt is generally not developed till the sulphate has been exposed to the atmosphere, when the iron compounds oxidise to give basic compounds which tarnish the surface of the salt. With neutralisation the iron is immediately thrown out and on oxidation gives a creamy tint to the salt.

REFERENCES

D. V. Hollingworth and E. J. Fottrell. Statistics of Production of Ammonia, etc. *Gas Journal*, 1920, **149**, 557.

Alkali, Etc. Inspector's Reports. Losses of Ammonia and Use of Paraffin Oil in Storage Wells. 1914, 17 ; 1915, 42.

W. B. Davidson. Liquid Purification. *Trans. Inst. Gas Eng.*, 1913. *Gas World*, 1913, **58**, 867.

Alkali, Etc. Inspector's Reports. Analysis of Liquor. Reports for years 1909, 1917, 1918, and Tech. Index to Reports, 1894–1917.

H. G. Colman and E. W. Yeoman. Analysis of Concentrated Liquor. *J.S.C.I.*, 1918, 319T.

Alkali, Etc. Inspector's Reports. Estimation of Pyridine. 1919, 49.

G. Malatesta and A. Germain. Use of Cadmium Chloride for Estimation of Pyridine. See Malatesta's *Coal Tar, etc.*

T. F. Harvey and C. F. Sparks. Estimation of Pyridine. *J.S.C.I.*, 1918, 41T.

Ladd. Estimation of Pyridine by Hypobromite method. *J. Ind. Eng. Chem.*, 1919, **11**, 552.

S. H. Collins. Calcimeter. *J.S.C.I.*, 1906, 518.

S. Young. Distillation, Principles and Processes. 1922.

C. S. Robinson. Elements of Fractional Distillation. 1922.

E. Piron. Relation between Composition of Vapour and Liquor in Distillation. *Chem. and Met. Eng.*, 1922, **26**, 317.

P. Parrish. Ammonia Stills, Design and Steam Consumption. *J.S.C.I.*, 1922, 229T.

R. Lessing. Scrubber Packing. *J.S.C.I.*, 1920, 321A.

E. G. Donnan and I. Masson. Theory of Packing Scrubbers. *J.S.C.I.*, 1920, 236T.

A. Edwards. Measurement by Weirs. *Gas Journal*, 1917, **138**, 187.

CHAPTER IX

OXIDE PURIFICATION

Properties of Ferric Compounds. The existence of definite hydrates or hydroxides of iron is still a matter of controversy. It is certain, however, that if any definite compounds of this nature exist there must be a very large number. This being so, any statement as to the content of ferric hydroxide or ferric hydrate in oxide materials is unjustifiable and misleading.

Ferric compounds are known to possess the property of polymerisation and are subject to condensation, whereby high chemical complexes are reached. The behaviour of ferric chloride may be taken as an illustration. This compound gives an acid solution ; and if it is attempted to neutralise the " free " acid by addition of alkali the solution remains acid up to the point when the alkali added is chemically equivalent to the total acid radicle of the ferric chloride taken. Moreover, up to this neutral point, by adding the alkali very slowly and shaking well, the iron may all be kept in solution. The iron salt must gradually lose its acid radicle to the alkali added, but as it remains in solution as a salt it is to be regarded as a highly polymerised base $(Fe_2O_3)_x\ (H_2O)_y$, combined with an equivalent of acid. Naturally, as acid is thrown out by the alkali, the iron oxide becomes more and more highly polymerised, till at last the whole of the acid is neutralised and the whole of the iron is immediately precipitated as hydroxide. There is little doubt that in these complexes water enters into the molecule, and it is not until the oxide is heated to over 1,000° C. that the last remnants are expelled. Fortunately, it appears that so long as even a trace of water is present, in combination, whether in a physical or chemical sense, the oxygen of the molecule may be replaced by sulphur, under suitable conditions of temperature ; and under the same conditions may be again exchanged for oxygen with liberation of free sulphur.

This mutual replacement appears to take place without affecting the constitution of the molecule ; for the physical and chemical appearance of the oxide after this double reaction is, so far as can be seen, the same. Hence for all complexes containing oxygen there must exist corresponding compounds containing sulphur. Regarding the matter from a catalytic point of view, these various complexes of iron sulphide, water and acid radicle play the part of intermediate compounds in the reaction—

$$3\,H_2S+3\,O=3\,H_2O+3\,S.$$

Intermediate Compounds. The nature of the intermediate compound formed depends on the original oxide used and on the temperature conditions. By varying the latter, a successive series of compounds are formed, and as the temperature rises they become more complex and unstable. The reaction becomes quicker, until at last the " Claus Kiln " effect is observed. As this point is approached, intermediate compounds are not visible. The higher intermediate compounds may be regarded as sulphides of the type $(FeS_2FeS)_x\ (H_2O)_y$, which oxidise in the presence of water, giving two-thirds of the sulphur as sulphate and one-third as free sulphur. When, however, the oxidation is carried out at a higher temperature (above 100° C.), instead of sulphate, sulphur dioxide and hydrogen sulphide are the products, and an equilibrium is established.

$$SO_2+2\ H_2S=3\ S+2\ H_2O.$$

Increase of temperature favours the reaction from right to left and in practice produces a limit when sulphur dioxide, as in the Claus Kiln, appears in the exit gases. Sulphur itself is slightly volatile even at ordinary temperatures, and more so as the temperature rises. The sulphur vapour formed can decompose water vapour, reaching an equilibrium in the reverse way.

Temperature. It will be realised that if a certain temperature is necessary to induce sulphur to exchange with oxygen in the iron oxide molecule, a corresponding temperature will be necessary to enable the reverse change to be accomplished with equal ease, since it has been found that no molecular changes necessarily take place. The heat liberated by the reactions is the chief means available to maintain the temperature, and it is obvious that the larger the area exposed the more likely it is for intermediate compounds to appear and the more difficult it is to maintain temperatures. Similarly, the smaller the concentration of the hydrogen sulphide in the gas the more difficult it is to obtain a quick reaction, and the removal of the hydrogen sulphide becomes very difficult. There is, probably, a definite minimum purifying area for each variety of material at each particular temperature. Without artificial heat, and under present-day conditions, with most materials the minimum appears to be about 0·3 square foot per 1,000 cubic feet of gas per 24 hours.

The reaction—$3\ H_2S+3\ O=3\ H_2O+3\ S+159{\cdot}9$ cal.—at lower temperatures may be regarded as divided into two portions, although in the presence of oxygen the two reactions always take place simultaneously, to some extent :—

$$(1)\ldots.3\ H_2S+Fe_2O_3=3\ H_2O+Fe_2S_3.$$
$$(2)\ldots.Fe_2S_3+3\ O=Fe_2O_3+3\ S.$$

For the sake of simplicity, the water combined in the oxide molecule is omitted. If in place of the ferric sulphide another sulphide is formed, the total heat liberated will always be the same for the same end products. It must be realised that oxides in use are not homogeneous, and that particles of oxide playing a catalytic rôle may be raised to a far higher temperature than that indicated by the thermometers, which only give the average temperature of a relatively large volume. This probably explains the fact that a mixture of oxygen and hydrogen sulphide will combine in the presence of oxide in small proportion, which is apparently inactive to hydrogen sulphide alone, without visible heat effect or change of appearance of the oxide. The phenomenon appears to be due to concentration of the reacting gases on the surface, which in reality causes a high local temperature. The heat liberated may be sufficient to cause a neighbouring particle to reach a sufficiently high temperature to enable it to react, and under such conditions the whole mass of oxide may pass into use.

Influence of Water. Apart from the influence water may have on the original constitution of the ferric oxide, subsequently it seems to only provide a limitation on the possible rise in temperature. It is obvious that oxide suspended in water to which oxygen and hydrogen sulphide is admitted cannot rise in temperature locally, and therefore is very limited in its reaction. The heat liberated is insufficient to drive the water off in vapour form. Oxides which in a dry state exhibit a very high activity when suspended in water may be inert. Generally speaking, oxide to be capable of reaction in water must have been precipitated, or, in other words, contain in its composition a very large amount of water.

Both ferric and ferrous sulphides are completely hydrolysed by water at 100° C. with evolution of hydrogen sulphide. The reaction is the reverse of the absorption. Ferric disulphide ($FeS.S$) and the higher sulphides, $\{(FeS_2)\ (FeS)\}$, are stable under these conditions, but these compounds will only oxidise very slowly in presence of excess of water and then pass largely to sulphate. In practice, when excess of water is present the temperature must be strictly limited. The alternative is to remove the excess of water, and by obtaining higher temperatures the higher sulphides may be used as intermediate compounds. The oxidation must then be carried out at a similar temperature.

Natural Oxides. A large variety of natural deposits exists, containing 20–30 per cent. of oxide of iron, calculated as Fe_2O_3. The exact form in which the iron occurs is unknown.

Massive and crystalline varieties are not available for purification as their preparation is too costly. The natural deposits which can be used are all derived by solution and re-deposition of iron from the parent rock or by natural weathering (degradation). They may be classified as (1) True Bog Ores, and (2) Degraded Iron Ores. The former, which are chiefly obtained from Ireland and the German-Dutch frontier, are formed from iron solutions flowing into bogs, the iron being deposited on the peat fibres by partial oxidation, chemical and bacterial actions. As mined, the iron is in a reduced state, and only turns brown on drying and atmospheric oxidation.

Bog ore is suitable for cold alkaline purification and may retain over 60 per cent. of water without appearing wet or sticky. This property is, in fact, a good criterion of true bog ore. Nearly the entire content of iron is available, and its distribution over the surface of the peat can hardly be imitated artificially. Under favourable conditions it can be worked to a content of 50 per cent. of sulphur without change, as it gives little back pressure. On the other hand, the density and iron content per cubic foot is remarkably small, so that a certain volume will not purify the same volume of gas as the more dense oxides will.

Many local deposits of degraded iron ores exist in this country, derived from ferruginous rocks, such as limestones, basalts, rotten ironstone veins, etc. A few of these, such as Westbury ore, are used to a considerable extent. Naturally, they vary extensively in iron content and in the availability of the iron which is present. Occasionally, as in Lincolnshire and Belgium, vegetation growing on the surface provides a considerable amount of fibre, which loosens the structure and gives an imitation of bog ore. Usually the oxide has to be broken, crushed, or ground and mixed with sawdust or fibre to lighten it before use. These oxides will rarely contain more than 35 per cent. of moisture without appearing sodden, and many of them are simply mud when the water content is above 20 per cent. The type of iron compound contained also varies considerably. Yellow ochres, too gritty for the paint trade, provide very useful material when suitably prepared. Sometimes, when derived from a limestone by the leaching out of the lime, they possess a curious minute honeycomb structure, which enables them to appear almost dry although containing 30 per cent. of water. When a lump is squeezed water trickles out. As it is usually necessary to crush and mix the material in the wet state, the advantage of this structure is largely lost. Occasionally deposits of precipitated oxide can be obtained locally from colliery water, and these can be usefully used as an enriching material.

Oxides of this class do not, as a rule, give good results with low temperatures, but if the heat of the reaction is allowed to accumulate in the mass surprisingly good results can be obtained, and the activity is then all that can be desired.

Artificial Oxides. The basis of most of the artificial oxide used is burnt spent oxide, which is usually prepared for use by rendering alkaline with lime or soda ash and mixing with sawdust or fibre. The addition of the alkali liberates a certain amount of " precipitated " hydrate from the sulphate of iron originally contained. Often, extra sulphate of iron is added to increase the amount thus formed. The idea that this small amount of " active " iron is responsible for the whole of the work done by the oxide is hardly correct, but there is no doubt that it is extremely useful in imparting an initial activity to the oxide which gives rise to sufficient heat to bring the bulk of oxide into use. Burnt spent oxide itself is not immediately reactive, and if suspended in water is quite inert ; but continued exposure in the dry state brings about an activity which often exhibits itself suddenly and after a lapse of time. The commencement of this activity is promoted by raising the temperature, and the whole of the iron present may be converted to sulphide and subsequently oxidised. The temperature and duration of burning has a considerable effect in retarding the immediate response of the burnt oxide when put into use and of raising the temperature at which it can be satisfactorily used, hence when the cycle between the acid works and the gasworks has been completed three or four times, the oxide becomes difficult to use. The oxide, as prepared for use, is usually much more dense than other materials, and unit volume will consequently remove a greater amount of hydrogen sulphide before it is finally spent ; but it must, necessarily, be worked at higher temperatures, and unless carefully watched gives rise to excessive back-pressure.

Oxides from other chemical processes have been tried from time to time, and even the inert " Bauxite mud " can be used if the temperature conditions can be maintained. It is better to use such material where the concentration of the hydrogen sulphide in the gas is greater than in coal gas—for example, in the waste gas purifiers of a sulphate plant.

Various preparations of precipitated oxide are used for strengthening or promoting initial activity or where the concentration of the hydrogen sulphide is lower than usual. Ferrous sulphate may be decomposed with lime or soda ash or ammoniacal liquor. Pickling liquors may be similarly treated. Light metal scrap may be covered with freshly discharged spent oxide, when heat will develop and the mass gradually oxidise to an energetic mass.[1]

Precipitated oxides which have not been dried at a temperature much above normal are energetic even in the cold and presence of excess of water.

The selection and valuation of oxide involve the determination of moisture, loss on ignition, total iron, and the absorption value.

109*a*. *Moisture.* It is often necessary, in the case of wet oxide, to obtain a rough sample for moisture which is broken and handled as little as possible, and to obtain a separate sample, which is crushed and quartered, as usual, for the remaining analysis. Moisture samples are immediately divided, bottled, corked, and sealed. For the determination, the sample is roughly spread out on a glass plate, and quickly mixed, 200–300 grams are exactly weighed into a tared weighing dish provided with a good cover. On completion of drying, at 100–105° C., the cover is placed to close the vessel, and the whole cooled and weighed. Dried oxide is very hygroscopic. Loss represents moisture.

The residue from the determination of moisture, if accurately representing the bulk (otherwise a fresh sample is taken), is ground and the fibres chopped, placed in a covered vessel and dried again. The cover is replaced, and the whole kept in a desiccator.

109*b*. *Loss on Ignition.* For the determination of loss on ignition, about 1 gram of this dry and ground sample is weighed exactly into a platinum crucible, covered with lid and the volatile matter cautiously driven off. The lid is then removed, and the crucible is raised to a red heat for about 15 minutes, when the residue should be red and free from carbon. The lid is replaced and the whole cooled in a desiccator and weighed.

If required, an approximation to the contained fibre may be made by burning off 1 gram of the dried oxide in a combustion tube and estimating the carbon as carbon dioxide in a similar manner to a combustion of coal. The carbon is then calculated to cellulose $C_6H_{10}O_5$ or wood tissue—$5C_6H_{10}O_5$, $C_{19}H_{18}O_8$. The difference gives an approximate figure for combined water, but this figure is of little value as other compounds than those of iron are present, which may hold combined water. Moreover, it is almost certain that part of the moisture is combined, i.e. enters in the composition of the oxide molecule.

109*c*. *Iron.* The residue from the determination of loss on ignition may be used for the determination of iron by adding about 2–3 grams of anhydrous sodium carbonate, mixing carefully with a spatula, taking care to remove oxide from the

---

[1] F. H. Walker—private communication.

base of the crucible. The mixture is then covered with about 5 grams of sodium carbonate. The crucible is covered and ignited very gently at first. The temperature is gradually increased to a dull red heat till the melt clears. A Méker burner is advisable, and no risks should be taken of getting a reducing flame on the base of the crucible. Over-fusion should also be avoided, or some iron may become insoluble. The melt is cautiously dissolved in dilute sulphuric acid, the crucible and lid washed clean and removed. The solution is evaporated, as far as possible, on the water bath, when the residue should be white and clean. If otherwise, it must be filtered and the residue refluxed.

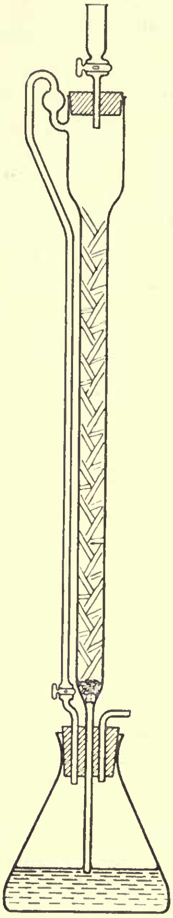


Fig. 25.
Modified Jones' Reductor.

The solution is then diluted, made up to 250 c.c., and portions of 50 c.c. withdrawn, reduced, for example, with zinc and titrated with N/10 potassium permanganate. The iron is conveniently reduced in a reductor, consisting of a vertical condenser tube with a plug of glass-wool at the base. This tube is filled with pieces of zinc rod and the solution passed through, followed by four or five washings with very dilute acid. The reduced solution, of which a drop should not give a coloration with potassium sulpho-cyanide, is filtered free from lead (from the zinc) and from silica by the glass-wool, and passes to a conical flask, in which, after addition of 10 c.c. per cent. of dilute sulphuric acid and warming, it is titrated. A rather more elaborate form of reductor is illustrated (Fig. 25). By manipulation of the taps, the hydrogen gas liberated can be passed to the reduced solution to displace air or used to create a pressure and cause the solution to pass rapidly through the column.

$$K_2Mn_2O_8+10\ FeSO_4+9\ H_2SO_4=5\ Fe_2(SO_4)_3+2\ MnSO_4 \\ +2\ KHSO_4+8\ H_2O.$$

An allowance should be made for iron in the zinc used by titrating a blank test, using the same quantities of acid.

The iron is returned as ferric oxide (Fe_2O_3) on dry and wet basis.

In some cases, the iron may be obtained in solution directly by digesting with hydrochloric acid, in which case the iron is precipitated with ammonia after oxidation, filtered, washed several times with water, and then re-dissolved in sulphuric acid before reduction.

If a complete analysis is required, the melt, obtained as above, may be dealt with as described for the analysis of refractory materials.

110*a*. *Absorption Test.* Various methods of estimating the activity of oxide have been used. The following is one of the simplest.

A calcium chloride tube is fitted with rubber tubing and glass rod stoppers to close each end, and into it are introduced 5 grams of the dried oxide to be tested (or oxide with a known quantity of moisture may be used). The air is displaced with coal gas, which has been passed through alkaline pyrogallol to remove carbon dioxide and oxygen, and the glass rod stoppers inserted. The whole is weighed and attached to a supply of hydrogen sulphide dried over calcium chloride. To the outlet of oxide is attached a weighed calcium tube, in which air has been similarly displaced. Hydrogen sulphide is then passed slowly through the tubes. The behaviour of the oxide is noted. The fouling is continued for an hour, when the oxide tube should feel quite cool. The tubes are disconnected, filled with coal gas as before, the stoppers replaced, and the tubes weighed. The total increase in weight gives the hydrogen sulphide absorbed. This increase may be calculated on 100 parts of oxide as received, and on 100 parts of the Fe_2O_3 contained. The latter, divided by 63·7, the theoretical amount of hydrogen sulphide capable of being absorbed, gives the " efficiency " of the iron oxide present.

It is sometimes of use to repeat the test, adding to the dry oxide an amount of water to correspond to the water content of the oxide in actual use. The spent oxide derived from the test may then be turned out of the tube, moistened and allowed to oxidise. It should be completely revivified in 24 hours and the free sulphur determined after drying at 105° C., as in the case of spent oxide. (See **118***b*.) After extraction of the sulphur the oxide residue may again be fouled and the efficiency again obtained, and this may be repeated as desired. Or, the oxide may be allowed to attain 50 per cent. of sulphur by repeated fouling and oxidation before extraction of the sulphur. Probably little is gained by carrying this procedure out, as the continued efficiency depends on the working conditions more than upon the original oxide. As a rule, the efficiency falls off gradually, till with a 50 per cent. sulphur content the absorption is only about 5 per cent., and this is largely due to the fact that the fouling and revivification are intermittent. The heat liberated on oxidation is not available for raising the temperature to promote the activity under test conditions. On the other hand, the temperature is allowed to develop according to the heat of the sulphiding reaction, subject only to natural cooling of the surrounding atmosphere. To observe the effect of increase in temperature, the absorption tube may be immersed in a beaker of hot water. Usually, in practice, the temperature is similarly allowed to accumulate, and is only restricted by the cooling effect of the gas passing through and radiation and conduction losses. Should this be such as to only allow a very low temperature in the boxes, the method of valuation of oxide should be altered accordingly. The oxide should be wetted with water to give a moisture content approximating to works' practice, and the tube kept cool by immersing in cold water. Further information may be obtained in this respect by placing a known volume in a U-tube of standard dimensions and passing ordinary crude gas through at a given rate and noting the time during which the gas at the outlet of the tube remains free from hydrogen sulphide. This test is a strictly comparative one.

A more elaborate method and apparatus for determining the absorption volumetrically is described in the Alkali Inspector's Report for 1911.

The absorption values of partially spent oxide may be obtained in a similar way.

Control of Purification. In the case of overtaxed purifier plant, when the temperature of the oxide is tending to become too high, relief may be obtained by increased circulation of liquor through the scrubber, so as to reduce the hydrogen sulphide content at the inlet of the purifiers.

While a certain amount of control can be exercised in regulating temperature at the inlet of the purifiers, this always varies considerably between summer and winter. With tower scrubbers in the open, little can be done except to provide steam-heating coils at the bottom of the boxes. The water used at the scrubbers may be warmed to, say, 60° F. Open steam, admitted to regulate moisture content, adds very little heat to the purifying mass unless in such quantity as to be otherwise detrimental. A great deal may often be done in conserving the heat of the reaction by protecting the boxes from exposure to cold winds and rain.

If the temperatures are low, the moisture content of the oxide charged is reduced as far as possible, and it is advisable to bring oxide required for charging in wintertime under cover during the autumn. The temperature of the gas rises during its passage through working boxes, and this is the chief means of removing excess of moisture in the oxide and that formed by the reaction. With three million cubic feet per day passing in at 60° F. and out at 80° F., the amount of water taken away will amount to nearly 1 ton per 24 hours.

It is obvious that if the last box is allowed to get cold condensation will quickly render the oxide waterlogged. Rotation is arranged to avoid this, and is regulated by taking into account the relative absorption of hydrogen sulphide in each box. It is preferable not to arrange a definite rotation, but to move the boxes " backwards " or " forwards," according to the data obtained.

The admittance of air is carefully controlled from the point of view of the regulation of temperature, the cleaning of the gas, and the effect of the inert gas so admitted. It is admitted in the first box if this is not too active. The supposition that oxidation and sulphidation will not occur at the same time is a fallacy. It should be remembered that the larger part of the heat is released on oxidation, and the air is therefore to be admitted where the heat is needed. The air should, of course, be admitted at the purifiers. If drawn in at the condensers part of the oxygen will be absorbed by the tar and will not be available for purification.

The first box generally absorbs about two-thirds of the total hydrogen sulphide entering, and as soon as this falls off materially, it should be changed round to another position. When the absorption in the first box falls off rapidly, after one or two days in that position, the time has come to empty and re-charge it. By carefully examining the purifying boxes in this way, a great deal of expense in emptying and recharging may be avoided. Very often the necessity arises to empty boxes, owing to back-pressure troubles, but this may largely be avoided by admitting steam with the gas stream so as to keep a continual and uniform dampness of the oxide. The back pressure usually arises through the oxide becoming dry. The fibres in it when dry and charred will not be effective in keeping the mass open. Boxes allowed to cool in presence of moisture also set hard, particularly if the volume of gas passing through is greatly reduced. Trouble in this respect often occurs with a varying load.

The admittance of ammonia should be strictly limited, for economy's sake, to one or two grains per 100 cubic feet at the most, and even this is only necessary when for some reason the temperatures have fallen. Spent oxide while revivifying almost always turns acid, and sometimes the amount of soluble iron salt may be sufficiently high to make it worth while to add an alkali to throw out the iron hydrate. Lime may be added for this purpose, and should be freshly slaked. It is mixed with the oxide and the whole allowed to stand some time before charging. Ammonium salts in the oxide are decomposed in this way, and the ammonia in turn releases the iron hydrate. It may be noted that calcium carbonate will not precipitate a ferrous salt. Lime added in this way is strictly limited, as it adulterates the oxide and adds to the trouble in keeping back-pressure down. Cyanogen is largely removed in the purifiers, and while it may throw a certain proportion of the iron out of use as a catalyst for hydrogen sulphide, in view of the corrosive properties of cyanogen compounds in the gas their removal is a matter to be encouraged. A good deal emerges in the drainage liquor as thiocyanate when revivification " in situ " is used.

Carbon disulphide in the gas may also be considerably reduced under circumstances not very clear, but possibly by catalytic decomposition, as in Guillet's process.

$$2\,H_2O+CS_2=CO_2+2\,H_2S.$$

This and the reaction of sulphur vapour with steam :

$$3\,S+2\,H_2O=SO_2+2\,H_2S$$

account for the occasional appearance of traces of hydrogen sulphide in purified gas at the outlet of the purifiers. In freshly turned-out spent oxide, which is warming up by oxidation, both sulphur dioxide and hydrogen sulphide can be detected. It will be realised that should the temperature get out of control the latter reaction becomes a very serious matter, and in one instance known by the author there was a very copious evolution of hydrogen sulphide, ammonia, steam and sulphur dioxide at the outlet of the box. The hydrogen sulphide and ammonia were several times greater in amount at the outlet than at the inlet. In fact, the box had practically turned into a Claus Kiln.

The working up of oxide is, necessarily, carefully watched. A good plan is to divide new oxide into parcels sufficient to fill a box and label each parcel. A record is then kept of the composition, behaviour, final analysis, and, as far as possible, of the weight of each parcel at different stages. The parcel, of course, increases in weight and bulk, and after use, is too large for one box. The residues may be roughly credited to the respective parcels, and finally mixed to form a new parcel.

A cost balance can be struck when each parcel is finally sold, which will go far to bring purification on to the profit side of the works' costs.

Analytical methods used for obtaining the necessary information are detailed below.

113*a*. *Temperature*. A system of temperature control is essential for proper working, particularly with limited purifier space. This should include the recording of the temperature of the inlet and outlet gas from each purifier section and the temperature of the oxide in each box. An installation of electrical resistance thermometers is very convenient. In any case, the thermometer bulbs must be well into the gas stream or 2 feet into the oxide, and if metal protection covers are used round the thermometer these should be insulated from the outside so as not to conduct an appreciable amount of heat away. If steam or other means of heating are used, the position of the thermometers must be such that they are not directly influenced. When hurdle grids are in use the thermometers inserted in the oxide are placed over or through the central double grid so that the other grids fall away on each side from the stem. The expansion and consequent movement of the oxide towards the sides will not then break or bend the thermometer stem. The thermometers are withdrawn before emptying the box. The temperatures recorded are the average temperatures of the neighbouring oxide, and are certainly lower than the maximum temperature of individual particles.

114*a*. *Moisture.* The moisture content of the gas at different points is generally equivalent to saturation at the temperature obtaining, but this is not always the case, particularly in summer-time. The most convenient method of estimating the moisture is by using some form of hygrometer and obtaining the dew-point. Reference to Glaisher's Tables will then give the corresponding water content. (See **141***a*.)

Hydrogen Sulphide. The hydrogen sulphide content of the inlet gas varies considerably, according to condensing and scrubbing arrangements. It may be as low as 300 grains per 100 cubic feet, or as high as 500 grains. The only convenient and accurate method of determination is by absorption in ammoniacal zinc chloride solution.

114*b*. *Method* (*after Linder*). A sampling connection of glass tubing is arranged direct to the gas main, with as few rubber connections as possible, and as short as convenient. Such rubber connections as are necessary are made so that the glass of each end-piece is pushed through the rubber to touch. The whole is blown out with the test gas for 5 or 10 minutes. Two absorption bottles are connected, each containing 25 c.c. of an N/5 solution of zinc chloride to which has been added conc. ammonia till the precipitate is just re-dissolved. A test meter is attached to the outlet. All connections are wired. One cubic foot (or more) is passed through in an hour (or longer), and the absorption bottles are then disconnected, the precipitate of carbonate and sulphide transferred to a filter, and washed once or twice with warm water. The filter paper is then perforated and the precipitate washed through into a conical flask containing 50 c.c. N/10 iodine solution acidified with dilute hydrochloric acid. The filter paper and the absorption bottles are cleaned up with drops of very dilute hydrochloric acid and washed into the iodine solution. The contents of the conical flask are then shaken vigorously for 10 minutes and the excess of iodine titrated with N/10 thiosulphate, using starch indicator near the end-point.

$$ZnS+I_2=ZnI_2+S.$$

The gas measured will be smaller in volume by the amount of carbon dioxide and hydrogen sulphide absorbed. The volume may be corrected by the total percentage absorbed in caustic soda, as determined experimentally, in an Orsat or Hempel apparatus. This is not necessary if the percentage is required on purified gas.

If the precipitate is too bulky and clogs the inlet tubes of the absorption bottle, or if a smell of hydrogen sulphide is observed on mixing with the iodine solution, the reagent is used in greater dilution and less gas is passed.

An acid solution of cadmium chloride may be used in place of the zinc chloride. The precipitate is filtered off, oxidised with bromine water, and the sulphate precipitated as barium sulphate.

The direct use of iodine leads to erroneous results, as unsaturated hydrocarbon vapours are also oxidised. For rough indications of the working of the purifiers the following method may be used. The results are approximately correct only so far as difference in the values obtained are taken.

115*a*. *Approximate Absorption Test.* Short glass connections are arranged at the inlet of the purifier section and at the outlet of each box. A bottle holding about 4 litres is fitted with rubber cork (vaselined on the underside) and delivery tubes, one of which is a short tap-funnel, and the other a tube with stop-cock reaching to the bottom (Fig. 26). The capacity of the bottle is determined to the cork by filling with water and emptying into a measure. The dry and clean bottle is filled with the test-gas by connecting to the inlet tube and allowing gas to pass full-bore for 5 to 10 minutes. The taps are then closed and the bottle removed to the laboratory, where excess (50 c.c.) of N/10 iodine solution is added through the tap-funnel. The whole is well shaken for 5 minutes. The tubes may then be removed, when lead acetate paper exposed inside should show no stain.

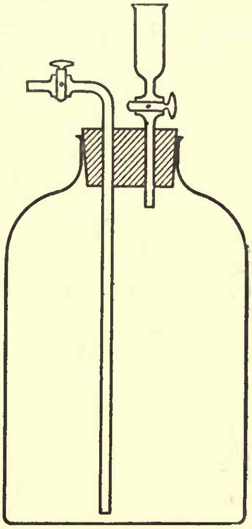


Fig. 26.—Bottle for Estimation of Hydrogen Sulphide.

The excess of iodine is titrated back with N/10 thiosulphate, adding starch indicator near the end. This test is made at the inlet to the section of purifiers and at the outlet of each box. Since the outlet of the last box is presumably free from hydrogen sulphide the titre is the iodine value of the gas, and is subtracted from the titre at other points to give the hydrogen sulphide by difference. The difference between the figures arrived at for the inlet and outlet of each box gives an approximate figure for the hydrogen sulphide absorbed. The hydrogen sulphide may also be determined volumetrically by absorption. The most suitable reagent is a slightly acid 10 per cent. solution of cadmium chloride. The gas is measured in a Hempel or other burette and passed over the reagent. The absorption is noted. As the percentage by volume only amounts to about 1–2 per cent., the figure obtained is not very exact.

Ammonia. The ammonia in the gas can be taken as that at the outlet of the scrubber system. Usually it will be found completely absorbed in the purifiers.

Tar. Tar in the gas from the outlet of the scrubbers may be estimated, as already described, but since the amount of tar is small more gas is used for the determination. (See **81***a*.)

116*a*. *Oxygen*. The oxygen at the inlet and outlet of each box can be obtained by analysis in an Orsat or other apparatus in the usual way. A complete analysis, or a determination of nitrogen, at the inlet and outlet of the sections, is a good check on the air admitted. (See **135***a*, **135***b*.)

116*b*. *Carbon Disulphide and Organic Sulphur Compounds*. The estimation of these compounds in crude gas is a matter of considerable difficulty. One method is to estimate hydrogen sulphide by passing the gas through a U-tube containing precipitated iron oxide, with a guard tube of ammoniacal zinc chloride, and then through a meter, finally estimating the sulphur remaining in the Referees apparatus. (See **142***a*.) In place of the Referees apparatus a calcium chloride tube, to dry the gas, and two absorption bottles, each containing 10 c.c. of perhydrol (100 per cent. H_2O_2) and 75 c.c. conc. caustic soda may be substituted, and placed before the meter. A crystalline compound, possibly $Na_2O_2 \cdot 8\ H_2O$, separates. The sulphur compounds, excepting thiophene, are oxidised to sulphuric acid. The solution is acidified with hydrochloric acid, heated to boiling-point, and the sulphuric acid estimated by precipitation with barium chloride. (See **23***a*.)

The whole of the sulphur compounds, including the hydrogen sulphide, may be oxidised, either by combustion or after absorption in caustic potash, and a separate determination of the hydrogen sulphide will give the sulphur compounds by difference.

Carbon disulphide may be estimated after eliminating hydrogen sulphide with oxide and moisture with calcium chloride, by passing the gas through two absorption vessels, each with 25 c.c. of alcoholic potash (a saturated solution of potash in absolute[1] alcohol), at rate of about 1 cubic foot per hour till 2–3 cubic feet have passed. The bottles are then washed out and the solution made up to 250 c.c. with water, 100 c.c. withdrawn, the alcohol boiled off, excess of sodium peroxide added, the solution boiled, and after cooling and acidifying the sulphur is precipitated as barium sulphate. An error arises through sulphur present in the materials used, which should be allowed for, and also owing to possible absorption of carbon disulphide in the purifying train. Gastine recommends passing the gas through conc. caustic soda solution, followed by conc. sulphuric acid, and then through the alcoholic soda. The thiocarbonate formed in the first vessel is decomposed by copper or zinc sulphate, and the vapour distilled off through sulphuric acid into alcoholic soda. The latter is combined with the bulk. The whole is slightly acidified with acetic acid, mixed with excess of sodium bicarbonate and titrated with a solution of iodine containing 1·68 grams per litre, when 1 c.c. is equivalent to 1 mgm. of carbon disulphide.

Harding and Doran's method consists in absorbing the carbon disulphide in alcoholic potash, as given above. The solution is then boiled, cooled, and acidified with acetic acid. The whole is diluted to 500 c.c., and a portion is precipitated with a known excess volume of standard copper acetate solution. After filtration and washing, potassium iodide is added to the filtrate and the liberated iodine titrated back with thiosulphate, giving the excess of copper present. By difference, the copper precipitated as copper xanthate, $(CS \cdot S \cdot OC_2H_5)_2\ Cu$, is found.

$$CS_2 + KOH + C_2H_5OH = CS_2 \cdot OC_2H_5K + H_2O.$$

---

[1] See p. 100.

Cyanogen and Hydrocyanic Acid. Two methods have been advocated—the " polysulphide " and the " ferrocyanide." Probably the former is least troublesome.

117*a*. *Polysulphide Method.* In this 50 to 100 c.c. of polysulphide solution (prepared by allowing pure sulphur to stand in a 10 per cent. solution of ammonia freshly saturated with hydrogen sulphide) are placed in each of three absorption vessels, and 10 cubic feet of gas are passed through at a rate of 1–2 cubic feet per hour. The gas is measured after the absorption, and the measurement may be corrected for loss of volume in the reagent by determination of the per cent. loss in caustic soda in a gas analysis apparatus. It is usual, however, to report results on the purified gas, and this correction is then unnecessary. The meter is protected by a guard tube, with dilute acid and an oxide scrubber to remove hydrogen sulphide. The solution resulting is made up to 500 c.c. with distilled water, and 50 c.c. are taken and acidified with dilute sulphuric acid. The bulk of the hydrogen sulphide is expelled by warming on a water bath for 15 minutes. The solution is then made nearly neutral with dilute caustic soda, and a small excess of lead carbonate is added. The whole is heated to boiling, filtered, and the residue washed. Excess of sulphurous acid is added to the filtrate to give a decided acid reaction, and it is then heated to about 60° C., and excess of copper sulphate added. The solution is kept hot until the white thiocyanate settles, when it is filtered rapidly and washed till free from sulphate. The precipitate is thrown into a beaker, 50 c.c. of boiling water with 20–30 c.c. of normal caustic soda added, and the whole is boiled, filtered, and the precipitate washed till free from thiocyanate. Dilute nitric acid in excess is added to the filtrate with a few drops of 10 per cent. iron alum (as indicator). The solution of thiocyanate is then titrated with N/10 silver nitrate. Owing to interaction of carbon disulphide and polysulphide the results may be a little high.

$$AgNO_3+NaCNS=AgCNS+NaNO_3.$$

117*b*. *Ferrocyanide Method.* In the ferrocyanide method about 25 c.c. of 10 per cent. ferrous sulphate solution is placed in each of three absorption vessels and an equal quantity of 20 per cent. caustic potash solution added. The gas is passed through at about 1 cubic foot an hour until 3 cubic feet have passed. The contents are rinsed into a beaker, 25 c.c. caustic potash solution added and heated to boiling. The whole is filtered and washed with hot water until a few drops show no blue colour when acidified and tested with a drop of 1 per cent. ferric chloride solution. The filtrate is diluted and made up to 500 c.c. and shaken well. One hundred c.c. are removed and dilute sulphuric acid (sp. gr.=1·5) is gradually added with constant stirring until the solution is slightly acid to litmus. It is then titrated with zinc sulphate solution (about 5 grams per litre) previously standardised against potassium ferrocyanide solution (10 grams $K_4Fe(CN)_6{\cdot}3\ H_2O$ per litre). The end-point is determined by " spotting " on filter paper against a drop of ferric chloride. In doing this, the precipitate of zinc ferrocyanide must not come into contact with the ferric chloride. About 30 seconds are allowed for the colour to develop.

$$2\ Zn\ SO_4+K_4Fe(CN)_6{\cdot}3\ H_2O=Zn_2Fe(CN)_6{\cdot}3\ H_2O+2\ K_2SO_4.$$

The precipitate is not exactly of the composition shown, but this difficulty is obviated by standardisation against pure potassium ferrocyanide.

Instead of the titration with zinc sulphate the ferrocyanide may be decomposed and the cyanogen distilled off in the presence of cuprous chloride, as suggested by Williams. The solution and precipitate obtained from the absorption is warmed gently, with slow addition of sulphuric acid, till the bulk of the hydrogen sulphide has been removed. To the still alkaline solution is added lead carbonate to remove the last traces of sulphide. The filtered solution is acidified in a distillation flask with sulphuric acid, and about 0·2 gram of cuprous chloride, free from basic compounds, dissolved in a few drops of hydrochloric acid, is added. The whole is distilled gently into excess of dilute caustic soda. As the distillation proceeds the solution clears—any precipitate produced by the cuprous chloride being gradually decomposed.

The alkaline distillate is titrated with N/10 silver nitrate, after addition of a few drops of 10 per cent. potassium iodide, with constant shaking until the first permanent opalescence occurs.

$$2\,NaCN + AgNO_3 = NaAg(CN)_2 + NaNO_3.$$

Spent and Partially Spent Oxide. As a method of analysis for moisture, sulphur and tar in spent oxide has been agreed upon between buyers and sellers, this may form the basis of control analysis.

118*a*. *Moisture.* The estimation of moisture is made by drying 5 grams in a steam bath at 100° C. for 1½ hours, cooling and weighing in the usual way. The sample is reduced to pass a 20-mesh sieve. A small loss of sulphur occurs, as hydrogen sulphide, in wet samples.

Before estimating the sulphur the oxide must, of course, be completely "revivified." After drying the oxidation is usually complete, but if doubt exists the sample should be slightly moistened and dried again slowly at 100° C.

118*b*. *Sulphur and Tar* (*Marsden Method*). The dried residue from the moisture determination is extracted for 2 hours in a Soxhlet apparatus (Fig. 27) with freshly distilled carbon disulphide. The latter is then distilled off, the flask cautiously blown out with air and gently warmed to fuse the sulphur, care being taken that no loss by overheating occurs. After the flask has cooled completely, it is again blown out with dry air, and weighed. This gives the total sulphur plus tar. Fifteen c.c. of conc. (95 per cent.) sulphuric acid are poured on to the sulphur in the flask, and the whole heated for 2 hours at 100° C. in a water oven. After cooling, the contents of the flask are diluted, filtered, and the purified sulphur washed free from acid and dried. The filter paper and contents are then extracted in the Soxhlet again with carbon disulphide, and the latter distilled off. The residue is fused as before, cooled and weighed as pure sulphur. The tarry matter is obtained by difference.

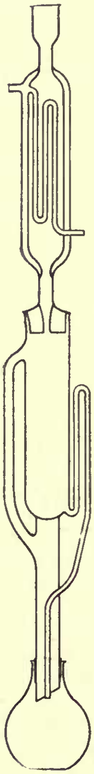


FIG. 27. SOXHLET APPARATUS.

In place of the rather expensive extraction "thimbles" a filter paper, folded into a cone, may contain the oxide or sulphur. A plug of cotton-wool is placed over it and the top edges of the filter paper turned over. The whole is then compressed and slid gently into the Soxhlet apparatus.

Other methods of determining sulphur and tar consist of combustion and volumetric cyanide methods.

119*a*. *Ammonium Salts and Soluble Iron Salts.* Ten grams of the wet sample are washed with cold water if alkaline, and with hot water if acid, till free from ammonia and iron. The filtrate is made up to 500 c.c. and 250 c.c. are made alkaline with caustic soda and distilled into excess of standard acid to estimate the ammonia, while the remainder is oxidised by warming with a few c.c. of hydrogen peroxide (10 volumes). The iron is precipitated with excess of ammonia, filtered and washed. The precipitate is dissolved in a little dilute sulphuric acid, reduced, and titrated with permanganate. (See **109***c*.)

119*b*. *Ferrocyanide.* Ten grams of the undried sample are well ground in a mortar with an equal weight of caustic soda, and sufficient water to make a thin paste. The contents of mortar are transferred to a Büchner filter and the filtrate collected in a 250 c.c. flask. The residue is well washed with cold water to make up to the mark. Twenty-five c.c. are taken; the free caustic soda is neutralised by addition of ammonium sulphate, and the whole then well mixed with cream of lead carbonate to remove sulphide. The mixture is filtered and washed. The filtrate is warmed and a little ferric alum added, so that the settled solution shows a blood-red colour. The precipitate of prussian blue is filtered and washed, transferred to a beaker, 25 c.c. of normal caustic soda added, and the iron filtered off. The filtrate contains the sodium ferrocyanide equivalent of the ferrocyanide and carbonyl ferrocyanide originally present. The hydrocyanic acid is distilled off in presence of cuprous chloride, caught in caustic soda and titrated with silver nitrate, as in Williams' method. (See **117***b*.)

The cyanide found is usually calculated as $Fe_7(CN)_{18}$.

119*c*. *Thiocyanate.* The thiocyanate may be estimated in the filtrate from the prussian blue, by acidifying, with addition of sodium sulphite and copper sulphate to precipitate cuprous thiocyanate. The thiocyanate is decomposed with caustic soda and passing into solution is estimated, after acidifying with nitric acid, by titration with N/10 silver nitrate in presence of ferric alum. (See **8***b*.)

119*d*. *Carbonyl Ferrocyanide.* By addition of five times the volume of alcohol to a portion of the original solution, the ferrocyanide, sulphates, and carbonates, may be precipitated, leaving the carbonyl ferrocyanide in solution. By determining the ferrocyanide in the precipitate the carbonyl ferrocyanide can be obtained by difference.

119*e*. *Naphthalene* (*Metro.*) Ten grams of the original sample of oxide, roughly pulverised, is digested with 100 c.c. of 90 per cent. alcohol in a small closed flask for three or more hours at about 30° C. The liquid containing the naphthalene is filtered into a larger flask and the residue washed with alcohol. Four to five hundred c.c. of picric acid solution (nearly saturated) is added, and after shaking and standing a short time, the picrate formed is filtered and washed into a flask with the smallest quantity of picric acid solution. Absolute alcohol is added to dissolve the entire precipitate. Finally, the naphthalene is thrown down as picrate by addition of a large excess of picric acid solution and the picrate filtered off, decomposed with hot water and titrated with N/10 caustic soda as described elsewhere. (See **143***a*.)

REFERENCES

Carnelley and Walker. Constitution of Ferric Hydrates. *J. Chem. Soc.*, 1888, **53**, 59.

P. Nicolardot. Constitution of Ferric Hydrates. *Ann. Chim. et Phys.*, 1905, (1), **6**, 334.

L. T. Wright. Ferric Hydrates and Purification. *J. Chem. Soc.*, 1883, 156.

G. Weyman. Molecular Structure, etc. *J.S.C.I.*, 1918, 333T.

Eastwood. Bog Ores, etc. *Gas Journal*, 1882, **39**, 469.

Rodt. Iron Disulphide, etc. *J.S.C.I.*, 1918, **37**, 732A.

Gedel. Oxide Purification. *J.S.C.I.*, 1905, 664 ; 674. *J. Gasbeleucht*, 1905, **48**, 412 ; 428.

Stavorinus. Oxide Purification. *Gas World*, 1905.

H. Bunte. Oxide Purification—Thermal Aspect, etc. *Gas Journal*, 1903, **83**, 676, 749, 812.

Debus. Sulphur Dioxide and Hydrogen Sulphide. *J. Chem. Soc.*, 1888, **53**, 278.

Cross and Higgins. Interaction of Sulphur and Water. *J. Chem. Soc.*, 1879, (1), 250.

Alkali, etc., Inspector's Reports. Oxide Purification. 1911, 1912, 1913, 1915, 1916, 1918, 1920, 1921.

Alkali, etc., Inspector's Report. Absorption Apparatus. 1912, 18.

G. Weyman. Oxide Purification. *Gas Journal*, 1920, **149**, 301 ; **150**, 256, 489.

H. G. Colman and Yeoman. Analysis of Spent Oxide. *Gas Journal*, 1919, **145**, 68 ; 112 ; 169.

H. E. Williams. Chemistry of Cyanogen Compounds. 1915.

H. E. Williams. Estimation of Cyanogen. *J.S.C.I.*, 1912, 468.

H. G. Colman. Estimation of Ferrocyanide, etc. *Analyst*, 1908, 261 ; 1910, 295.

F. W. Skirrow. Estimation of Ferrocyanide, etc. *J.S.C.I.*, 1910, 319.

O. Guillet. Reduction of Carbon Disulphide. *J.S.C.I.*, 1913, 78.

CHAPTER X

TOWN GAS

Under the Gas Regulation Act (1920), a gas concern may determine practically any value for the calorific value of Town gas to be supplied. In view of the findings of the Board of Trade Committees on inerts and on carbon monoxide (1921), gas of practically any composition may be supplied, provided that it is free from hydrogen sulphide, and possesses a distinctive odour. Whatever be the values fixed for calorific value and composition, they must be maintained consistently, and with as little variation as possible. Under the Act, penalties may be enforced for reduction of calorific value below the declared value, and the introduction of recording calorimeters will allow variation without penalty over only a very short period of time.

To avoid penalties, the gas supplied is necessarily of a higher calorific value than the declared value, and the difference is a loss of thermal value to the gas concern. Hence uniformity is an essential feature of modern gas supply, and this must be of the greatest advantage to both gas concern and the general public. Only under such conditions can the maximum thermal efficiency be obtained in the use of gas for all purposes.

The declared value is necessarily fixed, having regard to the maintenance of a uniform supply. It has also to be remembered that the rate of thermal supply to the consumers' apparatus has to be maintained. Since the distribution system can be regarded as fixed, and usually is on the small side, it is obvious that a reduction in the calorific value of the gas is a question for serious consideration in view of the increased pressure necessitated. Again, the condition of the manufacturing plant has to be considered. While no less than 15,500 cubic feet of straight coal gas, of a calorific value of 550 B.Th.U. per cubic foot, can be obtained from a ton of coal in a coal-testing plant with metal retort—a yield of 85 therms per ton—in this case, the nitrogen content of the gas is less than 1 per cent., a condition which can hardly be approached with fireclay retorts. Yields of over 70 therms per ton can be obtained in practice, but the yields of gas per ton or the calorific value are considerably lower. It is not practicable to maintain plant entirely in a new state, and upon the average condition of the plant over a considerable period will depend the maximum possible calorific value.

Lastly, and most important, is the question of that particular quality and composition of gas which supplies the least costly therm in the gaseous form. This depends on both local and general conditions, which vary from time to time. The relative costs of the production and value of blue and carburetted water gas, of benzol, and tar products, of ammonia, and of coal itself, have to be balanced in order to ascertain in which direction economy lies. It may be pointed out, however, that the increased economy which can be obtained by a change in manufacturing operation must be substantial to outweigh the disadvantages and costs of altering a settled policy.

As a rule the number of manufacturing units is very large. Many different types of gas are manufactured in most works, much being produced in intermittent plant, and the quality varies accordingly. Mixing effected in purification plant, and in the holders, is sufficient as a rule to take up hourly variations, but is not sufficient to tide over daily fluctuations. Constant determination of the calorific value and quality of all the different streams of gas made and distributed is essential, and shows the periodical variations in the manufacture in different units which are obscured by hourly fluctuations to those in charge of the different units.

The provision of adequately equipped and properly situated testing stations is necessary, and here it may be pointed out that a little extra care and expense in placing and fitting up such stations will make all the difference in the accuracy of the results, and will reduce enormously the time and trouble required to obtain the necessary information. In spite of the ingenuity which has been exercised in their design, the accuracy of scientific instruments, particularly recording instruments, remains dependent on the maintenance of fairly equable atmospheric conditions, and, in many cases, the supply of clean water at even temperature and pressure. Care is to be taken in leading the gas into the station. The pipe used is screwed so as to penetrate for a distance of, say, one-third of the diameter of the main into the gas stream, at some point in the middle of a straight length of the main. The lead is made as short as possible and is covered all the way. There should be no possibility of condensation occurring in the lead, and a constant stream of gas should be always passing through. Governors are necessary in most cases to reduce the gas pressure to about 2 inches w.g. Sometimes considerable difficulty is experienced in keeping the pressure uniform when the lead is taken from a large main at high pressure. A mercury governor may be followed by a diaphragm, or a balanced-weight governor. Trouble occurs where large fluctuations are experienced, as in the case of the automatic-lighting pressure waves, in the jamming of the valves of the governors. Periodical cleaning of the valves and the introduction of a vessel, say, of 3 or 4 litres, to act as a "shock-absorber," will overcome this. Additional governors are almost always provided on the instruments. The insertion of a small orifice will often take up sudden changes, but there is danger in the orifice becoming choked with dust.

Testing stations are placed at the outlet of each section of the works' purifiers, on the mains leading from the holders, at the district governors, and in different parts of the district.

122*a*. *Calorific Value.* The calorific value of gas is almost universally determined in instruments of the water-flow type. The Boys Calorimeter has been defined as the official instrument, and is accurate. For works' use, however, it suffers from somewhat over-elaboration, and the water coils need a considerable amount of repair and maintainence. At the present, there is no instrument so reliable, quick, and simple as the Junker Calorimeter.

There is no need to describe these instruments, as detailed accounts will be found in the official *Notification of the Metropolitan Gas Referees*, and other works, but some notes as to their use may be of service.

For even ordinary accuracy all calorimeters have to be kept clean and the bright parts polished. The thermometers require checking from time to time by removing them, and comparing the readings when both are placed in the same vessel of water, maintained for an interval of time at different temperatures. Their accurate calibration is not essential, but there should be no great difference in the readings within the limits of use, and for this reason it is much to be preferred if no correction at all has to be introduced into the calorimetric calculations. The bulbs of the thermometers should not exceed 0·25 inches in diameter. (*Metro.*)

The meter will require periodical cleaning and checking. A standard bottle is used which delivers $\frac{1}{12}$ cubic feet when the air in it is displaced with water between two marks. When connected to the meter, which is open to the atmosphere at the outlet, the meter hands should show exactly one revolution for each volume of the bottle delivered to it. The temperature is adjusted to 60° F. An improved form of the bottle has been designed by Coste and James.

Meters rarely give the correct registration for all parts of a revolution, but each complete turn should read correctly within the limits of observation. Incorrect registration is brought to the correct value by adjustment of the water level, which is re-marked so that the same level can again be found.

The pressure of the gas at the outlet of the meter may be found by a pressure gauge and added to the observed barometric pressure before correcting the volume of the gas for the atmospheric conditions. It is convenient to arrange this pressure at the outlet of the meter (after the governor) to be constant at, say, 2 inches w.g. (or 0·15 inches mercury), so that the same correction can always be made. (*Metro.*)

It is advisable to instal a small ball-cock cistern a few feet above the working bench, which will contain sufficient water for an hour's run, and will help to maintain an equable temperature and pressure of the water supply. When bringing a new Boys Calorimeter into use it may be necessary to fill the coils with water from a high-pressure supply to remove air-locks.

Usually, for ordinary work, it is only necessary to correct for the volume of the gas used saturated with moisture to 60° F. and 30 inches pressure, but for more accurate work other corrections are introduced by the Gas Referees, which sometimes make a difference of as much as 5 B.Th.U.

In the first place, the products of combustion escape from the calorimeter carrying an amount of water vapour corresponding to saturation at the temperature of their exit. While the gas used for the test is saturated at the in-going temperature, the air is usually only partly saturated. The temperature of exit of the products of combustion may not be the same as that of the atmosphere, and the volume may be less than the total volume of air and gas used. The Gas Referees take one volume of gas as burning with seven volumes of air to give 6·6 volumes of products. The moisture-content of air is determined by use of a wet and dry bulb hygrometer, while those of the gas and products of combustion are taken as the amounts corresponding to saturation at the meter and effluent gas temperatures respectively. If the amounts in grains of water per cubic foot are a, b, and c respectively, then $6{\cdot}6\,c.-(7\,a+b)$ will be the excess of moisture carried away, and as the latent heat of water (15·5° C.—100° C.) may be taken as 1,070 B.Th.U. per lb., or $\frac{1070}{7000}=0{\cdot}15$, one grain will carry away about 0·15 B.Th.U., whence the correction : $0{\cdot}15\ \{(6{\cdot}6\,c-(7\,a+b)\}$.

The temperature of the products escaping may not be the same as that of the air used for combustion, and heat may be carried away or gained as sensible heat in the products. The specific heat of the products may be taken as 0·237. The heat lost or gained in the 6·6 volumes of products is approximately $\frac{0{\cdot}237}{7000}\times\frac{6{\cdot}6}{1}\times d\times e=0{\cdot}00022\,d\,e$, where d is the weight in grains of a cubic foot of saturated products at the temperature of the exit gases, and e is the temperature difference between the effluent gases and atmospheric air. The weight of a cubic foot of saturated products is taken as the same as for air, and found from Glaisher's Tables. Tables to facilitate the corrections have been constructed by the South Metropolitan Gas Company.

Calorimeters of the water-flow type are expensive and are not portable. The quantity of gas used is also large. To overcome these difficulties, and to provide a means of checking recording calorimeters, instruments of the " still-water " type may be used. They can be obtained fairly portable, and in any case use a comparatively small quantity of gas, so that the sample can be brought in a container from the sampling place to the laboratory. They require considerable care and skill to obtain consistent results, and the operator should always accustom himself to their use by practice against a calorimeter of the water-flow type.

In the Simmance-Abady portable instrument a calorimeter vessel is provided with a hollow shaft in which a measured volume of gas is burnt. The gas sample is taken in an aspirator vessel and is displaced by water through the burner. The burner is lighted outside the calorimeter, and when the water level passes a certain mark, the burner is quickly inserted in the calorimeter, which contains about one litre of water at known temperature. As soon as the water level has reached a second mark the burner is extinguished, and the calorimeter taken up and swung in the hand to equalise the temperature. The maximum temperature to which the water rises is noted, and the calorific value calculated as the product of the rise in temperature, and the total water equivalent divided by the gas used. By suitable adjustment of the amount of gas burnt (about 0·05 cubic foot), and of the water placed inside the vessel, the rise in temperature can be made to correspond to $\frac{1}{100}$th part of the calorific value. The instruments require standardisation against flow-calorimeters. The values obtained need the usual corrections of the volume of gas used for atmospheric temperature and pressure.

Very accurate results can be obtained with small quantities of gas in a bomb-calorimeter, provided with connections for filling the bomb with the gas. The result obtained is the calorific value at constant volume, which is about 4 B.Th.U. lower than the result at constant pressure.

125*a*. *Recording Calorimeters.* Several different types of recording instruments are available which permit of a continuous record of the calorific value being obtained. All of these are empirical, and although largely automatically corrected for changes in gas volume from 60° F. and 30 inches, are necessarily checked frequently against a value obtained by direct observation. When placed in suitable surroundings and supplied with gas of fairly uniform pressure and temperature, consistent results can be obtained over long periods, but it is essential that careful and frequent attention be given. The Gas Investigation Committee of the Institution of Gas Engineers and the Fuel Research Board have examined several of the instruments in detail. The subject is dealt with elsewhere.

For works use, perhaps the " Sarco " instrument, in which the record is *not* corrected for gas volume, is as reliable and useful as any, and is not quite so subject to surrounding conditions, except as regards draughts. Such instruments are exceedingly useful and practically essential for the control of the quality of the different streams of gas. It must be remembered, however, that they record the calorific value of the gas passing at any time, but this has no relation with the volume passing. Hence in averaging the value for a period from the records, a true average can only be obtained by multiplying the calorific value, as seen from the chart, by the make of gas passed for each small period, adding and dividing out by the total quantity of gas. When the records are obtained from gas during, or prior to, purification, it is frequently observed that the averages do not correspond to the average obtained in a similar way from the purified gas ; the former being considerably higher. This is due in the first place to the fact, that when the calorific value is low, the volume of gas passing is low, and conversely during the periods of maximum output of gas the calorific value is high. As the gases pass through the plant the variations are reduced, and the average comes nearer the truth. The integrating device recently described by Professor Boys, in connection with his new calorimeter, may overcome this difficulty. There is also a natural depreciation in calorific value due to diminution of hydrocarbons during purification, and to air which may be admitted for the purpose of revivification "in situ."

Specific Gravity. The specific gravity is of great importance in the use of the gas, both as regards the question of distribution and design of burners and apparatus. It may be determined by directly weighing the gas in a glass globe of known capacity. The globe should be balanced by a similar globe to avoid correction for air displaced in weighing. The one globe is then evacuated, and filled with the gas and the difference in weight again taken.

125*b*. *Schilling's Apparatus.* It is much more convenient to make use of the fact that the rate of efflux from a small orifice is proportional to the square root of the density—the temperature and pressure being constant. Schilling's apparatus (Fig. 28) consists of a glass cylinder closed at the top, save for a small orifice pierced through a platinum disc. An inlet connection for filling

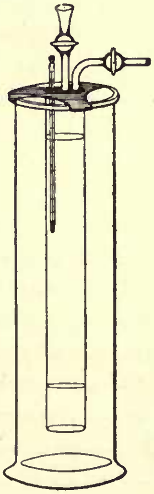


FIG. 28. SCHILLING APPARATUS.

the cylinder is placed at the top and the cylinder is immersed in a jar of water. An aspirator may be attached to this connection and the jar first filled with air. By removing a cap over the orifice the air passes out and water flows into the cylinder. When the level of the water passes a mark at the foot of the cylinder a stop-watch is started and it is stopped when the water level has reached the top mark. The experiment is repeated until three consecutive readings of the time of efflux agree. The apparatus is then filled with the gas and the rate of efflux determined in the same way. The specific gravity is then given by $\frac{T^2}{t^2}$ where T is the time of efflux in seconds for the gas and t for air.

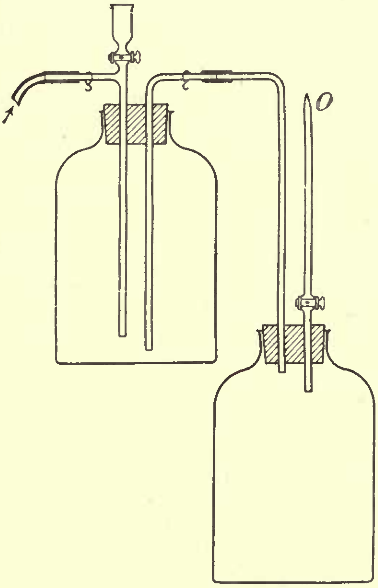


Fig. 29.—Apparatus for Sampling Gas under Pressure.

Owing to the effect of the inert constituents in raising the specific gravity of coal-gas, recording indicators can be of great service in controlling the retort-house gas.

126*a*. *Analysis of Gas—Sampling.* As a rule, in checking the composition of purified gas, average samples will be required. For this purpose a gas stream may be slowly drawn into a 12 or 20 cubic feet gas-holder, mixed and a small sample drawn off; or a continuous sampling arrangement may be used such as indicated in Fig. 29. In this case the Marriott's bottle is employed to aspirate the gas at constant pressure, while a small orifice at the end of the tube O regulates the volume passed. The sample is sealed off by the gas pressure forcing water up the tube O when the full sample has been accumulated. If the pressure on the inlet varies, the arrangement shown in Fig. 30 (due to A. Edwards[1]) can be introduced. The fine capillary tube A determines the volume of gas passed at pressure maintained constant on the inlet side by the governing principle. This latter consists of a U-tube, with limbs of unequal area—the bottle and the tube E. Pressure applied through B causes the fluid (mercury or oil) to rise in E without materially lowering the level in D. Increase in pressure merely causes a greater seal on the tube C. The

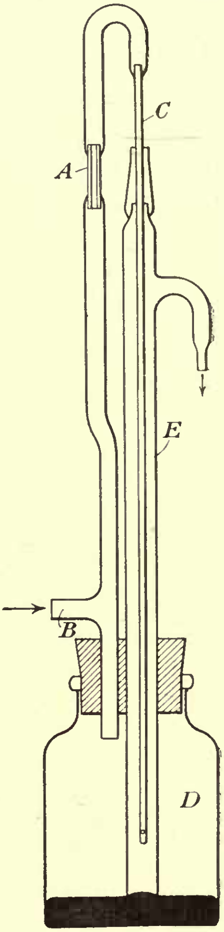


Fig. 30.—Edwards Gas Pressure Regulator.

---

[1] Private communication.

effective pressure acting upon *A* is fixed by the height of the end of the tube *C* above the fluid in *D*.

The sampling arrangement used by the South Metropolitan Gas Company is very similar, consisting of a pressure regulator, a seal to prevent diffusion, and a Marriott bottle containing brine, which drips through a regulated orifice into a second vessel open to the atmosphere. Arrangement is made so that a portion of the sample may be drawn off for transference to the laboratory.

Snap samples may be taken in tubes provided with taps at each end if they are not required to be kept for more than a few hours. Such sampling tubes are tested for tightness by filling with water and holding vertically. The lower tap is opened and any leak will show by water dripping out. The tube is then inverted and the other tap tested in a similar way. Even when proved tight in this way the cocks cannot be relied upon to store samples for any length of time. If a little mercury is placed in the tube before use and allowed to fill the capillary tube adjacent on each side of the taps, after the sample has been taken, the tube can be relied upon to store the gas for a considerable time. The tubes may be filled with water or brine, or a mixture of glycerine and water, and the gas allowed to flow in as the liquid runs out of the other end. Or the gas may be allowed to blow straight through to displace the air for, say, 10 minutes. Special tubes may be obtained in which provision is made for filling the capillary tube outside the tap with liquid before using the sample.

When a large number of samples are required at one time, plain cylindrical pipettes can be used. The gas is allowed to blow through the whole of the tube for, say, 10 minutes at full pressure when the tube is capped off at each end with rubber tubes and clips. The tube can then be removed to a small flame and sealed off at the constrictions. In opening the tubes to draw off the sample, each end is snapped off under mercury, or in a rubber tube filled with mercury.

Absorption. Whatever the apparatus used for analysis, the carbon dioxide, oxygen, unsaturated hydrocarbons, saturated hydrocarbons, and usually the carbon monoxide, are absorbed in liquid reagents in the order given with one or two exceptions, which will be mentioned later. Hydrogen and methane are estimated by processes of combustion and nitrogen by difference.

The reagents used for the absorption are made as described below :—

127*a*. *Caustic Potash for Carbon Dioxide.* About 10 sticks, or 150 grams, are dissolved in 450 c.c. of water, keeping the containing vessel cool under the tap. The solution is stored in a bottle with a rubber cork. Solutions of caustic soda can be used, but if the reagent is concentrated, crystals of carbonate may separate while in use and block the tubes of the apparatus.

The solution used must not be too concentrated or the gas will be dehydrated, and an undue amount of hydrocarbon may also be absorbed. The absorption is rapid and complete in 2 or 3 minutes. The solution given above will absorb 1 or 2 litres of carbon dioxide per 100 c.c. of reagent.

127*b*. *Pyrogallol for Oxygen.* The compound 1 : 2 : 3 trihydroxybenzene in alkaline solution possesses a high reducing power and will absorb considerable quantities of oxygen. A clear white solution in caustic potash gives on contact with oxygen a blood-red, and finally almost black, colour. A stock solution of 10 grams of pyrogallol in 300 c.c. of water is made, and immediately before use an equal volume of caustic potash solution (1 part *KOH* in 2 of water) is added. After a time, and unless strongly alkaline, the solution may liberate carbon monoxide. Obviously carbon dioxide and acid gases must be removed before the reagent is used. The strongly alkaline solution may absorb hydrocarbons, and many prefer to remove the latter with bromine water before using this reagent.

The absorption is rapid, being complete in 3 to 4 minutes, and 100 c.c. of the pyrogallol solution can be used to absorb small amounts of oxygen from over 100 analyses if kept from contamination with the atmosphere.

128*a*. *Bromine Water for Unsaturated Hydrocarbons.* A solution is made consisting of water shaken up with a few drops of bromine and allowed to stand, in presence of excess of the liquid, for 24 hours. Or a normal solution of potassium iodide may be similarly saturated. (*Metro.*) It is then of a bright red colour. Pipettes are emptied when the colour becomes yellow, or if an oil consisting of the brominated compounds separates. A distinct red colour should be visible in the gas after standing in presence of the bromine water for about 3 minutes. The excess of bromine vapour is afterwards removed from the gas by passing the latter into the caustic potash bulb. Benzene vapour is not appreciably attacked, but may be partially removed in solution in the brominated compounds of other hydrocarbons.

128*b*. *Phosphorus for Oxygen.* Yellow phosphorus will absorb oxygen with ease. Once the reaction has started it goes to completion. A special pipette is required, which is filled with water. The sticks, which have been cut to the suitable length, are then introduced. Care is to be taken that particles are not allowed to become scattered, or left uncovered, or they may cause fire some considerable time later. The phosphorus bulb is either made of brown glass or covered with black cloth to protect the phosphorus from the action of sunlight.

The reaction takes place at about 20° C. with sufficient rapidity and is attended by white fumes. Hydrocarbons, such as ethylene, inhibit the reaction, and therefore in this case the olefines must be removed prior to the absorption of oxygen. On the whole the use of bromine water for hydrocarbons, followed by phosphorus for oxygen, appears to be the most accurate method.

128*c*. *Fuming Sulphuric Acid for Hydrocarbons.* Fuming sulphuric acid (sp. gr., say, 1·93, containing about 20 per cent. SO_3) is sometimes used in place of bromine water, but is hardly to be recommended. It will absorb benzene and similar hydrocarbons as well as the unsaturated ones. Oxygen may disappear from the gas in the organic compounds formed. Care must be taken to saturate the gas with water vapour before reading the burette after absorption, and to remove acid vapours in the caustic potash pipette.

128*d*. *Reagents for Saturated Hydrocarbons.* The correct absorption of benzene vapour is obviously desirable, but although many suggestions have been made, for example—the use of alcohol (Hempel), and ammoniacal nickel cyanide (Dennis and McCarthy)—there is as yet no generally accepted reagent.

129*a*. *Cuprous Chloride for Carbon Monoxide.* The cuprous chloride may be dissolved either in an acid or an ammoniacal solution. The former may be prepared by dissolving about 120 grams of cuprous chloride in hydrochloric acid of specific gravity 1·12. The reagent is kept in contact with copper gauze. Slight oxidation will not affect the results, but if the colour becomes green the solution is worthless until again reduced. The ammoniacal solution is made up by dissolving 250 grams of ammonium chloride in 750 c.c. of water and adding 250 grams of cuprous chloride. The whole is well shaken and stored in a well-stoppered bottle. Portions are withdrawn as required, and one-third of the volume of strong ammonia (sp. gr.=0·905) is added to the portion withdrawn. The gas after the absorption is freed from traces of ammonia by transference to a pipette containing acidified water.

It is now possible to obtain sufficiently pure cuprous chloride as the commercial salt, but this is expensive and it may be preferred to prepare the salt as follows. Scrap copper filings or turnings or the crude commercial salt are dissolved in conc. hydrochloric acid. The solution is heated to boiling-point and further copper added. After digestion for about an hour at boiling-point the solution is poured into about ten times its volume of water. After settling the white precipitate is rapidly filtered off under vacuum, or centrifuged, till substantially dry, washed with a little alcohol, and again subjected to vacuum or centrifuging. The powder can then be immediately used for making up the stock solution.

Solutions of carbon monoxide in cuprous chloride have an appreciable vapour pressure. The absorption is therefore never really complete. It is imperative that the gas should be treated with at least two separate quantities of solution, the last one being a substantially fresh solution. The first solution should absorb nine-tenths of the carbon monoxide present and is renewed as soon as it fails to do so. The second one will then absorb practically all the remainder of the carbon monoxide. The readings for each absorption are always taken, and when the second solution shows the presence of more than one-tenth of the whole it is used as the first reagent and a fresh solution is prepared for the final absorption.

Probably more errors occur through incomplete absorption of carbon monoxide than any other cause. The error is serious, as the carbon monoxide left may eventually be reckoned as methane, and this has the effect of reducing the hydrogen figure out of all proportion. The nitrogen, which is reckoned by difference, then becomes too high.

Many different forms of apparatus have been designed for accurate analysis, in which mercury is used as the confining liquid. The advantages are a matter of detail, and the most suitable form is that to which the operator is accustomed. Of those which, like the Hempel, measure the gas at constant pressure (atmospheric) the Sodeau provides an excellent example. The Bone and Wheeler apparatus, on the other hand, measures the pressure of the gas at constant volume.

129*b*. *Sodeau's Apparatus.* In this the 50 c.c. measuring burette is placed alongside a levelling-tube to which it is connected by a T-piece at the base. To the third limb of the T-piece is attached a reservoir of mercury, which is counterbalanced and can be raised or lowered at will. To the head of the measuring burette is attached a U-tube containing water which can be drawn along the capillary connecting tubes to wash out any dirty mercury or residue. (Fig. 31.) The pipettes consist of two cylindrical bulbs mounted nearly horizontally one above the other. The upper forms a reservoir to retain mercury when this is displaced from the lower bulb which

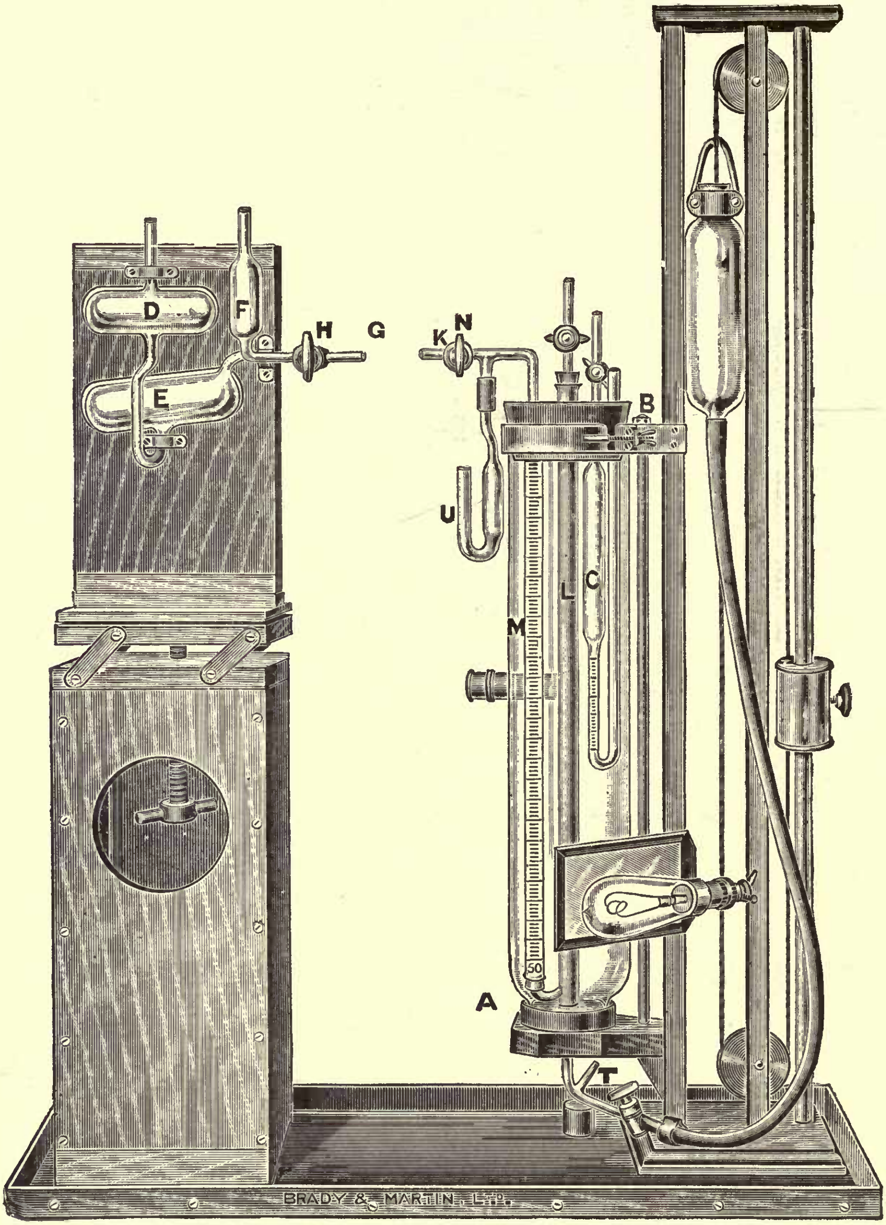


Fig. 31.—Sodeau's Gas Analysis Apparatus.

contains the reagent. A three-way cock on each pipette carries a little bulb to contain mercury, for washing out the capillary connections between the pipette and the measuring burette before and after each transference of gas. The pipettes are connected as required to the burette by pushing the capillary tubing of the pipette into a piece of thick-walled rubber tubing wired on to the end of the burette tube. It is important to grip only the two pieces of capillary tubing near the join when making the connection, so as not to bring any strain to bear upon the taps. The pipettes are mounted on stands which slide into grooves on the adjustable platform, and when not in use are stored in an inclined position so that the weight of the mercury does not fall on the taps. The burette and levelling-tube are mounted in a wide cylinder of water which maintains an even temperature, while a "Kew" correction-tube at the side allows of compensation being made for any alteration of atmospheric temperature and pressure during the analysis. A telescopic arrangement is fitted for reading the burette. A cylindrical explosion burette, and special forms of combustion pipette and phosphorus pipette are also provided. For absorption of unsaturated hydrocarbons with bromine-water, contact with mercury is not advisable. The determination may be carried out in the special form of tube illustrated.[1] (Fig. 32.) The gas is drawn into the bulb through *T*, which is then closed. By lowering the reservoir the burette, which only holds about 60 c.c., is emptied of mercury down to the tap *t*, which is then closed. The bromine water is introduced from the cup *C*. When the reaction is complete, caustic soda is admitted in a similar manner. The tap *t* is then opened and mercury admitted.

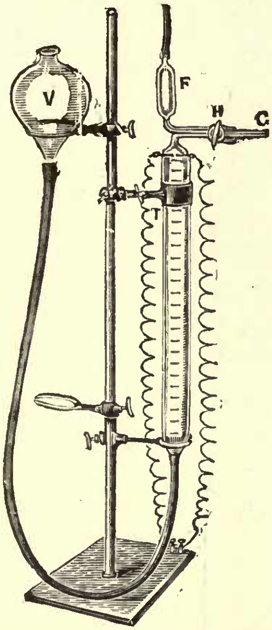


FIG. 31A.

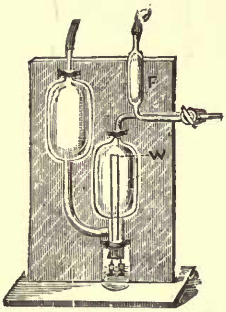


FIG. 31B.

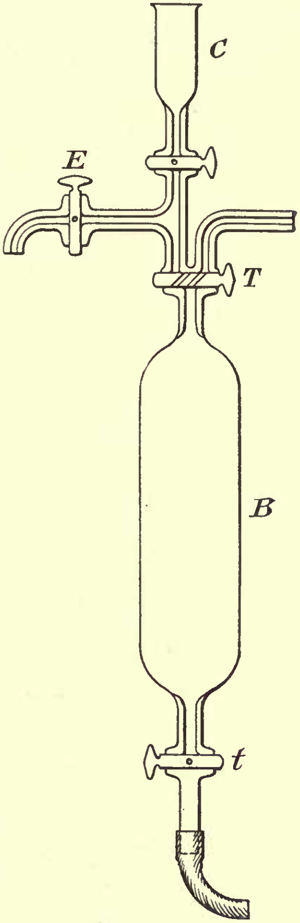


FIG. 32.—SPECIAL BURETTE FOR USE WITH BROMINE WATER.

---

[1] An arrangement used by Prof. P. P. Bedson.

The residual gas is transferred to the measuring burette till the liquid reaches *T*. This tap is then turned and the reagent expelled through *E*. Finally, the capillary to the burette is cleared by mercury from *B* and the gas measured. Obviously the tube can be used for other absorptions.

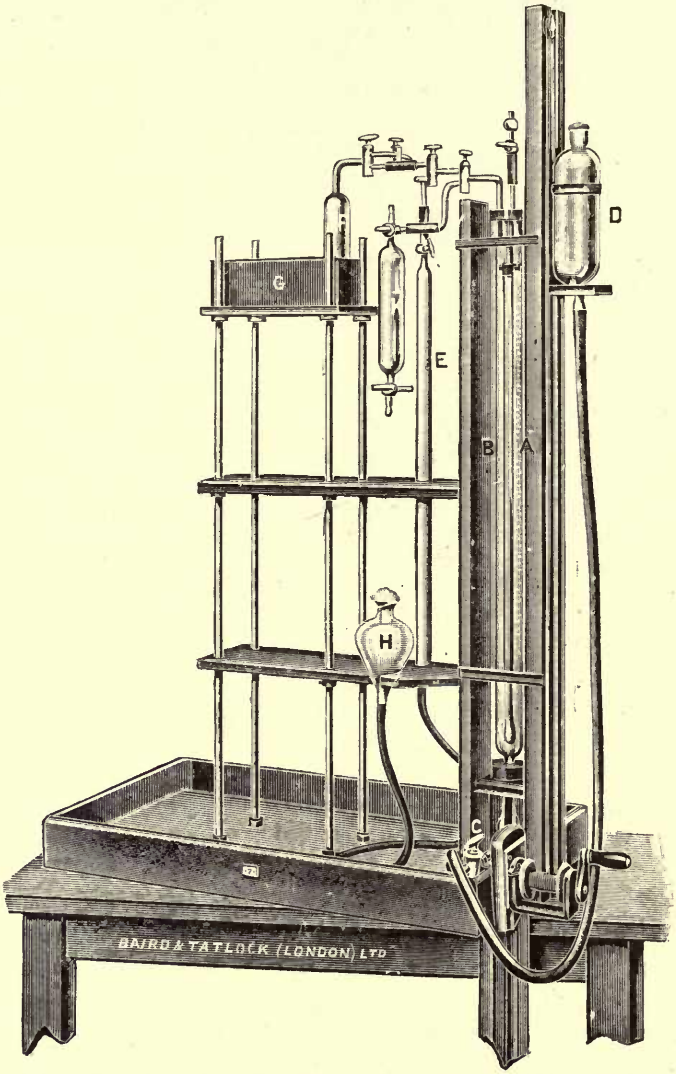


FIG. 33.—BONE AND WHEELER'S GAS ANALYSIS APPARATUS.

The method of analysis used with the Sodeau apparatus is similar to that described for the Hempel apparatus. (See **40***a*.) The precautions taken to clear the capillary tube connections, to keep the mercury of the measuring-tube clean, and the shape of the pipettes make the apparatus both accurate and quick.

133*a*. *Bone and Wheeler Apparatus.* In this apparatus (Fig. 33) the pressure of the gas saturated with water vapour is measured at constant volume. A pair of burette tubes, *A* and *B*, are mounted in a water-jacket and connected at the base by a movable mercury reservoir. The pressure tube, *A*, is graduated in mm. and closed by a tap with rubber connection at the top. The other is only marked to correspond at the 10 mm. intervals, and is connected as shown by a three-way tap to a mercury trough. *E* is the explosion burette and *F* is the reaction vessel. Before making an analysis the whole apparatus, including connections, is filled with mercury and the taps shut. On lowering the reservoir sufficiently the mercury should fall in each of the measuring tubes to correspond with barometric height. Care is taken to introduce sufficient water to saturate the space above the mercury in each case. On raising the reservoir the mercury will again reach the taps. The reservoir must not be raised too quickly, or the mercury will hit the bend at the top of the volume tube with sufficient force to fracture it. The other tube *A* is protected by the flexible tubing by which the tap is connected.

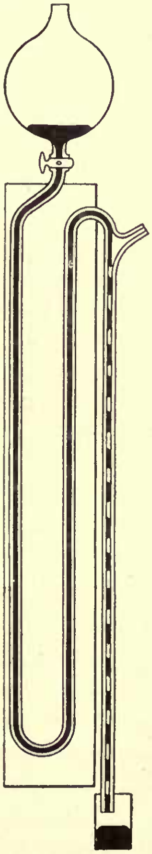


Fig. 34.
Sprengel Vacuum Pump.

The gas sample may be introduced through *K*. The tap is shut. The reservoir is moved so as to bring the mercury level in the tube to any convenient mark. This having been selected is adhered to for the remainder of the analysis. The pressure is then read off. A few c.c. of the reagent is introduced below the mercury in the trough so as to float up into the reagent vessel, either from a bent pipette, or a fixed tap-funnel of which the stem is bent to form a U. Any air admitted by accident can be got rid of through the branch at the top of *F*. The gas is then sent over into the reagent vessel and left for 3 or 4 minutes. The gas is drawn back to the burette until the liquid in the reagent vessel comes to the tap. The reagent is then withdrawn through side branch, followed by a wash of a few c.c. of acid water. For this purpose the side tube of the tap is connected to a drain bottle. The outlet from the top of the latter is connected to a vacuum which may be produced by a Sprengel pump affixed to the stand. A convenient form is illustrated. (Fig. 34.) The fall in height of the mercury must be greater than the height of the mercury barometer. Finally, the gas in the capillary tube is cleared into the burette by mercury from the reagent vessel, and the volume of gas adjusted to the chosen mark when the pressure is again read. If the pressure at the start was 500 mm. and after the absorption 450 mm.,[1] using the volume mark 10 (100 mm.), the percentage volume absorbed is:

$$\frac{400-350}{400} \times \frac{100}{1} = 12\cdot5 \text{ per cent.}$$

The remaining analysis is carried out on similar lines. It is advisable to see from time to time that the tube *A* remains clear of air, and that mercury completely fills it when the reservoir is raised. The

---

[1] The pressure corresponding to the constant volume mark chosen is deducted from each reading.

reaction with bromine water may be carried out in the vessel described for use with the Sodeau apparatus in order to avoid contaminating the mercury.

134*a. Explosion of Residual Gas.* If a sufficiently small amount of gas be taken for analysis in the first place, enough air may be drawn in to give an appropriate explosive mixture with the whole of the residue. For instance, with normal coal gas an amount of gas is taken so that the pressure at the zero constant volume mark is about 100 mm. After removal of the absorbable constituents the residue, giving a pressure of, say, 88 mm., is diluted by drawing in air till the pressure, after closing the burette tap and adjusting to the constant volume mark, is about 680 mm. The mixture is then exploded and the contraction and amount of carbon dioxide resulting measured in the usual way.

An alternative plan consists in connecting a two-way tap to the branch to *K* from the burette tap. To one of the two outlets thus provided may be fitted a mercury sealed tube or trough, in which a portion of the residual gas may be stored, while the remainder is being exploded. The second outlet is used in the usual way for the introduction of the gas sample, etc. A combustion pipette may also be fitted in this way, as suggested by E. W. Smith.

134*b. Estimation of Methane, Hydrogen, and Nitrogen. Explosion.* The determination by explosion has already been described (see **40***a*), and if the analysis has been skilfully performed this method generally gives the most consistent results. In the case of very rich gas objection has been raised as to its accuracy. It is unfortunate that usually only a proportion of the residual gas can be employed for explosion, in view of the large excess of incombustible material which must be present to avoid risk of oxidising nitrogen, as this multiplies any errors. The proportion of combustible to incombustible gas present should be kept, according to Bunsen, between 26 and 64 to 100; the combustible constituents include the oxygen required for complete combustion. Convenient proportions of residual gas and air are :—

Coal gas	12–14 c.c.
Carburetted water gas	15–20 c.c.
Blue water gas	18–22 c.c.
Mond producer gas	40–50 c.c.

made up in each case to about 95 c.c. with air. It is usually inadvisable to use pure oxygen. The residue, after combustion and absorption of the carbon dioxide formed, may be checked to see that an excess of oxygen remains.

With dry producer gas, and such gases as contain very small amounts of hydrogen, there is some difficulty in producing a mixture which will explode. In such a case air is added in excess and a few c.c. of electrolytic gas produced by the electrolysis of a little acidulated water. The explosion may then be regulated to the extent desired.

134*c. Combustion.* Hydrogen may be preferentially burnt in presence of palladium asbestos without the methane being materially affected, provided the temperature is not too high. The asbestos is contained in a small silica or quartz tube, and the residue, mixed with air, is passed through the tube heated to incipient redness. The temperature must not be allowed to rise so that the asbestos glows brightly for fear of burning methane. L. A. Levy has introduced a capillary, containing a platinum iridium wire, which is heated to redness by a current which is passed through. If carbon monoxide is present it will be partially burnt. When the contraction and amount of carbon dioxide so produced has been noted the wire may be raised to white heat and the methane and remaining carbon monoxide combusted. The contraction and carbon dioxide are again measured.

135*a*. *Jäger Method.* One of the simplest and most reliable methods consists in the fractional combustion of the gas residue over copper oxide, which supplies the necessary oxygen. The hydrogen is first burnt by passing the gas backwards and forwards over the copper oxide contained in a small silica or porcelain combustion tube at a temperature of 270° C., from a Hempel burette into a Hempel pipette filled with caustic soda solution. When the contraction which represents hydrogen has been measured, the temperature is raised to a bright red heat, when methane, as well as higher saturated hydrocarbons, such as ethane, are burnt. Since the caustic soda absorbs the carbon dioxide formed, the second contraction represents the methane present. If the residue is collected over mercury and the carbon dioxide afterwards absorbed and measured independently of the contraction due to hydrogen, the amount of hydrocarbons present higher in the series than methane will be indicated, since the ratio of the volume of the carbon dioxide formed to the volume of gas burnt is higher as the number of carbon atoms in the molecule increases.

It is possible for oxygen to be liberated from the copper oxide at the higher temperature, but this can be reabsorbed by reducing the temperature of the copper oxide and again passing the residual gas over it before the final reading is taken. A correction is necessary for the small amount of oxygen in the air filling the tube at the start of the analysis which is effected by actual determination—using pure hydrogen. Care in manipulation is necessary to prevent any caustic potash from entering the combustion tube, or the latter will crack. (See also **135***b*.)

135*b*. *Nitrogen.* It will be obvious that since the figure for nitrogen is found by difference that the errors of analysis are apt to make the result uncertain. The amount of nitrogen in coal gas is of fundamental importance, both in the control of the manufacture and purification, and also in the use of the gas. If nitrogen was accompanied by its equivalent of oxygen as it exists in the air it would not be detrimental, for an equivalent proportion must afterwards be admitted at the burner, but usually the amount of oxygen present in coal gas is very small.

While the determination of nitrogen as the residue after combustion of other constituents and the removal of carbon dioxide is not necessarily more accurate than the determination by explosion, a method has been evolved which is simple and accurate, and can be made in less time than by a complete analysis. It is found that the nitrogen determined by explosion shows abnormal results with gases of high calorific value owing to the varying effect of the intensity of the explosion.

The "Metrogas" apparatus[1] designed by E. V. Evans is illustrated (Fig. 35). It is suitably mounted for convenience and portability in a wooden frame. The opaque quartz tube *C* contains granulated copper oxide between two asbestos plugs.

---

[1] As made by Messrs. Townson and Mercer, Ltd.

Three to four inches of this are heated in the tip of the slot Bunsen flame, so that the base of the tube is maintained at red heat. Carbon dioxide generated in the Kipps apparatus, and purified in the bubbling tube, filled with sodium carbonate solution, is passed by *G* through the apparatus and out at the cup on *J*. Air is expelled from the sampling burette connection by drawing in carbon dioxide and again expelling it several times. Finally, by closing the tap *J* and opening *I* a sample of the carbon dioxide (100 c.c.) is drawn into the burette, which contains brine acidified with sulphuric acid and coloured with methyl orange as the sealing liquid. The measured volume is then passed to the alkali burette *A*, which contains caustic soda solution.

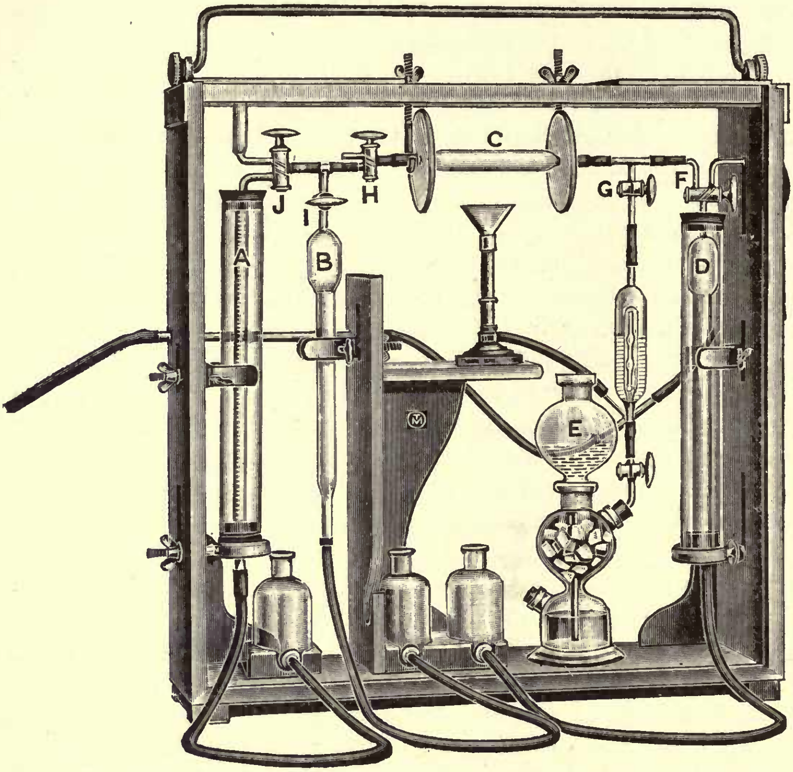


Fig. 35.—"Metro" Apparatus for Determination of Nitrogen in Gas.

The carbon dioxide is absorbed when the residue should not exceed a volume occupying 1 inch in length of the capillary tube (about 0·05 c.c.). This residue is expelled by drawing it back to *I* and thence to the atmosphere through *J*. The purity of the carbon dioxide and absence of air having been proved, the gas sample is introduced into the burette *D*, adjusted to 100 c.c., and the temperature of the water-jacket noted. The taps *J* and *G* are closed and the gas drawn and driven through the quartz tube into the acid burette at the rate of about 10 c.c. per minute. The gas is then drawn back and sent forwards again, so that the liquid from the sampling burette comes above *F*. The reduction in volume is made up in the acid burette by slowly admitting carbon dioxide from *G*. The tap *H* is shut and the gas passed backwards and forwards to the alkali burette until a constant volume of residue is obtained. This residue is taken as nitrogen and the volume may be corrected for any difference in temperature at which the measurements are taken. If desired, the residue may be diluted with carbon dioxide to 100 c.c. in the acid burette and submitted to further combustion.

The copper oxide is regenerated after every three experiments by passing air over from *J*. It requires renewal after being used about thirty times.

137*a*. *Care of Taps.* In all apparatus, which includes well-made taps impervious to gas under considerable pressure differences, there is considerable liability for the plugs to jam in the sockets, particularly if the apparatus is employed intermittently. A good lubricant consists of a mixture of equal parts of soft rubber shreds and vaseline melted together and stirred to an even consistency. Apparatus which is to be left for any length of time is best left with the plugs of the taps out of the sockets. Jammed taps can usually be successfully loosened in the following way: The tap is disconnected and placed with the top of the plug downwards so as to rest the shoulders of the socket on two hard surfaces; for example, the edges of a small vice, leaving the plug itself free to move, as illustrated in Fig. 36. A hard-wood pin, tapered so that the end is about the same diameter as the projecting base of the plug, is held on the end of the plug and given one or two sharp blows with the hammer. The plug will then drop out. It is advisable to protect the edges of the socket by placing a few folds of cloth between the glass and the hard surface.

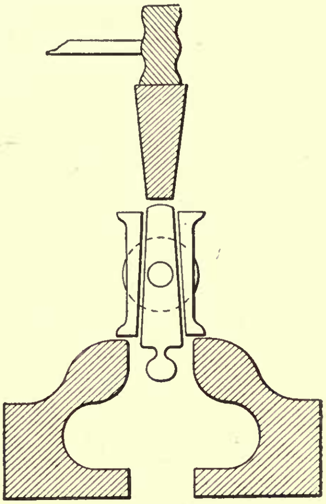


FIG. 36.—METHOD OF LOOSENING TAPS.

137*b*. *Calculation of Physical Properties from Analysis.* Many important physical properties, such as the specific gravity, specific heat, calorific value, oxygen requirements for complete combustion, are additive properties and may be calculated as the sum of the properties of the constituent gases. The product of the percentage of each constituent, and its particular value as known from determination on the pure constituent, is calculated. The sum of the products divided by 100 gives the average value for the gas. Some difficulty arises from the unknown composition of the hydrocarbons (other than methane). The composition is usually reckoned as equivalent to propylene, although ethylene is the chief constituent. Naturally the composition varies. In respect to the calorific value, the proportion of the whole due to the hydrocarbons is large, and considerable errors creep into any calculation of gas of which the origin is unknown. By determining the calorific value of gas and making a complete analysis a value may be deduced for the hydrocarbons present by working out the total due to other gases and deducting the result from that determined. So long as the gas is made and purified in the same manner, the value so found can be used for calculation with good results. Varying conditions of condensation, benzol washing and similar practices will alter the value. For example, using the values calculated from Thomsen (Table X) regarding the hydrocarbons absorbed by bromine as equal to propylene, it is found that with horizontal retort gas the determined value is nearly 30 B.Th.U. higher than the calculated, while with vertical retort gas the difference is 15–20 B.Th.U. With oil washing or tar washing the difference is reduced according to the extent to which the washing process is carried, and finally disappears.

Minor Constituents. In addition to the main constituents estimated in a volumetric analysis there exist a number of hydrocarbon vapours, sulphur and cyanogen compounds which are too small in amount to be observed in this way, but which exercise a very considerable influence on the use and distribution of the gas.

138*a. Liquid Hydrocarbons Present as Vapour in Coal Gas.* The only method of separating and estimating the various hydrocarbon vapours present in coal gas is to extract a considerable quantity of these from the gas and examine the liquid obtained by fractional distillation and similar methods. Deville has shown that the whole of the vaporous constituents may be extracted by cooling the gas to temperatures of about —50° C., but the method is not convenient in ordinary use, and recourse is usually had to methods of washing the gas with a suitable solvent for the vapours, or of absorbing these in prepared charcoal.

The most suitable solvent appears to be cresylic acid, used on the large scale by Brégéat, but both on the large scale and in the laboratory the usual solvent employed is creosote oil, which should be of low viscosity. Petroleum products, such as gas-oil, may also be employed, though of less efficiency and requiring a larger volume to effect complete extraction. In all cases, for laboratory estimation, the oils (other than cresylic acid) must be previously distilled to remove all constituents boiling below about 230–250°.

The simplest apparatus consists of a train of at least four wash-bottles, through which the gas is passed at the rate of about 1 cubic foot per hour, each bottle containing about 150 c.c. of oil. After each 10 cubic feet, or thereabouts, have passed, the bottle first in series is removed, emptied into a receptacle, refilled with fresh oil and put on last in series, and the test continued in this manner until about 200 cubic feet have been passed.

By this method, although only simple apparatus is required, the length of time required for a test is great. The back pressure due to the liquid in the bottles is high, and this frequently necessitates the use of an aspirator to draw the gas through the bottles.

To avoid these difficulties, a small scrubber may be employed in place of the absorption vessels. T. F. E. Rhead uses a vertical scrubber tower, consisting of a large number of superimposed trays. The wash-oil trickles down from tray to tray and the gas has to pass up in counter-current.

A useful scrubber may be made from a 4-feet length of 3-inch pipe, which is filled with $\frac{3}{8}$-inch Raschig or Lessing rings. With oil fed at about 700 c.c. per hour, the rate of gas throughput can be increased to 30 cubic feet per hour.

A further arrangement suggested by R. Lessing consists in using a scrubber packed with porous brick saturated with the wash-oil. When a certain quantity of gas has passed, the scrubber is used as a still and steam admitted to drive off the absorbed vapours, which are condensed and dealt with in the usual manner.

The benzolised oil obtained from the test, when using any of the above oils other than cresylic acid, is carefully distilled, for example, in the metal retort, already described, and the distillate up to 230° C. collected ; or steam may be passed through till the thermometer has reached 160°. Where cresylic acid is used (which should be practically free from constituents insoluble in aqueous caustic soda) the benzolised oil is distilled, using a 12-bulb pear column, a distillate collected equal to about 15 per cent. of the total volume of oil, and this is treated with aqueous caustic soda, to remove cresylic acid which has also distilled over.

The employment of absorbent charcoal for the purpose of absorbing the vapours has been fully described by Berl and Andress, and Müller.

A large glass U-tube, of about 3 cm. diameter, is filled for a length of about 30 cm. with 30–40 grams of active charcoal, such as that used for gas masks, and gas passed through this at the rate of about 8 cubic feet per hour in the case of a normal coal gas or coke-oven gas ; not more than about 10 cubic feet being passed in all. The U-tube is then placed in a bath heated to 110–120° C., and steam passed through the charcoal. The steam and spirits from the charcoal are condensed and collected in the usual manner. When spirit ceases to condense, air is blown through the tube—still kept in the bath to dry the charcoal—which is on cooling ready for use in a further test. With gas containing smaller amounts of vapour, such as the gases leaving the benzol scrubbers, a larger volume of gas is passed. The quantities obtained in the test being only a few c.c., it is not possible to make any analysis of the " benzol " obtained, but probably the apparatus could be enlarged if this were desired.

For many purposes, sufficient information as to the composition of the crude oil extracted by any of the above methods is obtained by subjecting the liquid to distillation in a round-bottomed flask fitted with a Young 12-bulb pear column, at the rate of 4 c.c. per minute, collecting and measuring the fractions obtained at different temperatures. If the temperatures are taken as 125°, 160°, and 190° C. the volumes obtained represent, approximately, the amounts of unwashed benzene and toluene, unwashed solvent naphtha, and unwashed heavy naphtha respectively.

For more exact information, the spirit obtained from the first distillation, when creosote or similar oils have been used, is distilled with a 12-bulb column and the distillate to 190° collected. This preliminary distillation is unnecessary where the oil has been extracted with cresylic acid or by means of charcoal. This spirit, up to 190°, is washed with 8 per cent. of its volume of conc. sulphuric acid (95 per cent.), then with caustic soda, and finally with water, and after drying, again fractionated with a 12-bulb column, collecting the fractions up to 125° ; 125–160°, and 160–190° C., the volumes obtained at these temperatures representing, approximately, the volumes of refined benzene and toluene, solvent naphtha, and heavy naphtha contained in the volume of gas washed.

The more exact determination of the amounts of benzene, toluene, etc., present, and the extent to which these are admixed with impurities, such as carbon bisulphide and paraffin hydrocarbons, may also be made. The method described by Colman and Yeoman depends on the separation from the crude spirits of a comparatively pure mixture of benzene, toluene, and xylene by fractional distillation, acid and alkali washing. The mixture obtained is distilled in a standard Engler apparatus, and the amount of the fractions collected below 104·7° C. and above 115·9° C. (corr.) determines the proportions of benzene, toluene, and xylene present. Such proportions are found as a percentage by reference to Tables. Considerable accuracy can be obtained by rigid attention to detail, and as this is the object the reader is advised to consult the original description.

In gasworks' practice it is usual to return the amount of vaporous constituents in terms of gallons per 12,000 cubic feet of gas.

140*a*. *Thermometer Corrections.* All thermometers used should be checked for accuracy, either by their being certified by the National Physical Laboratory or by comparison with a thermometer which has been so certified.

In addition, correction must also be made for the variation due to fluctuation in the height of the barometer, and for the emergent mercury column of the thermometer which is not heated by the vapour.

The barometer correction for any particular temperature is obtained from the formula :—

Correction$=0{\cdot}00012\ (760-p)\ (273+t^\circ \text{ C.})$ where p=barometric pressure in mm. with the mercury at 0° C., and t° C. = the interruption point.

The correction for emergent stem is given by the formula :—

Correction$=0{\cdot}000143\ (T-t)\ L$, where T = observed temperature of vapour, t = temperature of air around emergent portion of stem, and L = length of mercury column measured in degrees of emergent stem not exposed to the vapours.

For practical purposes this last correction may be avoided by having the thermometers graduated and standardised with only 100 mm. (or 4 inches) of the stem exposed to heat, as this is sufficiently close to the length of the thermometer which is heated during distillation in the great majority of cases.

Water Vapour. The gas may be taken as saturated with moisture at the outlet of the holders, but is usually below the saturation point by the time the gas reaches the consumers' premises. During passage through the distribution system the gas, in the first place, is usually reduced in temperature and water is deposited to run to the nearest syphon. But the gradual decrease of pressure and rise of temperature when the gas reaches the small services raise the gas above the dew-point.

Almost all the corrosion agents are ineffective in the absence of liquid water, hence the dew-point of the gas at different parts of the system is of considerable importance. A particular case may be quoted in connection with a high-pressure main which was used during part of the day for high-pressure gas and during the rest of the day for low-pressure gas. When the pressure was raised a film of water was deposited on the surface of the pipe causing considerable corrosion.

141*a*. *Hygrometer.* A useful modified form of Regnault's hygrometer is illustrated (Fig. 37). Gas is passed in and the temperature is noted on the thermometer placed in the inlet tube. The gas fills the outer jar and passes off by the outlet tube. The inner glass tube is capped at the foot with a polished silver cup, which contains ether or similar liquid, which can be vaporised by blowing air through with an aspirator to reduce the temperature of the silver cup. As the temperature falls to the dew-point, moisture condenses as a mist on the outside surface of the cup. At this point the temperature of the liquid in the cup is noted. The evaporation of the ether is then stopped and the temperature allowed to rise until the mist just disappears, when the temperature is again noted. The mean of the two observations can be taken as the dew-point.

The saturation of the gas with hydrocarbon vapours does not seem to interfere with the deposition of the water mist as oils form a clear film, but the mist takes somewhat longer to disappear if deposited at the same time as condensed hydrocarbons. The interior of the glass jar must, of course, be perfectly dry.

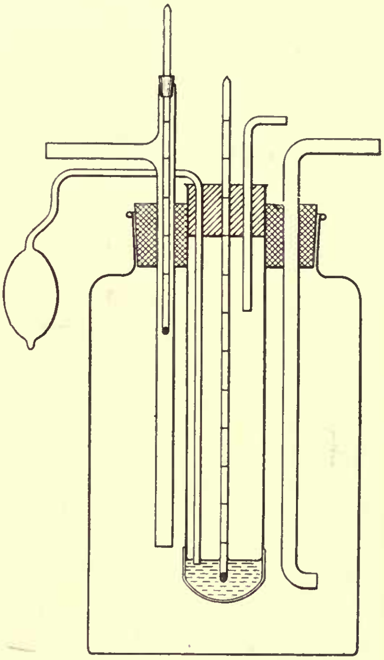


Fig. 37.—Form of Regnault's Hygrometer.

141*b*. *Ammonia.* The presence of ammonia is detrimental as not only representing loss in the recovery, but also as it is the most serious corrosive agent. The method of estimation consists in passing from 10–100 cubic feet of gas direct through two absorption vessels containing 25 c.c. of N/10 sulphuric acid divided between them. The gas is metered after the vessels. The connection should be short and consist of glass as far as possible. The solution may be titrated back to find the excess of acid. For very accurate work it is better to use stronger acid, and subsequently distil off the ammonia into standard N/10 acid, titrating back the excess in the usual way.

141*c*. *Hydrogen Sulphide.* The presence of hydrogen sulphide is proved by a yellow to brown stain on lead acetate paper exposed for 1 minute to the gas issuing from a jet at the rate of about 5 cubic feet per hour. Hydrogen sulphide to the extent of 0·5 grain per 100 cubic feet will produce a palpable brown stain. It is important that the gas should not have been heated in any way previous to exposure, as carbon disulphide will decompose in the presence of water vapour :—

$$CS_2+2\ H_2O=2\ H_2S+CO_2.$$

The above reaction may account for traces found in highly compressed gas which has become heated in the process.

Bacterial action in gasholder water can also produce traces of hydrogen sulphide. Similar stains can also be formed by oil or tar fog.

Free sulphur, the residue from some previous decomposition of sulphur compounds can produce a distinct trace of hydrogen sulphide with warm and moist gas. (Cf. **106**.)

142*a*. *Sulphur Compounds.* Carbon disulphide and other sulphur compounds existing in the gas are usually classed together. They are detrimental inasmuch as sulphur acids are formed on combustion. With a free-burning flame it has been shown that the chief product is sulphur trioxide, which quickly disappears in the presence of whitewashed walls, ceilings, etc. The presence of compounds in the gas corresponding to over 30 grains of sulphur per 100 cubic feet gives rise to a perceptible odour in badly-ventilated rooms, and is therefore very objectionable. The reduction of the sulphur content of the gas has been effected on a working scale by the nickel contact process of the South Metropolitan Gas Company and to a lesser extent by oil washing.

The estimation is usually made by the apparatus prescribed by the Gas Referees (Fig. 38), which consists of a test meter in which the gas is measured, a burner surrounded by lumps of ammonium carbonate, a trumpet tube to conduct the products to a condensing cylinder, and a chimney tube. The sulphur trioxide formed condenses in the cylinder filled with wet marbles and combines with ammonia from the ammonium carbonate to form sulphate of ammonia. The condensed liquid is collected in the beaker below the cylinder. The burner should give a practically non-luminous flame when passing about 0·5 cubic foot per hour. Usually 10 cubic feet are used, and the meter is provided with an automatic cut-off so that the gas is shut off when that amount has been passed. The condensed liquid is poured into a 500 c.c. flask, and the condenser and end of the chimney tube washed down about six times with water into the flask. The solution is made up to 500 c.c., and the sulphur estimated in an aliquot portion, either by precipitation with barium chloride (see **23***a*), or by Blair's method.

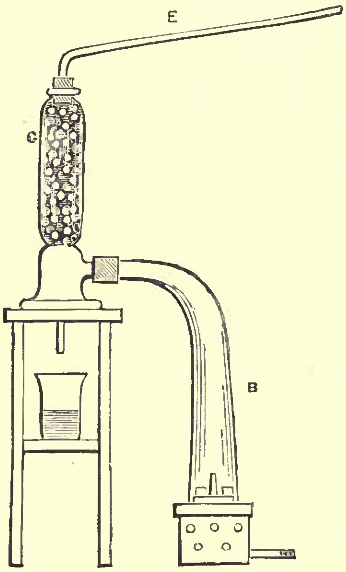


Fig. 38.—Apparatus for Estimation of Sulphur in Gas.

142*b*. *Blair's Method.* Several portions of 50 c.c. are taken, and to each is added about 100 c.c. of water. The whole is boiled for 5 minutes to expel carbon dioxide. About 10 c.c. of formaldehyde solution, which has been carefully neutralised with dilute (N/10) caustic soda, is added, and the boiling continued for 5 minutes. The solution is titrated hot with N/10 caustic soda, using phenolphthalein as indicator. The titre of the several portions should agree.

Formaldehyde liberates sulphuric acid from an ammonium salt, while the hexamethylene tetramine is driven off as vapour.

$$2\,(NH_4)_2SO_4+6\,CH_2O+4\,NaOH=(CH_2)_6N_4+10\,H_2O+2\,Na_2SO_4.$$

The caustic soda used is therefore equivalent to the sulphuric acid present in the liquor used.

The formaldehyde solution is made up from the 40 per cent. solution by diluting one part with two parts of water, adding phenolphthalein and neutralising with caustic soda till a faint purple tinge occurs.

The method is an extremely rapid and convenient one.

Cyanogen. The determination of cyanogen in gas has already been described. The importance of the presence of cyanogen depends on its corrosive properties. While it is true that syphon liquors contain considerable amounts of thiocyanates, and deposits often consist largely of ferrocyanide, it is not quite certain how far this corrosion is primarily due to cyanogen, or is the result of corrosion accomplished by other agents. Cyanogen would probably be ineffective in the absence of oxygen and ammonia.

Naphthalene. There is no need to emphasize the importance of the naphthalene content of the gas in view of the very heavy annual charges paid by gas concerns for the removal of naphthalene stoppages. The naphthalene usually exists in the gas above the amount corresponding to its vapour pressure, which is sufficient, according to J. S. G. Thomas, to cause about 4 or 5 grains to be present at a temperature of 15·5° C. in moist gas, but two or three times this quantity is often present. The naphthalene content depends on the conditions of condensation and purification as well as on the temperature of the gas. Unless oil washing has been resorted to, or the condensation is peculiarly effective from this point of view, there is always sufficient naphthalene formed in carbonisation from horizontal plants to send away at the ordinary temperature up to 15 grains per 100 cubic feet of gas. The gas from vertical retorts is usually not saturated in respect to naphthalene. To secure immunity from stoppages in the distribution system it seems imperative to reduce the naphthalene content down to less than 1 grain per 100 cubic feet, and allow a prolonged period for the influence of deposits already in the mains to pass away. This may be accomplished by oil washing, or by sudden severe chilling of the gas, for example, as is customary at coke-oven plants. Unfortunately, such drastic treatment of town gas, as in the latter case, is apt to result in very heavy depreciation of the hydrocarbon content, and would necessitate re-heating the gas, or using the direct process of ammonia recovery.

143*a*. *Estimation of Naphthalene.* About 10 cubic feet of the gas are passed by as short a connection as possible through an absorption bottle containing a little citric acid to remove ammonia and then through two vessels, each containing about 75 c.c. of a nearly saturated solution of picric acid (about 1 per cent. strength). It is imperative to avoid exposure of the gas to rubber in any connections. The gas is then measured in a test meter. The picric acid absorption vessels are disconnected and the contents washed through an 80 mm. filter paper, using a 0·2 per cent. picric acid solution as wash liquid. Finally, each vessel is rinsed out with about 1 c.c. of water, which is used to wash round the filter. Without further washing the filter paper and contents are thrown into a beaker, and any precipitate remaining in the absorption vessels is transferred, with a little hot water, into the beaker. The contents of the beaker are warmed slightly, 100 c.c. of water added, and the whole titrated with N/10 caustic soda solution, using phenolphthalein as indicator. A deduction of 0·2 c.c. from the titre is made to allow for picric acid left on the filter paper and bottle, after the washing. One molecule of caustic soda is equivalent to 1 molecule of naphthalene, $C_{10}H_8$. This method, in some cases, appears to be affected by the presence of other hydrocarbons than naphthalene, but, apparently, the "Metro. method," which consists of using 50 c.c. of a solution prepared by adding one part of alcohol to four parts of N/20 picric acid solution, in each of the absorption vessels, and then proceeding as before, is free from this objection. The original Colman and Smith method can also be relied upon.

144*a*. *Colman and Smith Method.* The gas is passed first through a 10 per cent. solution of citric acid to remove ammonia, particularly avoiding any bare rubber connections. The gas then passes through 100 c.c. of N/20 picric acid in one absorption vessel, through 50 c.c. of the same solution in a second vessel, and finally into an empty vessel to catch spray before passing to the meter. The picric acid solution is prepared by dissolving 35 grams in about 600 c.c. boiling water, pouring into about 1,800 c.c. cold water, cooling, filtering, and titrating 50 c.c. of the cold solution with N/10 caustic soda, using phenolphthalein as indicator. The strength may be then adjusted. The gas is passed at the rate of 1 cubic foot per hour till 10 cubic feet have passed, when the solution and precipitate are transferred to a bottle of nearly the same capacity as the total volume of solution. The bottle is fitted with delivery tube closed by a tap, and is evacuated under an exhaust. The bottle is closed up and placed in a cold water bath which is raised to boiling-point. Care should be taken not to allow the bottle to touch the heated bottom of the bath. The bottle is cooled with shaking so as to re-dissolve any naphthalene condensing on the upper part, and poured into a 250 c.c. measuring flask. After noting the total volume the solution is filtered through a dry filter paper. The first few c.c. are neglected and then 100 c.c. are collected and titrated with N/10 caustic soda, as in standardising the picric acid solution. From this the titre of the total volume measured is calculated. This is then the titre of the picric acid solution taken, less the picric acid equivalent of the naphthalene in the gas passed. One molecule of caustic soda is equivalent to 1 molecule of picric acid or of naphthalene. The naphthalene content is usually calculated in grains per 100 cubic feet.

Carburetting. There appears to be no reason for supposing that the introduction of the vapour of a liquid such as paraffin into the gas can keep naphthalene in the vapour state under conditions which would otherwise cause such deposition. The use of the expression "naphthalene carrier" seems to be founded on a misapprehension.

A liquid solvent may, however, be used to advantage, either for the purpose of condensing out at the same time as the naphthalene, dissolving it, and thus providing a liquid medium which will take the naphthalene to the nearest syphon, or it may be introduced as a liquid spray to remove in solution a naphthalene deposit already known to exist. In the first case, it is obvious that sufficient liquid must be used to saturate the gas completely, so that any reduction in temperature will cause deposition. The volatility of the liquid and its solvent powers must necessarily correspond, so that the amount deposited at any temperature will be more than sufficient to dissolve the naphthalene deposited at the same time. As a rule, the solvent power of the paraffin used is fairly high, and one of comparatively high vapour pressure may therefore be chosen. To use a light spirit is obviously uneconomical, as a large number of gallons per million cubic feet of gas would have to be used to dissolve a very small quantity of naphthalene.

A liquid used to spray or atomise may be heavy in nature and of low volatility so long as it is a good solvent.

145*a*. *Method of Examination.* The volatility or vapour pressure may be examined in the apparatus described by T. F. E. Rhead. Or, for comparative purposes, a weighed quantity may be placed in a wash-bottle. Dry air, at a regulated rate of, say, 1 cubic foot per hour, is drawn through and measured. At intervals the test is interrupted and the wash-bottle weighed back to ascertain the loss in weight. The process is repeated until over 95 per cent. of the oil has disappeared.

The solvent power of the liquid is perhaps easiest obtained by adding successive quantities of 5 grams of pure naphthalene to 100 c.c. of the liquid and shaking until a permanent residue is obtained. The total added, excluding the last 5 grams, may be taken as an approximate solubility figure.

REFERENCES

GAS REFEREES. Notification. 1918.

COSTE and ANDREWS. Fuel Gaseous, Liquid, and Solid. 1914.

COSTE. Calorific Power of Gas. 1911.

R. V. WHEELER. Combustion of Gases. *Gas Journal*, 1921, **153**, 615.

GAS INVEST. COMM. INST. GAS ENG. Fifth Report. Recording Gas Calorimeters. *Trans. Inst. Gas Eng.*, 1921, 127.

C. V. BOYS. A New Type of Recording Calorimeter. *Gas World*, 1922, **76**, 581.

W. H. SODEAU. Gas Analysis Apparatus. *J.S.C.I.*, 1903, 187.

W. A. BONE. Gas Analysis Apparatus. *J.S.C.I.*, 1908, 11.

E. W. SMITH. Modified Bone and Wheeler Apparatus. *Gas World*, 1919, **71**, 342.

JÄGER. Combustion Method. *J.S.C.I.*, 1898, 1190.

DENNIS and McCARTHY. Determination of Benzene, etc. *J. Amer. Chem. Soc.*, 1908, **30**, 233.

L. LEVY. Gas Analysis. *Gas Journal*, 1913, **122**, 455 ; 524.

E. V. EVANS. "Metrogas" Apparatus. *Gas World*, 1911, **55**, 814.

HEMPEL. Gas Analysis.

G. Lunge. Technical Methods of Gas Analysis. 1914.

T. Gray. Confining Liquids for Gas Analysis. *J.S.C.I.*, 1913, 1092.

J. S. G. Thomas. Vapour Pressure of Naphthalene. *J.S.C.I.*, 1916, 506.

D. Gair. Naphthalene Estimation. *J.S.C.I.*, 1905, 1279 ; 1907, 1263.

Knublauch. Naphthalene Estimation. *Gas Journal*, 1917, **137**, 61.

Jorissen and Rutter. Naphthalene Estimation. *J.S.C.I.*, 1909, 1179.

H. G. Colman. Estimation of Naphthalene. *Gas Journal*, 1918, **144**, 231.

Inst. Gas Eng. Res. Committee. Report on Corrosion by Gas. (Cyanogen, etc.) *Trans. Inst. Gas Eng.*, 1920.

T. F. E. Rhead. Benzol Recovery (vapour pressure apparatus). *Gas World*, 1917, **66**, 61.

T. F. E. Rhead. Estimation of Benzol in Gas. *J.S.C.I.*, 1917, **36**, 769.

R. Lessing. Estimation of Benzol in Gas. *J.S.C.I.*, 1917, **36**, 103.

CHAPTER XI

WATER GAS

WATER GAS plants form a valuable adjunct to carbonising plant. Owing to the ease with which plants of comparatively large capacity can be brought into use, such plants are largely used to take up daily variations in consumption. The properties of water gas as a fuel present very considerable differences from those of coal gas, and for this reason it cannot be considered good policy to permit sudden large dilution of the normal coal gas by water gas. The latter gives in the ordinary burner a very much shorter flame, and requires less air for its proper combustion than coal gas. A sudden alteration from coal gas to water gas without burner adjustment will therefore lead to poor lighting and heating efficiency with a tendency to back-firing. While adjustment of burners may prevent such difficulties, the consumer cannot be relied upon to make such adjustment. The best policy in the long run seems to lie in the manufacture of water gas all the year round, but the proportion of water gas to coal gas may be varied somewhat to meet daily variations in consumption.

Water Gas Reaction. In the manufacture of water gas, the object is to gasify the carbon, but it is desired to make gas of a type more concentrated in thermal value than producer gas. Since pure oxygen is not yet available, air has to be used to generate, by combustion of the coke, the necessary heat to gasify the carbon. But to reduce the nitrogen content to a minimum the actual gasification agent used is steam. The first stage is, therefore, to produce a high concentration of heat in the fuel bed, not by partial combustion of the fuel, as in the case of producer gas, but by the complete combustion of a portion of the fuel. The second stage is to utilise this heat for decomposing as much steam as possible.

The chemical reaction which it is desired to exclusively use in the first stage—the " blow "—is

$$C+O_2=CO_2+97{\cdot}6\ K.C.U.$$

but as the temperature increases the carbon dioxide first formed may be reduced with absorption, and consequent loss of both heat and carbon.

$$CO_2+C=2\ CO-38{\cdot}8\ K.C.U.$$

According to the attractive theory of Rhead and Wheeler, both carbon monoxide and dioxide are liberated simultaneously as primary products of combustion. The relative proportions existing in the gas will depend on equilibrium of the reversible reaction

$$CO_2+C=2\ CO$$

being attained (a matter of 4 or 5 seconds according to W. A. Bone) at the temperature prevailing. At 1,200° C. about 99 per cent. of the oxides of carbon present would be in the form of carbon monoxide. During the second stage the desirable reaction is

$$H_2O+C=CO+H_2-28{\cdot}8\ K.C.U.$$

but unfortunately, if the temperature is not sufficiently high (less than 1,000° C., say), other reactions produce detrimental results. The steam may not be decomposed to an adequate extent, or it may oxidise the carbon,—

$$C+2\ H_2O=CO_2+2\ H_2-18{\cdot}8\ K.C.U.$$

with consequent increase of the undesirable carbon dioxide in the water gas.

There is also the fact to be remembered that steam will react with carbon monoxide, and hydrogen with carbon ; and at existing temperatures an equilibrium may be obtained from the reversible reactions,—

$$\begin{array}{lll} CO_2+H_2 & =CO+H_2O & -10\ \ K.C.U. \\ H_2O+C & =CO+H_2 & -28{\cdot}8\ K.C.U. \\ CO_2+C & =2\ CO & -38{\cdot}8\ K.C.U. \end{array}$$

The curves shown in Fig. 39, illustrate the effect of temperature on the equilibrium attained.[1]

It will be seen that the development of too high temperatures in the first stage leads to loss by partial, instead of complete combustion. Temperature is also limited by the formation of clinker and risk of damaging the generator lining. On the other hand, a low temperature during the " run " leads to loss of undecomposed steam and production of carbon dioxide.

Not only have the thermal effects to be taken into account, but as the results are dependent on equilibrium being reached the time factor is of equal importance.

Temperature Control. There is, unfortunately, no means of continuously directly determining the temperature conditions inside the generator ; nor of appraising the amount of heat available in the fuel at the end of a blow. Control has, therefore, to be exercised by a visible appreciation of the conditions as seen at the generator top during charging and at the base during clinkering, supplemented by continual observation of the composition of the gas both during the run and during the blow.

It will be obvious that during the blow the temperature is rapidly increasing and during the run it is rapidly decreasing, and that coincidently the composition of the gas is changing.

The means of control are by adjustment of (1) the blast pressure, (2) the steam pressure, (3) the " cycle," or duration of blow and run, and (4) the direction of the run.

The adjustment of the blast and steam pressures is in effect an adjustment of the time factor and must have relation to the type of fuel (i.e. the " combustibility "), and to the size of fuel and depth of fuel bed. For example, the use of metallurgical

---

[1] Reproduced from the Sixth Report of the Research Committee of the Institution of Gas Engineers.

coke would necessitate a considerably increased blast pressure and (unless broken) a deeper fuel bed than gas coke. However, it is often convenient to vary the blast and steam pressure as a means of adjustment of temperature although some efficiency may be sacrificed.

An adjustment of the " cycle " is the chief means of regulating the temperature and amount of available heat, but for practical purposes it is somewhat crude. It is not convenient to use a cycle containing fractions of a minute, nor to use a cycle containing a period of less than 2 minutes. It is therefore very common to find that with a certain cycle the temperatures are on the balance either gradually rising or falling, and some means of counteracting this must be adopted.

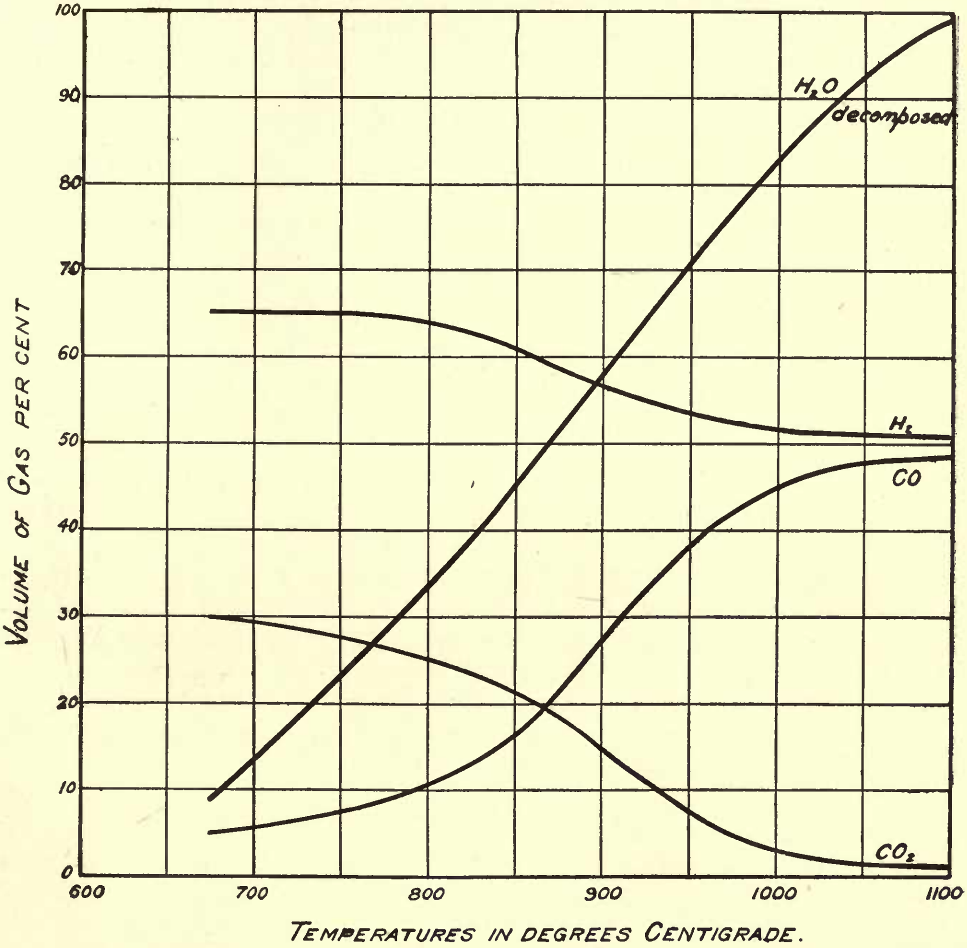


FIG. 39.—CURVES FOR STEAM-CARBON REACTIONS (BUNTE AND HARRIES).

In order to take advantage of the full depth of fuel bed it is important to maintain the required temperature over as large a depth as possible. This equalising of temperature can be accomplished by varying the direction of the steam current through the generator. Theoretically it might be best to use the steam always on the " down " run and the blast, in counter-current, upwards. The steam would then meet a gradually ascending temperature. This system can only be carried out to a limited extent by reason of the increasing formation of clinker, and the inconvenience and danger of having the maximum temperature too near the grate. It is usual to use " up-runs " for a time previous to clinkering, to cool the lower part of the fire so that clinkering conditions are easier. One or more " up-runs " are also beneficial immediately after charging so as to heat up and bring the newly charged fuel into use as quickly as possible.

Fuel. The quality of the fuel is of greatest importance. While there is no question that coke of a certain texture can be gasified very much quicker than other sorts, there is no known method of valuing this property. Close dense coke, such as blast furnace coke, needs a higher blast pressure and temperature for equal gasification rates, and if its use is attempted under the usual conditions for gas coke, large quantities will pass to the ashes unconsumed.

The size of the coke charged is also important. On the one hand, excessive breeze will deaden the fire and prevent contact with the larger lumps, besides providing an excessive amount of dust in the gas. Very large lumps are also detrimental, as the fuel bed becomes uneven and contact of gas and solid is reduced.

Moisture is a great drawback in the fuel, and water so present necessitates the supply of sufficient heat to raise it to boiling-point and convert it into steam. Obviously to charge a cwt. of cold water at a time into a generator will materially affect the results.

The amount and composition of the ash in coke is very important, but when its part in catalysis comes to be appreciated it may not always prove an unmixed evil. Often the ash of coke with a high melting-point (1,500° C.) is distinctly disadvantageous, as with the temperatures used partial fluxing results in a viscous plastic mass which hangs well above the fires and can only be detached by cutting down from above. By careful choice and use of coke with a more fusible ash this can usually be brought down in a state of flux on to the grate without stopping the plant.

The amount of volatile matter in the fuel is important, particularly when " blue " gas (uncarburetted water gas) is made, in view of the substantial increase in calorific value obtained from even small amounts of methane (1 per cent.) obtained by the decomposition of the volatile matter. It is possible that methane may also be formed catalytically.

It will be seen that periodical examination of the fuel is essential and involves the determination of size, moisture, specific gravity, calorific value, volatile matter, and ash. (See Chapter IV.)

Control by Gas Analysis. The chief control of the gasmaking operations is exercised by means of gas analysis. By systematic sampling and analysis the steam and air proportions may be adjusted and the duration of each period of the cycle fixed.

Obviously as little carbon monoxide as possible is desired in the " blow " gases, and as little carbon dioxide as possible is desired in the " run " gas. It would also appear desirable to estimate the amount of undecomposed steam, but this presents considerable difficulty.

Owing to the changing composition of the gas during the period of " blow " and " run," a series of gas samples are taken, each covering a definite period, of, say, 1 minute, and although the total volume of gas made in the same time is not known, nor the relation of the composition of the sample to that of the total gas, the analysis provides reliable indications of the rise or fall in the temperature conditions of the generator.

151*a*. *Sampling.* Sampling places are provided in the generator lid, in the base of the superheater, and at the base of the " downcomer " pipe, or inlet of the seal pot. Silica tubes may be inserted when desired, or left in place, but must be sufficiently long to avoid " dead " gas spaces. Samples are taken through the lower branch of a T-piece through which the gas passes to a bubbling bottle in which the seal is less than the gas pressure. In order to increase the rapidity of the gas stream, and the sensitiveness of the sample, an aspirator may be attached instead of the bubbling bottle.

151*b*. *Analysis.* The analysis of the uncarburetted and blow gases for control work may be made in an Orsat or Hempel apparatus if restricted to the determination of carbon dioxide, oxygen and carbon monoxide, and is carried out in a similar manner to the analysis of retort-house gas. (See **40***a*.) Precautions should be taken that the comparatively large amounts of carbon dioxide and monoxide are properly absorbed, and that the pyrogallol is not adding to the carbon monoxide content. Complete analysis may be carried out as described for coal gas. (See **129–137**.)

A method for the complete analysis of such mixtures containing practically only carbon dioxide, oxygen, carbon monoxide, hydrogen, methane, and nitrogen, consists in absorbing the carbon dioxide and oxygen. A portion of the residue, say, 12 c.c., is mixed with a measured excess of air, say, 80 c.c., and exploded over mercury in the usual way. The contraction is noted, and after the carbon dioxide resulting has been absorbed the oxygen remaining is absorbed in pyrogallol, and by difference from that taken the oxygen used can be found.

The relative amounts of carbon monoxide, hydrogen, and methane can then be calculated from the equations :—

$$CH_4+2O_2=CO_2+2\,H_2O$$
$$2\,H_2+O_2=2\,H_2O$$
$$2\,CO+O_2=2\,CO_2.$$

The hydrogen will be the total contraction less the volume of oxygen consumed, since the methane and carbon monoxide give their own volume of products, and the contraction on the combustion of these two gases represents the volume of oxygen consumed. The carbon monoxide will be $\frac{2}{3}$ [$2\times$vol. of carbon dioxide$+$($\frac{1}{2}$ the hydrogen$-$the oxygen used)] while the methane can be taken as the carbon dioxide found, less the volume of carbon monoxide found. Finally, the nitrogen is obtained by difference.

The nitrogen content is often required for checking the "scavenging" operations, or the general soundness of the valves, and may be determined separately by the combustion method. (See **135**a, **135**b.) As a rule it should not exceed 5 per cent.

Carburetting. The carburation of the gas by spraying petroleum oil on to brickwork contained in the "fixing chamber," which is kept at a red heat, is a very complex process. Comparatively little is known as to the "cracking" properties of oils, although considerable work was done during the war on this subject. The object of carburetting is to obtain as large a proportion of the thermal value of the oil as permanent gas. The total volume of gas is also saturated with the vapours of the various hydrocarbons formed. Unfortunately, most of the work done and published deals almost entirely with the photometrical aspect and omits thermal values. The results of carburetting depend largely on the nature of the oil, which varies considerably according to its place of origin. On an average, at least 1 therm in gaseous form should result per gallon of oil used.

Valuation of Water Gas Oil. It is very difficult to arrive at a satisfactory basis of valuation, all the more so, as the results from practice are so dependent on carburetting conditions which cannot be finely controlled. Little help is therefore obtained from practical working.

A great many methods of examination of water gas oil have been proposed from time to time. If it were possible by analysis to estimate the amount of each hydrocarbon, or even of each class of hydrocarbon, probably some satisfactory basis would be arrived at, but the oils are usually of such complexity that it is only possible in ordinary circumstances to make a partial examination to show the general nature of the oil, and to combine this with some comparative method for estimating the cracking properties of the oil. The oils contain in particular, paraffins, olefines, aromatic hydrocarbons, and naphthenes. R. Ross and J. P. Leather arrived at the general conclusions that open chain compounds are most suitable; double bonds diminish the value slightly; the presence of "ring" compounds is more detrimental, while benzene rings have practically no value. In respect to the latter, benzene and its homologues may add considerably to the thermal results if carried forward as vapour. Ross and Leather suggest that the specific gravity and refractive index of each fraction of the oil provide a good criterion of the value for gasmaking purposes; the lower these constants are the better the oil. With such physical examination is combined the results from an experimental "cracking" of the oil in an iron retort. The gas evolved is measured and its content of hydrocarbons determined by gas analysis.

The following methods of examination will be found suitable for most purposes :—

152a. *Water and Distillation Range.* The examination is conducted as in the case of tar oil (creosote). The specific gravity of each fraction may be taken.

152b. *Flash Point* is determined in the Pensky-Martin apparatus. (See **163**a.) The flash point should not be less than about 100° F. Ordinary railway carriage is prohibited with oil of less flash point than 73° F.

152c. *Calorific Value.* A bomb calorimeter is used and about 0·5 gram of oil weighed into the silica dish, where it is preferably mixed with sufficient "kieselguhr," or precipitated silica to form a lump. If this is not done, complete combustion may not occur unless very small quantities of oil are taken. The determination is carried out as in the case of coal. (See **26***a*.)

153*a*. *Sulphur.* The estimation is conveniently combined with the determination of calorific value as in the case of coal and coke. (See **23***a*.)

153*b*. *Comparative Cracking Test.* A silica tube about 1 inch diameter and 18 inches long is arranged upright and filled with little granular pieces of broken firebrick. A dropping funnel is arranged at the top. Connection is made to a supply of pure hydrogen. The outlet tube at the base passes through a bubbling bottle sealed with water to collect oil, and then passes to meter and gasholder. Alongside, or preferably inside, is placed a pyrometer thermo-couple. The tube is filled with hydrogen and heated from the outside to a temperature, say, of 800° C., and the hydrogen supply is regulated to a definite rate ; 50 c.c. of oil are placed in the funnel and arranged to drop at, say, 5 c.c. per minute. The increase in gas rate is then observed, and when conditions are constant a sample is taken for analysis. The oil collected in the condenser is noted and the tube afterwards examined for separation of carbon.

The test must be strictly comparative.

Carburetting. Adequate heat has to be maintained in the superheater and fixing chamber for the proper cracking of the oil used. Pyrometers are used for control of this, combined with periodical examination of the water gas tar for uncracked oil, and of the gas for its naphthalene content. With too high a cracking temperature the latter gradually rises till it approaches the content of high-temperature coal gas. Recording calorimeters are also of great use in checking the additional heat effect produced by the cracking, and the oil used may be varied from time to time and compared with the corresponding thermal effect. As may be expected, the first gallon of oil per 1,000 cubic feet gives considerably more effect than the second gallon. It is, of course, necessary that the complete analysis of the uncarburetted gas should be taken into account in computing the extra thermal value, due to carburetting, as a small percentage of methane from the coke used makes a considerable difference.

For the analysis, calorific value, and determination of minor constituents in carburetted gas the methods given for coal gas are applicable. Greater care is given to the absorption of the much larger properties of carbon monoxide, and unsaturated hydrocarbons. The specific gravity of water-gas is considerably higher than coal gas, and it is useful to have a continuous record of this property.

REFERENCES

E. G. Stewart. Efficiency of Water Gas Manufacture. *Gas Journal*, 1920, **149**, 750.

H. L. Nicholson. Water Gas Manufacture. *Gas Journal*, 1920, **150**, 85.

Gas Invest. Committee of Inst. of Gas. Eng.—6th Report. Blue Water Gas. *Trans. Inst. Gas Eng.*, 1921. 255.

Gas Invest. Committee of Inst. of Gas. Eng.—7th Report. Carburetted Water Gas and Waste Heat Boilers. *Trans. Inst. Gas Eng.*, 1922 ; *Gas World*, 1922, **76**, 529.

R. Ross and J. P. Leather. Composition and Valuation of Gas Oil. *Analyst*, 1906, **31**, 284. *J.S.C.I.*, 1902, 676.

R. Ross and J. P. Leather. Valuation of Gas Oils. *Analyst*, 1907, **32**, 241.

CHAPTER XII

STEAM RAISING AND WATER SUPPLY

Previous to the war, owing to the low value of the fuel—breeze—usually used, it was not worth while to spend time and money on control of gasworks boiler plants. Economisers and superheaters were conspicuous by their absence; but increase in the cost of the fuel, of wages, and of the capital cost of boiler installations, makes close control more economical where the boilers works are suitably grouped.

Fuel. The breeze which is usually used is not an ideal fuel, and boilers fired on breeze cannot be pressed in the way that they may be when fired on coal. To obtain good results the breeze should contain all sizes passing a fork, except dust, which is preferably removed. The flame as a rule is short, but with well-graded breeze stoked evenly over the grate the few inches' depth used in a boiler furnace may give a very excellent producer gas above the fuel bed. To complete the combustion, secondary air is admitted above the grate. This is strictly limited, as the best efficiency in breeze as a fuel seems to be obtained with a very slight excess of carbon monoxide. Too much secondary air shortens the flame to such an extent that contact is restricted to a very small portion of the boiler surface. The use of tarry breeze is to be deprecated, as it is impossible to prevent black smoke. This, to say the least, creates a bad impression of the contribution of gas as a fuel to smoke-abatement. The chief factors required in an examination of the fuel are the moisture, ash, calorific value, and grading test. (See Chapter IV.)

Firing the Boiler. Most of the improvements in boiler efficiency can only follow if the fuel bed is maintained even and regular over the entire grate. The steam jets used to give additional draught are watched carefully to see that the pressure is not sufficient to blow holes in the fuel bed. During clinkering time they must, of course, be entirely shut off, or an excessive amount of dust will be carried forward, to say nothing of cold air sent through to the chimney. The dampers should be partially closed. The steam jets often wear to a much larger size than originally intended and are examined periodically. The pressure on the jets should be definitely fixed and gauged according to the size of jet. A too liberal use of steam jets leads to blockage of the gas flues with dust.

If the clinkering is not carefully carried out the amount of unburnt carbon in the ashes will rise to an extraordinary amount in the case of breeze. In such cases the sampling of the ashes presents considerable difficulty. (See **59***a*.)

Regulating the Draught. The amount of draught required is largely dependent on the depth of fuel and ratio of boiler capacity to grate area. The draught at the base of the chimney may be obtained by a sensitive form of water-gauge with a connecting tube inserted midway into the base of the flue a few feet from the stack. The tube should be straight and terminate with the orifice at right angles to the flow of the waste gas. A fan anemometer may be used at the furnace front to measure the velocity of the air passing below the grate. The reading multiplied by the area of the opening will give the quantity of the air passing. It is difficult, however, to get exact measurements and the calculation is best regarded as comparative. With increased draught the thickness of fire may be considerably increased.

The dampers are regulated to give the minimum pull consistent with maintenance of the boiler capacity, and will vary from 0·5 to 1 inch with Lancashire boilers. With induced draught a slight pressure on the back of the furnace will considerably increase the efficiency, and tend to more even steaming. It is quite possible to obtain such a rapid current of air that time contact is insufficient to give complete combustion, and small amounts of carbon monoxide may appear in the waste gases in spite of a large excess of oxygen. This occurs particularly when the fire has been chilled with a fresh charge of fuel.

155*a. Temperature.* The control of the temperature throughout the boiler setting is a most important means of combining efficiency in the use of the fuel with the necessary steaming capacity. The rate of combustion will probably be too low unless the fire is sufficiently hot to fuse a part of the ash. The formation of some clinker may be taken as a satisfactory sign, but if the fire is pressed to an extreme temperature the capacity of the boiler will suffer from an uneven fire bed resulting from an excess of clinker.

The temperature of the gases at the inlet and outlet of the economiser and at the chimney base require indication, while that of the feed-water at the inlet and outlet of the economisers and of the steam from the superheaters will also be required. Mercury thermometers inserted in malleable iron pockets containing a little mercury to communicate the heat quickly may be used, but a set of distance thermometers with indicator in a place convenient to the fireman, will save a vast amount of climbing about with consequent damage to boiler lagging.

The water entering the economiser is kept not less than 45° C. to prevent sulphur acids in the waste gases condensing on the economiser pipes, while the temperature at the outlet is not allowed to exceed a figure 10° C. below the temperature of the steam at boiler pressure, in order to avoid risk of generating steam in the economiser.

The inlet temperature of the steam at the superheater can be calculated from the boiler pressure (see table), the difference between this and the temperature at the outlet being regarded as degrees of superheat.

155*b. Waste Gas Analysis.* The analysis of the waste gas provides the third means of control of the boiler. In conjunction with the means of obtaining the temperatures, sampling places are established at different places on the setting, especially on each side of the damper, and preferably at each end and in the centre of each side flue (Lancashire boilers) and at the base of the chimney. The gas samples may be taken from iron sampling tubes where the temperature does not exceed 300° C., and preferably from silica tubes where the temperature is higher. An iron tube is conveniently let into the brickwork to terminate on the inner face of the brickwork and closed by a loose screw iron plug. By the removal of this plug a thermometer or sampling tube may be inserted. Continuous samples may be obtained. (See **38***b*.) If accurate work is required the samples had best be taken over mercury. In this case the sampling arrangement described (**37***a*) may be used. The water in the aspirator draws a gas stream along while the sampling tube itself is filled with mercury and emptied drop by drop.

The analysis is made with Orsat or Hempel as described (**40***a*, **61***a*), or for more accurate work, which is rarely needed, in an all-mercury apparatus. (See **129**, **133**.)

Particular precautions are taken that the reagents are kept fresh and that the pyrogallol used does not liberate carbon monoxide, or fail to absorb oxygen.

As a rule it is considered advisable to work with an excess of air, and an average carbon dioxide content of 12 per cent. in the waste gas passing away would be good practice. With low-grade fuel like breeze it is better to reduce the excess of air and work with even a slight excess of carbon monoxide so as to lengthen the flame.

With the three indications of draught, temperature, and gas analysis, the boiler conditions can be easily controlled. Excessive leakage of air through the brickwork will be indicated by the rapidly declining temperature and increase in excess of oxygen. Thin firing results in a high temperature at the grate, but low temperature through the rest of the system; there is a low percentage of carbon dioxide and a high oxygen content and low draught readings. With dirty flues, owing to restriction of draught, carbon monoxide makes its appearance in the waste gases and the fires are dull.

Water Supply. The water supplied to boilers should be free from oil and grease. Hydrocarbon oil which distils without decomposition or residue is not so deleterious as animal or vegetable oil which decomposes, leaving solid matter often acidic in character. Contamination with the latter oils must be avoided at all cost. Oil of any nature leads to irregular steaming. Free acid is also to be avoided. Magnesium chloride is most objectionable. The permanent hardness (sulphates) is not allowed to exceed 3°, or the total hardness, say 5°, but with cheap fuel and a surplus boiler capacity somewhat higher figures may be permissible. Sometimes the boiler scale, though it may be thin, is extremely hard, and this considerably lengthens the time and trouble of scaling.

The water supply is sometimes taken from wells situated in the works. Often it is found convenient to use a Town supply after passing the water through condensers. Or water may be drawn from gasholder tanks into which exhaust steam drainage runs. It is a curious fact that water obtained from a gasholder tank, or otherwise partially saturated with coal gas, gives a very soft boiler scale which can largely be removed by sludging.

Since considerable amounts of water are used in gasworks not only for steam raising, but for condensing and scrubbing purposes, and the cost per 1,000 gallons is increasing rapidly, in most cases economy in the use of water is worth serious consideration, and definite schemes for collecting exhaust steam, condenser and gasholder water may result in considerably saving. For this reason the following methods of examination may be found useful :—

157*a. Sampling.* The chief precautions necessary in sampling are to ensure that the bottle used to contain the sample is clean to start with. It should be rinsed out with a hot solution of sodium carbonate, then with dilute warm sulphuric acid containing some potassium permanganate, and finally with distilled water of known purity until the washings are perfectly clean. The treatment, of course, includes the stopper. After well draining, the stopper is inserted till required. In dealing with natural supplies a series of samples are taken over a considerable period, varying the time of sampling according to the weather conditions so that the variation in quality may include alterations due to heavy rain or drought. It is convenient to report all results in parts per 100,000 parts of water. A close visual examination will often guide the observer as to what the subsequent examination should include.

157*b. Visual Examination.* The colour of the water is observed through 50 c.c. placed in a clean Nessler glass on a dead-white paper, or viewed through a column 1 or 2 feet in length. A tintometer may be used and the colour matched. Films of oil should be noted, and the nature of any suspended matter. The odour of the water is noted both cold and on warming 10 c.c. in a test tube. The reaction to methyl orange should also be observed and, if the water is peaty in character, lacmoid (0·2 gram in 100 c.c. of 10 per cent. alcohol) may be used to detect the acids.

157*c. Chloride.* The water may be titrated directly with silver nitrate only if organic matter is substantially absent. In the latter case the water is warmed to boiling-point and a few drops of neutral potassium permanganate added till a pink colour persists after boiling for a few minutes. The excess of permanganate is destroyed with a few drops of alcohol and, after settling, the manganese compounds are filtered off, the filtrate neutralised with bicarbonate and titrated.

If necessary, the water may be taken to dryness in a porcelain dish, carefully ignited, and the residue taken up with a little water acidified with nitric acid. After filtering, the solution is neutralised with bicarbonate and titrated.

The titration with silver nitrate is carried out in a porcelain basin, in the presence of 1 to 2 c.c. of 5 per cent. potassium chromate solution. A permanent red tinge marks the end of the titration. If necessary, a similar amount of water with the same amount of chromate solution, but with insufficient amount of silver nitrate to give complete precipitation added, may be used for comparison of the colour changes.

157*d. Sulphate.* A volume, say, 250 c.c., of the water is acidified with hydrochloric acid and evaporated down in a porcelain dish on the water bath. The residue is repeatedly moistened with hydrochloric acid and dried off. Finally, the residue is taken up with hydrochloric acid, filtered from silica, and after adding ammonium chloride to prevent precipitation of magnesium, the sulphate is precipitated with barium chloride, filtered, ignited, and weighed. (See **23***a.*)

157*e. Alkalinity.* A portion of the water, 250 c.c., is evaporated down to 50 c.c., filtered, the precipitate washed with freshly boiled water, and the filtrate titrated with N/10 acid in presence of methyl orange.

157*f. Acidity.* Water acid to lacmoid as indicator (0·2 gram in 100 c.c. of 10 per cent. alcohol) will usually act on lead. The acidity can be determined by titration with N/10 sodium hydrate, using phenolphthalein as indicator.

158*a*. *Total Solids.* Suspended matter is filtered off from a litre or more of the water, dried at 100° C. and weighed, deducting the weight of a filter paper treated with pure water, and dried in the same way. The residue is then ignited in a platinum crucible and the ash weighed back. The remainder of the examination is made on the filtered water.

158*b*. *Total Soluble Solids.* From 250 c.c. to 1 litre of the water are evaporated in a tared platinum dish, adding the water from time to time to make up the bulk as the evaporation proceeds. Care is taken to keep the water-line at least 0·5 inch from the top of the dish. The evaporation may be carried out by placing the dish on the top of a spouted beaker, the diameter of which is slightly smaller than the platinum dish, and with a large inverted funnel overhead to prevent dust falling in. In no case must the platinum be allowed to touch any metallic surface. The dish and residue is finally dried for 2–3 hours in the water oven and rapidly weighed. Care is taken that the outside of the dish is not contaminated. If platinum is not available a good quality porcelain dish may be used, but glass should be avoided.

Hardness. Strictly speaking, the total hardness of a water is the sum of the contents of calcium and magnesium oxides, expressed as parts of calcium carbonate per 100,000. For this purpose the calcium may be determined by concentrating, say, 250 c.c., to about 50 c.c., and precipitating from this the calcium as oxalate. (See **72**.)

The magnesium may then be determined in the filtrate as magnesium phosphate. (See **72**.)

A " degree " of hardness in this country is reckoned as 1 grain of calcium carbonate per gallon (70,000 grains), which is equivalent to 1·43 parts per 100,000.

Temporary hardness, due to the presence of bicarbonates which, on boiling, give a precipitate of carbonate, corresponds to the amount of calcium or magnesium carbonate precipitated on boiling and to the difference between the permanent hardness and the total hardness. The permanent hardness is due mainly to sulphates and chlorides. In most cases the following method (Hehner) is convenient.

158*c*. *Temporary Hardness.* The water, say, 100 c.c., is titrated with N/10 or N/5 sulphuric or hydrochloric acid, using methyl orange as indicator to permanent red, and the calcium carbonate equivalent of the acid is calculated.

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

158*d*. *Permanent Hardness.* Excess of a standard solution of N/10 sodium carbonate, is added to, say, 200 c.c., of the water and the whole evaporated to dryness, preferably in a platinum dish. The residue is taken up with water, filtered, and the residue washed several times. The total filtrate is then titrated with N/10 sulphuric acid or hydrochloric acid, using methyl orange as indicator.

The carbonate used in removing the permanent hardness is found by difference of the titres and the equivalent of calcium carbonate calculated.

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4.$$

159*a*. *Clark's Method.* The soap test for hardness, although approximate, is still largely used. The best method of preparing the soap solution is to take about 75 grams of "lead plaster" and grind it in a mortar with about 20 grams of pure potassium carbonate. A small quantity of 80 per cent. alcohol is added and the mixture worked up to a cream. With addition of further alcohol the mixture is rinsed into a large bottle and allowed to settle. The clear liquid is decanted off through a filter and the sediment washed with alcohol. The volume is then made up to 250 c.c., with equal parts of alcohol and water.

Or, the soap solution may be made by taking about 10 grams of white-shredded castile soap which are dissolved in a litre of 80 per cent. alcohol and allowed to stand a day or two till clear. It is then decanted through a filter and standardised against a standard calcium chloride solution. The standard chloride solution is prepared by dissolving carefully 0·2 gram of pure dry calcium carbonate in a covered vessel (a platinum dish) with dilute hydrochloric acid. The whole is evaporated to dryness on a water-bath several times with water till free acid is removed. The residue is then dissolved and the solution made up to 1 litre. Of this solution, 50 c.c. are transferred by pipette, avoiding contamination by carbon dioxide of the breath, to a clean-stoppered 250 c.c. bottle.

The soap solution is added from a burette 1 c.c. at a time, and later 0·2 c.c. at a time, and the whole well shaken after each addition. When the lather is permanent for 2 minutes with the bottle lying on its side the titration is finished. By observing the disappearance of the "metallic" scum on adding more soap, the false end-point produced by magnesium salts may be overcome. The strength of the soap solution in terms of calcium carbonate can then be calculated.

For the total hardness of a water, 50 c.c. of the latter are placed in the bottle and titrated with the soap solution as in the case of the standardisation. The hardness is calculated in terms of calcium carbonate per 100,000 parts of water. For very hard waters (over 20 parts per 100,000) a smaller quantity is taken and diluted to 50 c.c. by adding distilled recently boiled and cooled water, so that not more than 16 c.c. of soap solution are required.

The permanent hardness is obtained by placing 150 c.c. of the water in a 500 c.c. flask. The whole is counterbalanced on a rough balance. The flask is removed and the water gently boiled for 30 minutes, cooled, replaced on balance, and cold recently boiled water added to make up the balance. The water is filtered, if necessary, through a dry filter and 50 c.c. titrated as before with the soap solution. The temporary hardness is given by difference.

159*b*. *Water Softening.* The additions of soda ash and lime necessary may be ascertained very simply by the following (*Metro.*) method: The total hardness is determined by the "soap" method as given above, say, this is A degrees. The "magnesium hardness" is next determined by adding about 4 grams of ammonium oxalate to 120 c.c. of the water, shaking and allowing the mixture to stand for 15 minutes. After filtering, and assuring freedom from calcium salts, 70 c.c. of the filtrate is titrated with soap solution as before. The hardness may then be B degrees. The temporary hardness may be obtained by direct titration of 70 c.c. with N/50 acid, using methyl orange as indicator. This reading is called C. Another portion of 70 c.c. are taken and phenolphthalein is added. If no colour develops the water is titrated with N/50 sodium carbonate until a permanent pink is shown. This reading represents D. If the water is alkaline (sodium carbonate), the titration is carried out with N/50 acid solution, and the reading is called E. Then the soda ash required per gallon (pure) is 0·152 (A—C) lb., and the lime (pure) is either 0·08 (B+C+D) lb. or 0·08 (B+C—2 E) lb.

160*a. Lime and Soda Value* (*Drawe*). A method proposed for use in control work consists in finding first, the lime equivalent of the water by addition of a known excess of lime water and titration of the excess, after boiling and filtration, with standard hydrochloric acid. Excess of standard sodium carbonate solution is afterwards added to the neutralised solution, and after boiling and filtration the excess is found by a further titration with hydrochloric acid.

160*b. Soda Ash.* The purity of the soda ash may be ascertained by double titration. About 10 grams of the undried salt is dissolved in air-free water, filtered if necessary, and made up to 500 c.c. Of this 50 c.c. are taken, and phenolphthalein added. Normal sulphuric acid is run in until the colour is just destroyed. Methyl orange is then added and the titration continued to a permanent pink. The first titration neutralises hydroxide and converts carbonate into bicarbonate, while the second converts bicarbonate to sulphate. If the number of c.c used in the last titration be greater than in the first, the difference is due to presence of sodium bicarbonate. The titration should be carried out in the cold, and the burette tip dipped under the surface of the acid in the first titration, so as to avoid escape of carbon dioxide. (*Metro.*)

160*c. Boiler Water.* It is advisable to check the composition of the water from time to time to ensure that the proper amount of water is regularly " blown down." The sample taken can be examined by the methods described for feed water, but in particular the total solids should be determined and the alkalinity. The former should not exceed about 1,000 grains per gallon. The alkalinity may be determined by the double titration method using first phenolphthalein as indicator and then methyl orange.

REFERENCES

C. F. Wade. Efficient Boiler Management. 1919.

W. Inchley. Steam Boilers. 1912.

W. E. Dalby. Steam Power. 1920.

D. Brownlie. Steam Boiler Plants. *Engineering*, 1920, 759; *J.S.C.I.*, 1920, 69A.

A. A. Porritt. Scale Formation and Corrosion. *Chemical Age*, 1922, **7**, 76.

Thresh. Water and Water Supplies. 1913.

W. W. Scott. Standard Methods of Chemical Analysis. 1917.

CHAPTER XIII

LUBRICANTS

THE very considerable amounts of lubricants used in modern works, and the increasing use of machinery of all descriptions, make it well worth while devoting time to the examination of the different classes of oils and the use to which they are put.

The lubricants in general use largely consist of mineral oils (petroleum products) blended to a greater or less extent with the more valuable vegetable and animal oils. It is essential that both the constituent classes of oils should have been properly and carefully refined and free from such harmful adulterants as rosin oil and coal-tar oils. Oleic acid in large (say, over 0·5 per cent.) amount is considered injurious and mineral acids dangerous. The properties of a desirable oil naturally depend on the purpose for which it is desired.

All lubricants may well be examined for specific gravity, colour, free acid, viscosity, flash point and cold test. To obtain information for the purpose of selection the volatility, sulphur content, distillation range, gumming property, iodine value, and saponification value should be obtained; while, in the case of suspected adulteration, soaps, rosin and coal-tar oil may be looked for.

161*a*. *Specific Gravity.* The specific gravity may be determined by the use of a hydrometer, or specific gravity bottle, in the usual way. Except for purposes of calculating weight and volume it is of little use, save that a high specific gravity may indicate coal-tar and rosin oil adulteration. In the instances where pure oils are concerned the specific gravity becomes an important constant.

161*b*. *Acidity.* The total acidity is estimated by taking 5–10 grams of the oil in a 250 c.c. conical flask. The oil is shaken with 30–40 c.c. of previously neutralised 95 per cent. alcohol. The whole is warmed to boiling-point, agitated thoroughly, and titrated hot with N/10 caustic soda, using phenolphthalein as indicator and shaking vigorously after each addition. In the case of dark oils, the alcoholic extract may be separated, using a separating funnel and making several extractions. The acidity is expressed either as milligrams of alkali to saturate the free acid in 1 gram of oil, or reckoned as equivalent of oleic acid, $C_{17}H_{33}COOH$.

161*c*. *Mineral Acid.* The free mineral acid is detected by shaking 25 c.c. of the oil in a separating funnel with successive quantities of hot water to a total amount of about 25 c.c. The water is withdrawn through a wet filter into a conical flask, cooled and titrated with N/10 caustic soda, using methyl orange as indicator. The solution may afterwards be concentrated and examined for the particular acid, usually sulphuric acid, left by careless refining. In no case should mineral acid be present.

The presence of sulphonates may be shown by placing a quantity of the washed oil with water in a stout well-stoppered bottle. The stopper is tied down and the bottle placed in a water bath for 30 minutes. After cooling the stopper is removed and the acid resulting from the hydrolysis titrated. The presence of sulphonates is harmful, as in practice the compounds may be similarly hydrolysed with the production of free acid.

162*a*. *Viscosity.* The viscosity is one of the most important properties of lubricants and has been the subject of great discussion. A lubricant must be sufficiently viscous to retain its position in the bearing and must form a film capable of bearing the load at the running temperature. The viscosity of all oils diminishes rapidly with rise of temperature, and those oils, like castor oil which retain a large proportion of their initial viscosity at each successive rise of temperature, are the more valuable. As, however, the oils more viscous at normal temperature lose their viscosity more rapidly with increase of temperature than those less viscous to start with, all oils approach the same viscosity at high temperatures. It is customary to determine the viscosity at several different temperatures: the highest being the maximum temperature likely to be encountered in use. Temperatures of 20° C., 60° C., 100° C., and 120° C., are commonly taken.

The viscosity may be judged in a comparative manner by placing a water or oil-jacketed pipette full of the oil in a vertical position and noting the time which is taken by the level of the oil dropping from one fixed point on the scale to a lower one. In this country it is customary to determine the viscosity in a standard apparatus—the Redwood Viscometer (Fig. 40).

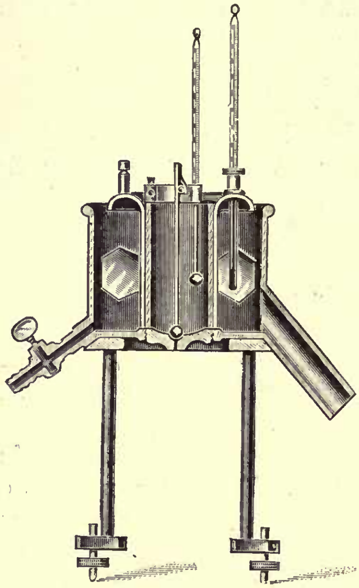


FIG. 40.—BOVERTON-REDWOOD VISCOMETER.

This instrument consists of a standard orifice placed in the base of a metal cup which is fixed inside a copper bath. The orifice can be closed by a ball on the end of a rod. The oil is dried over calcium chloride and filtered through a little glass-wool into the clean and dry cup, so as to bring the level up to the metal pointer fixed as a guide inside the cup. The temperature is then adjusted, and when constant conditions have been obtained, the stopper is removed and the oil allowed to run through the orifice into a 50 c.c. measuring flask placed beneath. Simultaneously a stop-watch is started and the time taken to fill the flask noted.

The viscosity of rape oil at 15° C. (60° F.) of sp. gr. 0·9142 is taken as a standard figure of 100.

The viscosity, then, is given by:

$$\frac{T \times S_T \times 100}{535 \times 0{\cdot}9142}$$

Where T is the efflux time in seconds of 50 c.c., S_T is the specific gravity of the oil at the temperature of the test. It is always necessary to state the temperature at which the determination has been made. Often, however, the time in seconds only is reported. The time of efflux of the standard rape oil with this instrument is 535 seconds.

Flash Point. The flash point is of value in the consideration of the possibilities of fire. A low flash oil with high distillation range is an indication of bad refining or adulteration with low boiling spirit. A minimum flash point of 350° F. is usually considered essential for all indoor machinery. The method in common use of obtaining the flash point is by means of the "closed test" carried out in the Pensky-Marten Apparatus. Flash point tests carried out in open crucibles are considerably higher and not very reliable.

163*a*. *Method.* The apparatus (Fig. 41) consists of a metal cup placed in an air bath which may be heated by a burner underneath. Stirring gear and thermometer are fitted through a lid which covers the cup. A movable slot in the lid permits of the flame from a small gas-jet to be brought down into the vapour space of the cup, and at the flash point the vapour is ignited in this manner and causes a visible "flash." The apparatus is carefully cleaned and dried before use. A small trace of volatile oil has a great influence on the flash point. The oil to be tested is dried over a lump or two of calcium chloride and is filled into the cup through a funnel containing a little glass-wool till the cup is full to the circular mark. The lid and thermometer are fitted in so that the small bulb of the latter just clears the lower part of the stirring gear. The heating burner and test flame are lighted; the latter being adjusted to the size of a pea. The rise in temperature is regulated to obtain a rise of 5° C. per minute. The oil is stirred very quietly and uniformly. As the flash point is approached the mill-head of the shutter is turned to open the slot and depress the test flame every 15 seconds. When the flame is seen to flash across the surface of the oil the temperature reading is taken as the flash point.

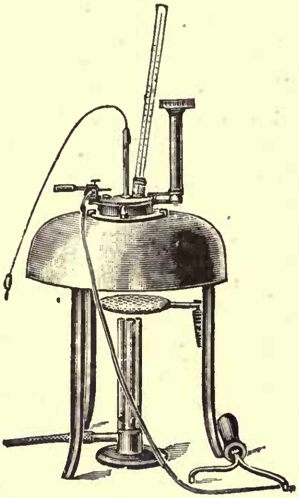


FIG. 41.—PENSKY-MARTEN CLOSED FLASH-POINT APPARATUS.

163*b*. *Cold Test.* Lubricating oils may contain sufficient waxy constituents to separate a scummy mass on standing in a cool place, or the oil may set to a semi-solid mass which is inconvenient to deal with, and which may not flow sufficiently well to find its way through the lubricating system.

The cold test consists essentially of gradually cooling the oil in an air bath and observing its behaviour. The temperature at which it becomes cloudy (cloud-test), at which a palpable amount of solid separates (separation-point) and at which it refuses to flow from one end of the tube to the other (the "cold test" or "pour test") are noted.

The oil should not be stirred or previously heated, and the temperature should not be reduced more than about 2° C. per minute.

The apparatus described for the crystallising point of creosote may be used. (See **89**_a_.)

164_a_. _Distillation Range._ Information as to the class of oil dealt with can often be obtained by a distillation carried out as for coal-tar oil (see **87**_b_), particularly if this be compared with the flash point and viscosity. If water is present, it should, of course, be separated and the oil portion of the distillate returned for a fresh trial.

164_b_. _Volatility._ The volatility bears no relation to either flash point or distillation range. It may be approximately determined by passing, in a comparative manner, air (a measured quantity at a fixed rate) raised to a definite temperature through a weighed quantity of the oil maintained at the same temperature (see **145**_a_), or its vapour pressure may be determined. Sometimes a known amount is simply placed in a dish in a heated oven for a definite time, and then re-weighed to determine loss in weight.

164_c_. _Gumming Power._ Some lubricants contain impurities which on heating in the presence of air throw down sticky deposits. Comparative observation may be made on the same quantity of two oils exposed in a thin film on similar watch glasses in a steam oven for 8–10 hours. The degree of " tackiness " can then be observed.

Saponification. The quantity of potash required to decompose the esters of the oils and fats expressed as a percentage is known by the title of saponification value. Most of the saponifiable oils have a value of 18–19 per cent., but a few are lower and some as high as 25 per cent. The waxes are very low in value, 7–12 per cent., and the hydrocarbon oils _nil._ Hence the value is of considerable use in determining the nature of a lubricant.

164_d_. _Method_ (_after Archbutt_). About 2·5 grams of the oil are weighed out into a small conical flask and 25 c.c. of semi-normal alcoholic potash, prepared by dissolving about 18 grams of "pure by alcohol" stick potash in 500 c.c. of pure alcohol, is added. The same volume of the potash solution is added to a similar flask to form a " blank " test. Both solutions are slowly simmered on a steam bath with reflux condenser, with constant gentle shaking so as to disperse the oil and promote saponification.

When the process is judged to be complete (say, an hour for mixed animal and fatty oils) the contents of each is successively titrated, with semi-normal hydrochloric acid, using phenolphthalein as indicator. By difference the number of grams of caustic potash required to saponify the oil taken is calculated, and finally that required for 100 grams of the oil.

If the mean saponification value of the fatty oils is taken as 20, the percentage of fatty oils can be roughly judged by multiplying the saponification value by 5. The difference from 100 is approximately the mineral oil.

164_e_. _Unsaponifiable Matter_ (_after Archbutt_). The hydrocarbon oils, together with small amounts of natural unsaponifiable matter, may be separated by extraction of the saponified solution with ether. Five grams of the oil are exactly weighed out into a deep evaporating dish. To this is added 4 c.c. of a mixture of pure clear caustic soda solution (containing about 2 grams of NaOH) in 50 c.c. of alcohol (free from naphtha). After digestion for 30 minutes the solution should have become concentrated to about 15 c.c. The hot residue is poured into a previously warmed separating funnel, and the basin rinsed round with hot water. The total volume should then be about 70 c.c. On the top of the solution is poured 100–120 c.c. of ether (re-distilled methylated ether, sp. gr. 0·725). The stopper is inserted and the whole is cooled under the tap with gentle shaking so as to mix, but not to emulsify, the ether and solution. Two distinct layers should separate. If an emulsion has formed more alcohol is added, while if three layers are seen, more water is added. After settling 10 minutes the soap solution is drawn off and shaken with more ether, and this is again repeated. The ether extracts are mixed, washed with 10 c.c. of a 1 per cent. caustic soda solution containing 10 per cent. of alcohol, and then thoroughly with water. The ethereal solution is run off into a tared conical flask and the bulk of the ether is distilled off. The remainder of the ether and water are evaporated off in the open on the top of a water oven, and the flask cooled and weighed. The drying is repeated to practically constant weight. The residue gives the unsaponifiable oil. Oils containing much hydrocarbon oil are best digested under reflux condenser with the caustic soda before concentration in the open dish.

Iodine Value. The absorption of halogen radicles by the oil provides an indication of the amount of unsaturated hydrocarbons present. Since the latter are the chief constituents liable to oxidise and gum, the lower the iodine value the better. It can be assumed that the radicle "ICl" is taken up by unsaturated compounds.

165*a*. *Wijs' Method.* A solution of iodine monochloride in acetic acid is prepared by dissolving 12·7 grams of iodine in 1 litre of pure glacial acetic acid. Twenty-five c.c. are titrated with N/10 thiosulphate. Chlorine (free from hydrochloric acid) is passed in until the titre of the solution has been increased to nearly twice the original amount. The colour will then be a rich orange.

The iodine value is determined on a portion of the oil which will absorb the equivalent of about 0·3 gram of iodine. Say, from 0·2 to 1 gram of the oil is weighed out and dissolved in 10 c.c. of carbon tetrachloride in a clean glass-stoppered bottle (8-oz. size) and mixed with 25 c.c. of the above reagent. It is shaken and allowed to stand 15 to 30 minutes (for linseed oil much longer). About 20 c.c. of a solution of potassium iodide (10 per cent. aqueous solution, free from iodate) is added and 100 c.c. of distilled water. The solution is then titrated with N/10 thiosulphate solution, using a little starch as indicator near the end-point. It is advisable to chill the bottle before opening the stopper and to shake well after each addition of thiosulphate. The iodine value is then taken as the iodine equivalent of the difference between the thiosulphate titre of a "blank" and the test solutions calculated per 100 grams of oil.

165*b*. *Rosin Oil.* A high acid value may indicate the presence of rosin oil. Oil containing rosin has a peculiar hard, astringent taste, which is markedly perceptible some minutes after the oil has reached the mouth. To detect these adulterants 8–10 c.c. of the oil are shaken with an equal volume of 70 per cent. alcohol. The solution is run off through a filter moistened with the alcohol and evaporated. If rosin is present, a resinous residue is left which is dissolved in 1 or 2 c.c. of acetic anhydride.

A drop of conc. sulphuric acid (sp. gr. 1·5) will give a violet colour. (Storch-Liebermann reaction.)

166*a*. *Coal Tar Oils.* Adulterants of this nature may be detected by nitration of the oil in presence of conc. sulphuric acid, when aromatic nitro-compounds, mainly insoluble in water, will be found.

166*b*. *Emulsification.* As a rule, emulsification of an oil when mixed with water is undesirable, but in the case of steam-engine cylinder oils a certain degree of emulsification is convenient, provided that when the emulsion is allowed to stand it will separate fairly rapidly into water and oil. Soaps are sometimes added to give consistency to an oil, and in this case the oil will emulsify very easily. Addition of dilute hydrochloric acid and separation of the acid layer will enable tests to be applied for the basic radicles (soda, alumina, iron, calcium, and magnesia).

Selection of Lubricating Oil. The oils used must necessarily be chosen with a view to the use to which they are to be put. For slow-moving machinery an oil or grease of high viscosity at ordinary temperature is used, and may be mineral oil if sufficiently viscous. With light loads and high speed as low a viscosity as possible is required, always provided the viscosity is high enough to form a film. Pure mineral oils are useful, or they may be mixed with a small percentage of fatty oils. For dynamos, motors, and high-speed turbine engines, pure mineral oil with twice the viscosity of rape oil is suitable.

For gas-engine cylinders a small amount of animal or vegetable oil blended with mineral oil, and of about the same or somewhat higher viscosity to rape oil, may be used. For motor cars and similar engines pure mineral oils are advisable of high viscosity. Pure mineral oils do not gum or oxidise at relatively high temperatures, in the way which the animal and vegetable oils do. In those cases where there is a chance of lubricating oil finding its way into boiler-feed water a pure mineral oil is preferable as not being subjected to hydrolysis.

In order to lubricate the interior surfaces of the drum and blades of exhausters, it is customary to use a light tar oil which will thin any pitchy tar collecting, and provide also a certain amount of lubrication. Petroleum oils are most unsuitable, as they precipitate pitch from tar and aggravate the trouble. A light creosote oil, distilling between 200° and 300° C., with a minimum of residue, is, perhaps, the most suitable. The naphthalene content should be low, say, 10 per cent., and the oil should be filtered through a gauze screen before use. The tar acids may be retained, but are preferably removed in view of their tendency to polymerise. Strained anthracene oil is also used and possesses more lubricating value, is more viscous, but has somewhat less solvent power for pitchy substances. The analysis may be made by methods given under Tar. (See Chapter VII.)

REFERENCES

L. Archbutt and Deeley. Lubricants and Lubrication. 1912.

Hamor and Padgett. Examination of Petroleum. 1920.

Dept. Scient. and Indt. Research. Report on Lubricants and Lubrication. 1920.

APPENDIX

TABLE I

International Atomic Weights. 1920. (Abbreviated list.)

Element	Symbol	Atomic Weight
Aluminium	Al	27·1
Antimony	Sb	120·2
Arsenic	As	74·96
Barium	Ba	137·37
Bismuth	Bi	208·0
Bromine	Br	79·92
Cadmium	Cd	112·4
Calcium	Ca	40·07
Carbon	C	12·005
Chlorine	Cl	35·46
Chromium	Cr	52·0
Cobalt	Co	58·97
Copper	Cu	63·57
Fluorine	F	19·0
Gold	Au	197·2
Hydrogen	H	1·008
Iodine	I	126·92
Iron	Fe	55·84
Lead	Pb	207·2
Magnesium	Mg	24·32
Manganese	Mn	54·93
Mercury	Hg	200·6
Molybdenum	Mo	96·0
Nickel	Ni	58·68
Nitrogen	N	14·008
Oxygen	O	16·00
Phosphorus	P	31·04
Platinum	Pt	195·2
Potassium	K	39·10
Selenium	Se	79·2
Silicon	Si	28·3
Silver	Ag	107·88
Sodium	Na	23·00
Strontium	Sr	87·63
Sulphur	S	32·06
Tin	Sn	118·7
Titanium	Ti	48·1
Tungsten	W	184·0
Uranium	U	238·2
Vanadium	V	51·0
Zinc	Zn	65·37
Zirconium	Zr	90·6

TABLE II

WEIGHTS AND MEASURES

Unit	Equivalent
1 inch	2·54 cm.
1 metre	39·37 inches
1 square inch	6·4516 sq. cm.
1 fluid ounce	28·41 c.c.
1 cubic inch	16·387 c.c.
1 cubic foot	6·23 gallons
1 cubic foot	28·317 litres
1 cubic metre	35·316 cubic feet
1 litre	61·024 cubic inches
1 gallon (8 pints)	4·5459 litres
1 gram	15·432 grains
1 ton (2,240 lb.)	1,016,050 grains
1 pound (16 oz.)	7000 grains
1 pound	453·59 grams

The cubic centimetre of water weighs 1 gram at 4° C. and 760 mm. ; the gallon contains 10 lb. of water at 62° F. and 30 in. One litre of water at 62° F. and 30 in. weighs 998·89 grams (Rosetti).

TABLE III

MISCELLANEOUS DATA

Unit	Equivalent
1 gram per litre	70·05 grains per gallon
1 grain per gallon	0·01429 gram per litre
1 Calorie (K) per cubic foot	3·968 B.Th.U. per cubic foot
1 Calorie (K) per gram	1·8 B.Th.U. per pound
1 B.Th.U. per cubic foot	0·1127 calories per cubic metre
NH_3 in 1 gallon 10 oz. liquor	1518 grains (1519·7)
1 per cent. nitrogen in coal	105 lb. sulphate of ammonia (theor.)
1 inch mercury pressure	0·4907 lb. per square inch
1 foot water column at 4° C.	0·433 lb. per square inch
1 lb. per square inch	2·31 feet of water column
1 cubic foot of hydrogen weighs at 0° C., 760 mm.	0·00559 lb.
1 cubic foot of water weighs	62·3 lb.
1 cubic foot of air at 0° C., 760 mm., weighs	0·0809 lb.
1 foot pound	13·825 cm. gram units or 13,562,000 ergs.
1 joule per second	1 watt. ; work of current of 1 amp. at 1 volt in 1 second ; 0·7373 ft. lb. per second
1 h.p.	33,000 ft. lb. per minute
1 Kilowatt	1·34 h.p.
Volume in cubic feet per hour	Velocity in feet per hour × square feet of area
Humidity of Gas at 15·56° C. ; partial pressure of water vapour	0·518 in. mercury (Metro)
Saturated gas at temp. t° F., h in. mercury and with vapour pressure of water, a in. mercury at t° F.	To correct volume divide by :— $\frac{459{\cdot}4+t}{17{\cdot}617\,(h-a)}$ (Metro)

TABLE IV

Temperatures of Saturated Steam

Pressures are Absolute

Pressure	Temperatures		Pressure	Temperatures	
lb. per □	°F.	°C.	lb. per □	°F	°C.
1	102	39	80	312	156
5	162	72	85	316	158
10	193	90	90	320	160
15	213	101	95	324	162
20	228	109	100	327	164
25	240	115	110	334	168
30	250	121	120	341	172
35	259	126	130	347	175
40	268	131	140	352	178
45	275	135	150	358	181
50	281	138	160	363	184
55	288	142	170	368	187
60	293	145	180	374	190
65	298	148	190	377	192
70	303	151	200	381	194
75	307	153	215	388	198

Atmospheric Pressure (14·7 lb. per sq. in.) corresponds to 212° F.=100° C.

To obtain temperature of steam at a working boiler pressure add 14·7 to the latter and refer to Table.

TABLE V

Strength of Liquor and Equivalent in Sulphate of Ammonia

Oz. Str.	NH_3grams per 100 c. c.	S/.A lb. per gal.	Gallons Liquor per ton salt.	Oz. Str.	NH_3grams per 100 c. c.	S/.A lb. per gal.	Gallons Liquor per ton salt.
1	0·2166	0·8421	26600	9	1·9498	0·7579	2955
2	0·4333	0·1684	13300	10	2·1665	0·8421	2660
3	0·6499	0·2526	8867	11	2·3831	0·9263	2418
4	0·8666	0·3368	6650	12	2·5998	1·0105	2217
5	1·0832	0·4210	5320	13	2·8164	1·0947	2046
6	1·2998	0·5053	4433	14	3·0331	1·1789	1900
7	1·5165	0·5895	3800	15	3·2497	1·2631	1773
8	1·7332	0·6737	3325	16	3·4664	1·3473	1662

TABLE VI

TONS OF SULPHATE OF AMMONIA—(theoretical)

Gallons of liquor	Grams of Ammonia (NH_3) per 100 c.c. of Liquor.											
	1·0	1·1	1·2	1·3	1·4	1·5	1·6	1·7	1·8	1·9	2·0	2·1
1000	·173	·191	·208	·225	·243	·260	·278	·295	·312	·330	·347	·364
1500	·260	·286	·312	·338	·364	·390	·416	·442	·468	·494	·520	·546
2000	·347	·382	·416	·451	·485	·520	·555	·590	·625	·659	·694	·729
2500	·434	·477	·520	·563	·607	·650	·694	·737	·781	·824	·867	·911
3000	·520	·572	·625	·676	·728	·781	·833	·885	·937	·989	1·041	1·093
3500	·607	·668	·729	·789	·850	·911	·972	1·032	1·093	1·154	1·214	1·275
4000	·694	·763	·833	·902	·971	1·041	1·110	1·180	1·249	1·318	1·388	1·457

Showing the theoretical yields of ammonium sulphate from various quantities of Liquor of different strengths.

TABLE VII

Specific Gravity and Equivalent Gallons per Ton of Tar

Sp. gr. Water=1.	Gallons per ton.	Sp. gr. Water=1.	Gallons per ton.
1·000	224·0	1·155	193·9
1·005	222·9	1·160	193·1
1·010	221·8	1·165	192·3
1·015	220·7	1·170	191·5
1·020	219·6	1·175	190·7
1·025	218·5	1·180	189·8
1·030	217·5	1·185	189·0
1·035	216·5	1·190	188·2
1·040	215·4	1·195	187·5
1·045	214·4	1·200	186·7
1·050	213·3	1·205	185·9
1·055	212·3	1·210	185·1
1·060	211·2	1·215	184·4
1·065	210·3	1·220	183·6
1·070	209·3	1·225	182·9
1·075	208·4	1·230	182·1
1·080	207·4	1·235	181·4
1·085	206·5	1·240	180·6
1·090	205·5	1·245	179·9
1·095	204·6	1·250	179·2
1·100	203·6	1·255	178·5
1·105	202·7	1·260	177·8
1·110	201·8	1·265	177·1
1·115	200·9	1·270	176·4
1·120	200·0	1·275	175·7
1·125	199·1	1·280	175·0
1·130	198·2	1·285	174·3
1·135	197·4	1·290	173·6
1·140	196·5	1·295	173·0
1·145	195·7	1·300	172·3
1·150	194·8		

TABLE VIII

Logarithms of the Reciprocal of the Correction of Gas Volume to 60° F. and 30 inches, Moist.

TEMPERATURE.			PRESSURE (Mercury).		
°F.	°C.	Log.	mm.	inches.	Log.
84	28·8	·0292	786	30·95	·9861
83	28·3	·0278	785	30·90	·9867
82	27·7	·0264	784	30·85	·9875
81	27·2	·0253	782	30·80	·9884
80	26·6	·0241	781	30·75	·9890
79	26·1	·0227	780	30·70	·9897
78	25·5	·0214	778	30·65	·9905
77	25·0	·0200	777	30·60	·9914
76	24·4	·0186	776	30·55	·9920
75	23·8	·0175	775	30·50	·9927
74	23·3	·0164	773	30·45	·9933
73	22·7	·0152	772	30·40	·9940
72	22·2	·0141	771	30·35	·9948
71	21·6	·0127	770	30·30	·9957
70	21·1	·0114	768	30·25	·9963
69	20·5	·0103	767	30·20	·9970
68	20·0	·0092	766	30·15	·9978
67	19·4	·0079	765	30·10	·9987
66	18·8	·0066	763	30·05	·9993
65	18·3	·0055	762	30·00	·0000
64	17·7	·0044	761	29·95	·0006
63	17·2	·0033	759	29·90	·0013
62	16·6	·0022	758	29·85	·0022
61	16·1	·0011	757	29·80	·0031
60	15·5	·0000	756	29·75	·0037
59	15·0	·9989	754	29·70	·0044
58	14·4	·9978	753	29·65	·0052
57	13·8	·9967	752	29·60	·0061
56	13·3	·9957	750	29·55	·0067
55	12·7	·9946	749	29·50	·0074
54	12·2	·9935	748	29·45	·0081
53	11·6	·9924	747	29·40	·0088
52	11·1	·9914	745	29·35	·0097
51	10·5	·9903	744	29·30	·0106
50	10·0	·9893	743	29·25	·0112
49	9·4	·9882	742	29·20	·0119
48	8·8	·9872	740	29·15	·0128
47	8·3	·9861	739	29·10	·0137
46	7·7	·9851	738	29·05	·0143
45	7·2	·9840	737	29·00	·0150
44	6·6	·9830	735	28·95	·0157
43	6·1	·9819	734	28·90	·0164
42	5·5	·9809	733	28·85	·0173
41	5·0	·9799	731	28·80	·0182
40	4·4	·9788			

To correct gas volume subtract the log. numbers above from the log. of the uncorrected volume. A value (e.g. calorific value) may be corrected by adding the above logs. to the log. of the value.

TABLE IX

SPECIFIC GRAVITY AND STRENGTH OF SULPHURIC ACID

(Lunge, Isler and Naef.)

Sp. gr. 15°C compared to water at 4° (in vacuo).	°Tw.	100 pts. by wt. contains parts by wt. of		lb. of H_2SO_4 per gallon.
		H_2SO_4	Acid 142° Tw.	
1·600	120	68·51	87·79	10·97
1·605	121	68·97	88·38	11·07
1·610	122	69·43	88·97	11·18
1·615	123	69·89	89·56	11·29
1·620	124	70·32	90·11	11·40
1·625	125	70·74	90·65	11·51
1·630	126	71·16	91·19	11·61
1·635	127	71·57	91·71	11·71
1·640	128	71·99	92·25	11·82
1·645	129	72·40	92·77	11·93
1·650	130	72·82	93·29	12·03
1·655	131	73·23	93·81	12·12
1·660	132	73·64	94·36	12·23
1·665	133	74·07	94·92	12·31
1·670	134	74·51	95·48	12·45
1·675	135	74·97	96·07	12·57
1·680	136	75·42	96·65	12·68
1·685	137	75·86	97·21	12·79
1·690	138	76·30	97·77	12·90
1·695	139	76·73	98·32	13·02
1·700	140	77·17	98·89	13·13
1·705	141	77·60	99·44	13·24
1·710	142	78·04	100·00	13·36
1·715	143	78·48	100·56	13·47
1·720	144	78·92	101·13	13·58
1·725	145	79·36	101·69	13·70
1·730	146	79·80	102·25	13·83
1·735	147	80·24	102·82	13·94
1·740	148	80·68	103·38	14·05
1·745	149	81·12	103·95	14·17
1·750	150	81·56	104·52	14·28
1·755	151	82·00	105·08	14·40
1·760	152	82·44	105·64	14·52
1·765	153	82·88	106·21	14·66
1·770	154	83·32	106·77	14·78
1·775	155	83·90	107·51	14·90

TABLE X

CALORIFIC VALUE OF GASES: B.TH.U. GROSS AT 60° F. AND 30 IN., MOIST

Gas.	Lunge (after Thomsen).	Coste.
Ethylene	1605	1559
Propylene	2358	2301
Benzene	3771	3738
Carbon monoxide	326	318
Methane	1020	992
Hydrogen	326	320
Hydrogen sulphide	657	—

TABLE XI

THE SPECIFIC GRAVITY OF GASES AND THE WEIGHT OF ONE CUBIC FOOT AT 60° F AND 30 IN. PRESSURE—MOIST

Gas.	Sp. Gr. Air=1.	Weight of 1 cub. ft. lb.
Carbon dioxide	1·529	0·1163
Oxygen	1·105	0·0841
Ethylene	0·969	0·0737
Benzene	2·79	0·2123
Carbon monoxide	0·967	0·0736
Methane	0·553	0·0421
Hydrogen	0·0695	0·00529
Nitrogen	0·972	0·0740
Air	1·000	0·0761
Hydrogen Sulphide	1·192	0·0907
Ammonia	0·590	0·0449
Water vapour	0·622	0·0473

TABLE XII

HEAT CAPACITY OF GASES

Heat Capacity in B.Th.U. per cubic foot, at 60° F. and 30 in.—moist.
t=Temperature, °C. less 15·5° C.

Gas.	Heat Capacity.
Hydrogen and Nitrogen	$0{\cdot}032t + 0{\cdot}00000187t^2$
Oxygen and Carbon monoxide	$0{\cdot}0322t + 0{\cdot}00000234t^2$
Carbon dioxide	$0{\cdot}0418t + 0{\cdot}0000117t^2$
Hydrogen sulphide	$0{\cdot}0381t + 0{\cdot}00000468t^2$
Ammonia	$0{\cdot}0403t + 0{\cdot}0000131t^2$
Methane and Cyanogen	$0{\cdot}043t + 0{\cdot}0000453t^2$
Olefines	$0{\cdot}0723t + 0{\cdot}0000889t^2$

Heat Capacity in B.Th.U. per lb.
t_{100}=temperature °C. less 100 °C.
t =temperature °C. less 15·5 °C.

Water (vapour)	$0{\cdot}915t_{100} + 0{\cdot}000215t^2_{100} + 1116$
Coke	$0{\cdot}414t$
Ashes	$0{\cdot}36t$
Tar (vapour)	$0{\cdot}80t + 180$

The value for water includes the latent heat and heat capacity from 100° to 15·5° C.

The above values are those selected by the Gas Investigation Committee of the Institution of Gas Engineers, which Committee includes representatives of Leeds University.

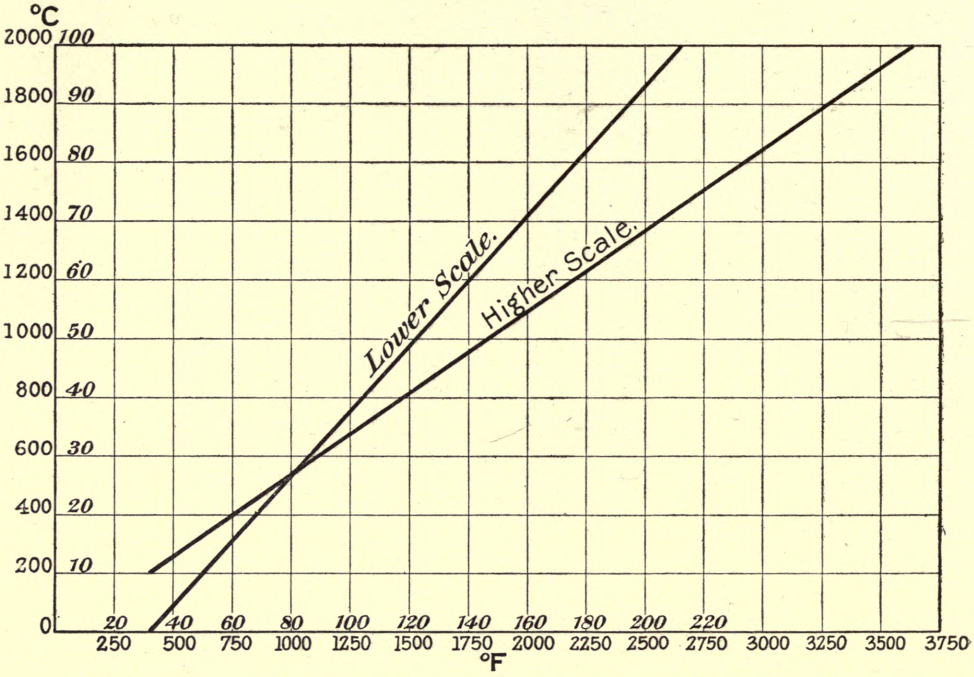
(See *Trans. Inst. Gas Eng.* for 1919–1920 and 1921, 1922, 4th, 6th and 7th Reports.)

TABLE XIII

MELTING POINTS OF SEGER CONES

Cone No.	Cent.	Fahr.	Cone No.	Cent.	Fahr.
022	600	1112	9	1280	2336
021	650	1202	10	1300	2372
020	670	1238	11	1320	2408
019	690	1274	12	1350	2462
018	710	1310	13	1380	2516
017	730	1346	14	1410	2570
016	750	1382	15	1435	2615
015a	790	1454	16	1460	2660
014a	815	1499	17	1480	2696
013a	835	1535	18	1500	2732
012a	855	1571	19	1520	2768
011a	880	1616	20	1530	2786
010a	900	1652	26	1580	2876
09a	920	1688	27	1610	2930
08a	940	1724	28	1630	2966
07a	960	1760	29	1650	3002
06a	980	1796	30	1670	3038
05a	1000	1832	31	1690	3074
04a	1020	1868	32	1710	3110
03a	1040	1904	33	1730	3146
02a	1060	1940	34	1750	3182
01a	1080	1976	35	1770	3218
1a	1100	2012	36	1790	3254
2a	1120	2048	37	1825	3317
3a	1140	2084	38	1850	3362
4a	1160	2120	39	1880	3416
5a	1180	2156	40	1920	3488
6a	1200	2192	41	1960	3560
7	1230	2246	42	2000	3632
8	1250	2282			

TABLE XIV



Curves for Conversion of Thermometer Scales.

INDEX

NAME INDEX