dimethyl derivative of hydroquinone phthalein and the methyl derivative of phenolphthalein, and although the latter only contained half the amount of methoxy group, the compounds formed were more unstable. It seemed as if the methyl ester of phenolphthalein might partially decompose without losing colour, but if it were allowed to stand with alcohol for any length of time the colour disappeared.

Mr. H. G. BENNETT said the subject was of considerable practical importance in leather dyeing. He had tried the methyl ester as an indicator and found that although there was apparently no difference in aqueous solutions it was more sensitive in alcoholic solutions than phenolphthalein. He suggested that some of the higher esters of the series such as the ethyl or propyl ester might be more stable than the methyl compound, and might possibly be equally or more sensitive as indicators.

Mr. C. P. FINN said that some years ago some French chemists were working on the absorption spectra of the triphenylmethane dyestuffs, and he would like to know if researches in this direction had thrown any light on the probability of the truth of the quinonoid theory.

Prof. A. G. GREEN, in reply, said that phenolphthalein was of course no exception to the law of ionisation, but colour was not produced by ionisation. Reasoning *a priori*, why should a colourless salt on dissociation give a coloured ion? Colourless salts of phenolphthalein could be obtained, which might be dissociated in solution but would only give a colourless ion. The physical chemist considered the colour change was due to ionisation, but colour chemists thought that a change in the structure of the benzene molecule took place. The stability of the phenolphthalein ether largely depended on the absence of all acid, but the presence of the merest trace would render it unstable. The colour did not change at first although Mr. King said it might lose methyl. He thought it probable that fading of dyestuffs might be due to a change from the quinonoid form to the benzenoid form. The triphenylmethane dyes were most fugitive, but fading could not take place unless at least a trace of moisture was present. Mr. Bennett had suggested that some of the higher homologues of the methyl ester of phenolphthalein might be more stable and he thought that this would probably be the case. Such a member as the amyl or benzyl derivative would most likely retain exactly the same properties as the methyl ester along with superior stability.

Meeting held at Leeds on Monday, December 9th, 1907.

[MR. F. W. BRANSON IN THE CHAIR.]

AN ACCURATE FORM OF GAS ANALYSIS APPARATUS FOR COMMERCIAL AND OTHER PURPOSES.

BY WILLIAM A. BONE, PH.D., D.SC., F.R.S. AND RICHARD V. WHEELER, M.SC.

The authors make this communication in response to repeated requests for a convenient and not too costly adaptation of the gas analysis apparatus used throughout their researches on combustion, which shall meet the daily requirements of a commercial research laboratory.

The authors' research apparatus, which was erected ten years ago, (*vide* Bone, Proc. Chem. Soc., 1898, 154), embodied, in its essential features, the principles of that originally devised by the late Sir Edward Frankland, and subsequently modified by Professors Herbert M'Leod and H. B. Dixon. Since its erection it has been in continuous daily use in the laboratories of Owens College, Manchester (1898—1906) and the University of Leeds (1906/7), for upwards of 3000 analyses, including explosion analyses of mixtures of oxygen with such hydrocarbons as methane, ethane, ethylene, acetylene, propane, propylene, trimethylene, butane, and butylene, as well as the analysis of the products of the partial combustion of these hydrocarbons, and of different forms of producer gas, water gas, natural gas, oil gas, coal and coke-oven gas,

septic tank gas, blast furnace gases, etc. It has proved to be so admirably adapted to all these varied requirements, that the authors decided to introduce such modifications in details as would, without sacrifice of its essential features, bring it within reach of most technical laboratories, and now after more than a year's daily trial of the modified apparatus, they feel that it can be confidently commended to all who desire a thoroughly reliable instrument.

The essential requirements of a "commercial" apparatus, with any claims to precision are (1) accuracy of measurement, including, of course, the maintenance of a constant temperature in the eudiometer, (2) sufficient capacity to allow, in an explosion analysis, of the proper dilution of the "explosive mixture" ("Knallgas") with excess of air or oxygen, (3) absorption arrangements such as will permit of the use of small volumes of freshly prepared (*i.e.* previously unused) reagents, (4) rapidity of action, (5) adaptability to gases of widely different compositions and richness, and (6) simplicity and general convenience of design and working arrangements. Many, if not most, of the forms of apparatus commonly in use are very deficient in regard to the second, third, and fifth of these requirements, however satisfactory they may be in other respects, whilst some of them involve the use of absorption vessels which are either needlessly elaborate or liable to fracture. The authors have duly considered all these points, their aim being to

reduce everything to its simplest terms consistent with convenience and accuracy of working.

The general character and arrangement of the various parts of the apparatus will be readily understood, with the aid of the accompanying diagram, by all who are familiar with the methods of gas-analysis. It comprises, essentially, three parts, viz. (1) a water-jacketed combination of measuring and pressure tubes, A and B, communicating, through the glass tap, C, with the mercury reservoir, D, (2) an absorption vessel, F, standing over mercury in a mahogany trough, G, (3) an explosion tube, E, fitted with firing wires, and connected with a separate mercury reservoir, H. All the connections between A, E, and F are of capillary bore throughout, with suitable glass taps wherever necessary. The diagram also shows how connection is made between the measuring tube, A, and the special "sampling tube," K, whenever the latter is employed for the introduction of the sample under examination. The sample may also be introduced into the apparatus, from an ordinary test-tube, under the wide open end of the absorption vessel, F, which has been previously filled with mercury. Before commencing an analysis, the whole of the apparatus, including all the connections between A, E, and F, is completely filled with mercury, and, needless to say, the whole of the subsequent operations are conducted over mercury.

The various parts of the apparatus are suitably mounted on a strong wooden stand (mahogany, oak, or teak), with four vertical steel rods supporting the shelf upon which the mercury trough, G, rests, the same rods also carrying another shelf for reagent bottles. Proper provision is made for the raising or lowering (to the ground level, if required) of the mercury reservoir, D, by means of a wooden carrier with suitable pulley and ratchet wheel. The whole apparatus stands in a wooden tray 2 ft. 4 in. by 1 ft. 6 in. with 1 in. raised sides.

The salient features of the working of the apparatus are as follows:—

(1) The principle of measurement employed is that first introduced into gas analysis by Regnault, and subsequently adopted by Sir Edward Frankland, viz., the measurement of the pressure of the gas (in m.m. of mercury) at constant volume. For this purpose the gas is brought to a certain "constant volume" mark in the measuring tube, A (by suitable manipulation of the mercury reservoir D and the tap C) and its pressure read off on the pressure tube, B. There are a series of such "constant volume" marks on A, each coinciding with a 100 mm. mark on the pressure tube, B (i.e., with 0, 100, 200, &c., mm.), so that the actual pressure of the gas is given by subtracting from the "pressure reading" the numbers 0, 100, or 200, etc., according to the particular constant volume mark selected for the analysis. The tubes A and B are made in one piece, which is surrounded by a water jacket, and their inner surfaces are kept moist with very dilute sulphuric acid (1 in 20) as a precaution against the accidental fouling of the measuring tube, with alkalis, and it is obvious that the wetting of A and B with the same liquid eliminates the influence of water vapour upon the gas measurements, the various pressures representing those of the dry gas under examination. The tap closing the upper end of the pressure tube is connected with it by means of stout rubber pressure tubing, a device which gives a perfectly tight joint with sufficient elasticity to prevent fracture in case the mercury in B is inadvertently allowed to run up the tube with unusual velocity. The tap in question also allows of the vacuum being easily made in B whenever necessary. The advantages of this mode of measurement over the more usual method of determining the volume under atmospheric pressure are twofold, viz. (1) it allows of the use of smaller volumes of gas for an analysis—thus from 5 to 10 c.c. of gas can be made to have a pressure of 100 m.m., according to the particular volume mark selected, and this pressure can easily be read off to within 0.2 mm. without employing a telescope, and (2) the measurements are, of course, independent of the barometric pressure and at the same time are unaffected by tension of aqueous vapour.

(2) The length of the pressure tube, B, (about 700 mm.) amply provides for the proper dilution of the

"explosive mixture" in an explosion analysis.* Thus in the analysis of a coal gas containing (say) carbon dioxide, 0.5, unsaturated hydrocarbons, 5.5, carbonic oxide, 6.0, hydrogen, 55.0, and methane, 33.0 per cent. respectively, if an amount of gas were originally taken corresponding with a pressure of 120 mm. at the constant volume mark, O, then after removal of carbon dioxide and monoxide, and unsaturated hydrocarbons with suitable absorbents, the residual 105.6 mm. of methane and hydrogen would give 217.8 mm. of "*Knallgas*," which could be diluted with the 350 mm. of *excess* oxygen necessary to ensure accuracy in the subsequent explosion. The importance of capacity is, of course, even greater in the case of a rich oil gas, or in the analysis of acetylene, where very large dilutions are necessary.

(3) The arrangements for the various "absorptions" are of the simplest. Instead of using a number of large absorption vessels each containing a particular reagent which is used unchanged many times over in successive analyses, all the absorptions are carried out over mercury in the one absorption vessel, F, in each case with a comparatively small volume of the particular reagent which is always used fresh and is at once discarded after use.

To facilitate the introduction of the various reagents, and the rinsing out of the absorption vessel with water or dilute sulphuric acid *in situ* between each successive reagent, the wide (open) end of the vessel is immersed under the mercury in the trough, G, whilst the top terminates in a capillary three-way tap, K. One of parallel branches of this tap communicates, through a stout rubber joint, with the measuring vessel, A, and the other with a water pump, a large bottle being inserted between the pump and the absorption vessel to serve as a trap for either the mercury or the reagent which is being discarded after use. The insertion of a tap between the pump and the bottle obviates the necessity of the continuous exhaustion of the latter, a single exhaustion at the outset of an analysis being all that is required.

From 2 to 5 c.c. of the particular reagent to be used is introduced into the absorption vessel (previously filled with mercury), by means of a suitable pipette, from below the surface of the mercury in the trough. Any minute bubble of air accidentally introduced with the reagent can be got rid of by cautiously opening the branch of the tap, K, leading to the above mentioned exhausted bottle; the same device allows of the complete withdrawal of the reagent after use, without taking down the absorption vessel, and also of the rinsing out of the latter *in situ* with water, or dilute sulphuric acid, before the next reagent is used.

In this way, using small quantities of each successive reagent always in a fresh condition, and washing the vessel out *in situ* between each reagent, a series of absorptions can be quickly carried out without disturbing a single connection in the apparatus. It may also be added that long experience has proved that the use of such reagents as a solution of bromine (in potassium bromide) for the absorption of unsaturated hydrocarbons, is unattended with difficulty.

(4) In point of rapidity of action, combined with accuracy, the apparatus will compare favourably with any other type. An analysis of producer gas can be easily carried out in 45 minutes, and one of coal gas in about an hour.

(5) There are no complicated parts about the apparatus to occasion trouble, and the several parts can be readily detached for cleaning purposes.

(6) The apparatus is well adapted for the analysis of almost every kind of combustible gaseous mixture, ordinarily met with in technical practice.

DISCUSSION.

Mr. J. W. Cobb said that no branch of technical analysis had developed more in the past few years than the analysis of gases, on account of the growing conviction that

* If the apparatus is required for the analysis of such diluted gases as producer gas or blast-furnace gas only, the length of the pressure tube need not exceed 400 mm., in which case the lengths of the measuring tube, A, and the explosion tube, E, could be correspondingly diminished, with consequent reduction of the total height of the apparatus above the working bench. But such a reduced apparatus would be unsuitable for the analysis of richer gases.

scientific control was essential for the economical use of fuel. The development was however, mainly in quantity and not in quality. The Hempel apparatus was a good form for control work on ordinary combustion processes, and was easy to manipulate, but others must have felt the need that he himself had experienced, for some more delicate apparatus, what he might call a reference apparatus, for use in determining with certainty the effect of comparatively slight alterations in the conditions of some process. He assumed that this apparatus was intended for reference rather than for control purposes. In comparing the results obtained by the authors in the analysis of producer gases with those generally obtained from the Hempel apparatus, the methane seemed to come out always higher, usually about 1 per cent. Why was this? Could comparison be made between the heating power as calculated from analysis, and the same as determined by gas calorimeter; he had always found the results from gas calorimeters, although comparable with one another, to be low compared with those from analysis, and more so than could be explained by the radiation losses of the calorimeters. Finally he should like to compliment the authors on some of the novel details of the apparatus, and to welcome the paper as the first contribution from the new Fuel and Metallurgical Department of the Leeds University, to the Society of Chemical Industry.

Mr. T. FAIRLEY pointed out that the apparatus was by no means a portable one. It was suitable for an expert chemist to use. The washing out of the vessels by means of the vacuum bottle was an advantage, and the use of mercury made possible greater accuracy. Water was very convenient when the apparatus had to be carried about, and for certain work the results were near enough.

Mr. F. W. RICHARDSON welcomed the apparatus since he had to suffer a good deal from the shortcomings of other forms of apparatus for gas analysis. He noticed the large number of taps but was pleased to hear these were not likely to get out of order. He asked what lubricant Prof. Bone used, and if the apparatus was suitable for extracting dissolved gases from liquids. Had Prof. Bone found trouble by the action of bromine on the mercury used? Mercury was clean and gave accurate results, and he was surprised to see how often water or brine was recommended in its place.

Mr. W. LOWSON inquired what amount of concordance could be obtained between the results obtained by exploding the unabsorbed residue of a coal gas in three or four fractions.

Mr. C. P. FINN asked what time was necessary for the gas to remain in contact with the absorbent and if shaking was required. He had always found two treatments with separate lots of ammoniacal cuprous chloride in separate Hempel pipettes necessary to remove carbon monoxide completely.

Prof. W. A. BONE, in reply, said that all the points raised during the discussion had been carefully considered in designing the apparatus, and many years' experience with his own research apparatus, of which the present form was an adaptation, had convinced him of its reliability.

It was not perhaps an apparatus to put into the hands of a works foreman, or possibly even into the hands of a novice in the laboratory, but anyone with ordinary manipulative skill and practice could be entrusted with it. It had been in daily use as a control apparatus in connection with a large producer plant under Mr. Wheeler's supervision for more than a year, and had given the greatest satisfaction. The Hempel apparatus was, in his opinion, quite unreliable and useless, except for very rough work, and he was not surprised to hear about the low methane results for producer gas obtained with it. He should never think of placing any reliance on results obtained with either the Hempel or the Orsat apparatus, where the estimation of small quantities of any given constituent was concerned, or where small differences in composition had to be detected. He had successfully applied the most rigid tests to his research apparatus with hydrogen containing known small percentages of methane. Moreover, whenever he had had occasion to supplement gas analyses by calorimetric tests during producer trials, he had found close agreement between the two sets of results. Comparative analyses of the same sample of gas with the research apparatus and with the present apparatus showed good agreement, and although the latter was not quite capable of the same degree of refinement as the research apparatus, which, indeed, was much more costly, it was nevertheless, so far as his experience went, a thoroughly reliable instrument. With regard to the absorption of carbon monoxide by means of an ammoniacal solution of cuprous chloride, everything depended upon the care taken in preparing the solution. He always used a freshly prepared (i.e., unused) solution, containing ammonium chloride, of such activity that it absorbed carbon monoxide almost as rapidly as caustic potash absorbs carbon dioxide. Careful experiments had shown, moreover, that after two successive treatments of a gaseous mixture containing large quantities of carbon monoxide with such an active solution, the amount remaining unabsorbed was negligibly small. He often used a solution of bromine in potassium bromide for the absorption of unsaturated hydrocarbons, but found no difficulty at all with it. With regard to taps, if these were carefully selected by a competent judge, and kept lubricated with a solution of india-rubber in vaseline, and especially if the whole apparatus was regularly washed out with dilute acid after each analysis—an operation which could be performed in less than two minutes—no trouble would arise. People who experienced trouble with stop-cocks sticking had largely their own carelessness to blame. There could be no doubt but that gases must be analysed over mercury if accuracy was desired, and he personally never used any other liquid in a gas analysis apparatus: the best substitute for mercury would perhaps be a mixture of equal volumes of glycerin and water. He could not agree that water by itself was "good enough" for even rough work. In these days when gaseous fuels played so important a part in industrial operations the need of exact methods of gas analysis could not be too much insisted on, and the present apparatus was designed to meet that need.

Journal and Patent Literature.

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I.—PLANT, APPARATUS, AND MACHINERY.

PATENTS.

Drying and grinding materials. O. Imray, London.
 From Soc. of Chem. Industry, Basle, Switzerland.
 Eng. Pat. 9741, April 26, 1907.

A HORIZONTAL cylinder with open ends closed by perforated plates is surrounded by a heating jacket and is mounted so that it can be rotated within an air-tight casing in which a vacuum is maintained. Within the cylinder are a number of balls, or "grinding bodies" of steel, or other

suitable material, which crush the material as the cylinder is rotated. The material to be treated, which may contain any quantity of moisture, is fed by suitable means, continuously and without breaking the vacuum, into one end of the cylinder. It is ground and dried and continuously discharged from the other end of the cylinder into the first of two valved chambers, which form an air-lock, so that the dried material can be continuously extracted without breaking the vacuum. The vapour given off is discharged from that end of the casing at which the moist material enters and it travels in the