

BE IT FURTHER RESOLVED.—That these resolutions be printed and a copy be sent to each Senator and Representative of the United States who is a member of the Senate or House Committee on Patents.

MINERAL WASTE

The importance of the conservation of the mineral resources of the United States is again emphasized by the recent appearance of "Notes on Mineral Wastes," Bureau of Mines *Bulletin*, 47, by Charles L. Parsons, Mineral Technologist for the Bureau.

Wastes of fuels, the common metals, fertilizers, combined nitrogen, sulfur, arsenic, the rare earths; losses in the mining and treatment of ores and minerals; failure to make use of native ores; our need of potash, the platinum metals, new alloys and new uses for by-products of our present industries; any one of these is alarming. But there is encouragement in the reports of the recent advances in the metallurgy of iron; the desirable properties of the new alloys; the successful application of the electrical precipitation processes to all smoke and fume problems; the conservation made possible by the cement industries; the possible use of native feldspars and kaolins in the silicate industries; the recovery of combined nitrogen from coal, as well as the fixation of atmospheric nitrogen.

While a certain amount of waste is absolutely neces-

sary, we are reminded that our prodigal annual use and destruction of our natural resources must cease. Ages were necessary for their accumulation and they must be made to serve for the ages to come.

In his preface to this bulletin, Dr. Holmes points out that the present generation will not stint themselves nor will they tolerate financial loss of any kind in utilizing their resources for their ever-increasing needs. The rights and duties of the Federal Government are recognized "as being limited to the carrying on of inquiries and investigations with a view to determining the nature and extent of this waste of resources, the means by which it may be diminished, and the setting forth of the facts in the case." A more detailed report on this subject is promised as soon as the necessary research can be carried out.

It is our opinion that this work is the most important now being done by the government. No scientific society is in a position to support the researches necessary to disclose the "facts in the case." It should be the first duty of chemists and engineers, individually and collectively, to cooperate with the Bureau of Mines in this investigation. Judging from the preliminary report, the Bureau is attacking this problem on broad lines and with most excellent talent. Dr. Parsons' wide personal acquaintance in the profession will assure him of the helpful cooperation of all chemists in this gigantic undertaking.

ORIGINAL PAPERS

THE PRODUCTION OF CHLORINE SUBSTITUTION PRODUCTS OF METHANE FROM NATURAL GAS¹

By CHARLES BASKERVILLE AND H. S. RIEDERER²

The attempts which have been made to effect a chlorination of methane in order to obtain satisfactory yields of substitution products have been discussed in a previous publication.³ It may be noted here that while the formation of methyl chloride, dichloromethane, chloroform and carbon tetrachloride from methane has been experimentally shown by several investigators operating with various methods, and a number of processes have been patented for the production of these and other halogen derivatives of methane,⁴ so far no process has been worked on a commercial scale. Since there is an abundance of natural gas containing 50-90 per cent. methane in this country, the problem is of some importance—one which we thought would bear investigation along lines differing in certain respects from those hitherto followed.

In general, it may be said that the ultimate object of those studying the matter has been to produce

a constant yield of an intermediate product. Bearing in mind the demonstration of Phillips⁵ that the tendency of methane, when chlorinated, is to constantly produce either methyl chloride or carbon tetrachloride, it occurred to one of us (C. B.) that it would be more advantageous to obtain the end-product, from which, among other products, chloroform could be prepared by reduction. Accordingly a number of experiments were conducted with a view of devising a commercial process for the production of carbon tetrachloride from natural gas.

EXPERIMENTS WHEREIN A SPARK DISCHARGE WAS EMPLOYED

In preliminary experiments, an apparatus similar in principle to that used by Phillips was employed. It was finally decided, however, to construct an apparatus with a closed circuit, producing a circulation of the gases by heat on the rise, cooling on the drop, and recovering the products in a trap at the bottom; suitable openings being made in the apparatus for the introduction of chlorine and natural gas, and for the insertion of spark terminals in such a manner as to bring the spark in the junction line of the gases (Fig. I). Several modifications were made in this apparatus during the course of the experiments, and in the later experiments a horizontal reaction chamber (Fig. II), provided with a glass pocket for the collection of any condensation products in a liquid form

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

² The authors have filed applications for patents on the novel features presented in this paper.

³ Baskerville and Hamor, *THIS JOURNAL*, 4, 216.

⁴ Mallet, U. S. Patent 220,397, October 7, 1879; Colin, U. S. Patent 427,744, May 13, 1890; Elworthy and Lance, French Patent 353,291, May 15, 1905; MacKaye, U. S. Patents 880,900, March 3, 1908, and 1,009,428, November 21, 1911; Walter, German Patent 222,919, November 5, 1909; and Pfeifer and Szaroasy, 12,058 D. Ann. P. 24,872, September 25, 1911.

⁵ *Am. Chem. J.*, 16, 362.

and with a hollow carbon terminal for the introduction of the natural gas,¹ was used. In the experiments wherein this form of reaction chamber was used, just

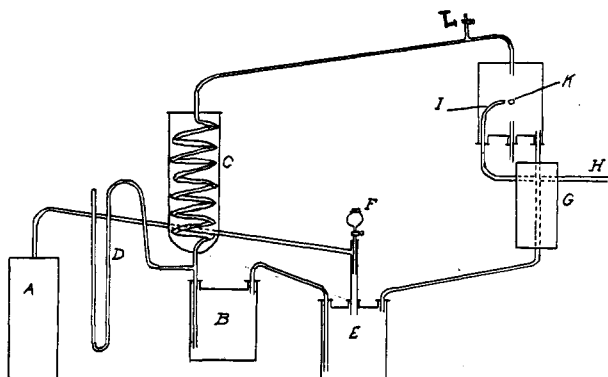


Fig. I

A, chlorine cylinder; B, receiver for substitution products of the reactions; C, condenser; D, pressure gage; E, hydrochloric acid absorption chamber; F, funnel for introducing water; G, electric heater; H, tube for introducing natural gas, which plays between carbon spark terminals I, K; L, cock for releasing pressure.

as in the case of the original form of chamber, bridging between the carbon terminals invariably occurred, although combustion ensued almost immediately upon starting the spark. A very small yield of products was obtained.

The first three runs, using the original form of apparatus, showed that chlorine substitution products could be obtained, although the character of the products could not be determined owing to the small yields. The spark in these runs generally showed a dual character, partly resembling an arc and partly presenting the true color of a spark. Undoubtedly there were considerable ultra-violet rays in this latter portion.

In the runs, using the reaction chamber illustrated in Fig. II, the spark showed little of the deep blue and more of the flame. Since the gas was continuously directed into the spark, it burned continuously.

In the first three runs it is doubtful if the flow of natural gas was continually into the direct line of the spark, as no continuous flame was observed as in the runs with

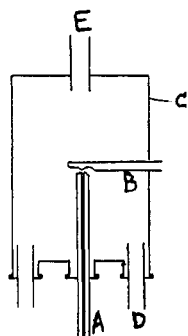


Fig. II

A, hollow carbon transmission tube for natural gas; this carbon is one terminal; B, solid graphite spark terminal; C, reaction chamber of glass; D, chlorine inlet; E, exit for gaseous products of reaction.

the modified apparatus, and it seemed reasonable to conclude that whatever chlorination was effected was through the agency of the ultraviolet rays and not by the combustion.

In all of the above experiments natural gas saturated with water was introduced into the circulating atmosphere of chlorine.

¹ Besides natural gas, methane, prepared by various methods, was used in preliminary experiments. In the following experiments, however, natural gas alone was used.

EXPERIMENTS WHEREIN ULTRA-VIOLET RAYS WERE UTILIZED

The apparatus used in the experiments which follow next was constructed as shown in Fig. III. The reaction chamber was a cruciform tube of glass, through two opposite components of which was inserted a quartz tube containing iron terminals.

In beginning, the apparatus was filled with chlorine, the heat and the spark started, and then natural gas (85 per cent. methane) was admitted. The pressure variations showed that a reaction occurred, but no product could be observed except a crystalline film suspended on the water in the receiving vessel. About 5 liters of natural gas were used. Even after continuing the run for 8 hours, during which time $3\frac{1}{2}$ liters of natural gas were used, no appreciable product was obtained. Accordingly, the apparatus was changed so that the natural gas was admitted below through the U-tube intended for a drain, causing it to bubble through the hydrochloric acid in the receiver.

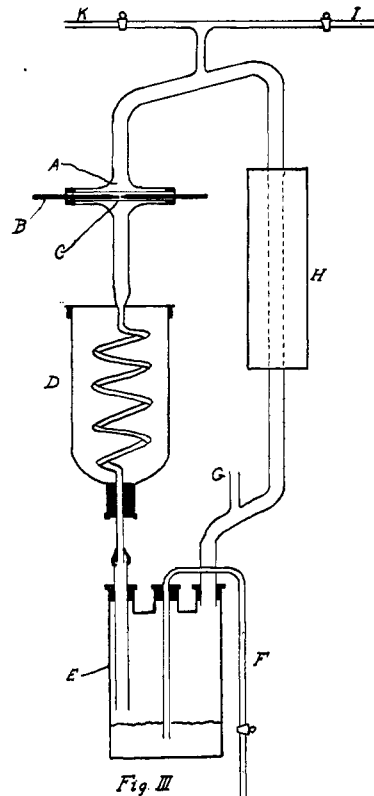


Fig. III

In the next experiment, a considerable quantity of product collected in the receiving vessel: $7\frac{1}{2}$ liters

of natural gas were used and the temperature of the heater was maintained so low that no vapors were observed in the rising tube above the furnace. After another run, in which $3\frac{1}{2}$ liters of natural gas were used, the apparatus was disconnected and the product was separated from the hydrochloric acid in the receiving vessel. Ten cc. of product were obtained; this was purified and fractionated. The first fraction came over at about 64°C ., and the fractions up to 76°C . were collected. A second fraction was then taken up to 88°C . and a residue remained in the fractionating bulb. The first and second fractions were colorless and clear, while the residuum possessed a yellow color. The first fraction amounted to about 75 per cent. of the total, the second and the residue to about 12.5 per cent. each. These experiments showed that approximately a 20 to 25 per cent. yield of carbon chlorides (chloroform and carbon tetrachloride) could be obtained from natural gas, using

a circulating atmosphere of chlorine in the apparatus described.

In the succeeding experiment the apparatus was made absolutely air-tight and a thermo-electric couple was introduced into the furnace to enable temperature readings. A run was made *without* a spark. Preliminary experiments showed that but a slight reaction occurred and that the crystalline product (hexachloroethane) formed was inappreciable, although very little natural gas was used; accordingly no further experiments were made without a spark with this apparatus.

In the following run, which lasted for 8 hours, considerable product collected, and the yield seemed to be in proportion to the natural gas used. The next runs were made after sweeping the apparatus with chlorine. After natural gas and chlorine were both added, the reaction proceeded smoothly and it was finally stopped by admitting chlorine alone. The product amounted to 14 cc. from about 10 liters of natural gas; this was purified and fractionated, and was found to consist of carbon tetrachloride and a small amount of chloroform and hexachlorethane.

For the next experiments, an outlet siphon for the hydrochloric acid produced and an inlet tube for natural gas were provided in the receiver. The apparatus was completely filled with chlorine, but no heat was used in the circuit. About 4 liters of natural gas were used in each run, and considerable product was obtained; the product was not separated, owing to the fact that it was in part distributed throughout the apparatus. It was determined that the product is very sparingly soluble in hydrochloric acid and chlorine water. Attempts were made to ascertain whether the ultraviolet rays have any influence on the reaction between chlorine and methane. Beginning with daylight, the ultraviolet source was then started and observations were made on the speed of the reaction. As in the preceding experiments, the issuing natural gas was saturated with water by passage through a water bottle. However, the variations in pressure were not sufficiently marked to lead one to infer that the ultraviolet rays have any effect on the reaction. In order to definitely establish this fact, a reaction chamber was constructed to accommodate an "Uviol" lamp to replace the spark section. Provisions were also made for exposing or not exposing the mixed gases to ultraviolet light, depending upon what was necessary to produce a reaction, for drying the gases by passage through sulfuric acid after the separation of the products of chlorination, and for passing the residual gases over quicklime. The form of apparatus used is shown in Fig. IV.

Beginning with a full charge of chlorine, the apparatus was run for one day and no appreciable reaction could be observed. From the experiments made, it seemed probable that the ultraviolet rays are not the necessary active rays required, for it was found that the reaction occurs in daylight, and the passage of the solar rays through glass would exclude ultraviolet light. From the observations made so far, it appeared that the solution of the problem was to find the proper rays.

Therefore, the "Uviol" lamp was removed and the aperture closed.

A tungsten filament lamp was mounted outside of the reaction chamber, surrounded by a reflector, and no appreciable reaction occurred, although runs were made under varying conditions. Using an incandescent gas mantle containing 10 per cent. of ceria, whereby the proportion of red rays was increased, with and without the aid of daylight, the reaction was practically *nil*, while with a mantle containing 3 per cent. of ceria only a slight reaction occurred. With the 3 per cent. ceria mantle, the reaction would take place when daylight was admitted, but would practically cease in the dark. At times a slight reaction was noted when working in the dark, but this was attributed to diffused light entering through the laboratory door. Dark here means the exclusion of daylight.

In the next series of experiments a projection lantern, using only one condenser lens and ordinary carbons was placed in such a position as to light the upper section of the reaction chamber. The lantern was run on an 8 ampere 235 volt current, and it was shown conclusively that the arc light cause the reaction

to take place. Colored screens were then interposed between the lantern and the reaction chamber, and in this manner the rays favoring the reaction were determined. A spectroscopic examination of the screens (solutions of coal tar dyes, blue, green, red and yellow, such as are used in the Pinotype color-photography outfit) showed that the blue screen passed through the green and gave but a dim indication in the deep red; that the green cut out every ray except the green with a blue fringe; and that the yellow and red screens

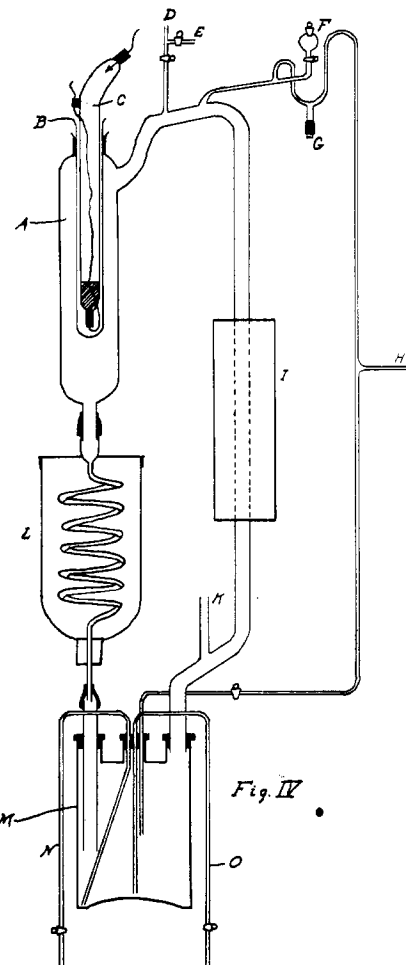


Fig. IV.
A, reaction chamber of glass; B, large thin-walled quartz tube; C, Uviol lamp inserted after current is started; D, tube connection to manometer; E, cock for releasing pressure; F, funnel for introducing water; G, trap; H, tube for introducing natural gas before or after the heater; I, K, chlorine inlet; L, condenser; M, receiver; N, syphon for removing heavy products of reaction; O, syphon for removing water solution of hydrogen chloride produced in the reactions.

excluded the blue end of the spectrum along with part of the green. A number of experiments demonstrated that the unscreened arc light and the arc light screened with the blue allowed a good reaction speed, while the interposition of the green, yellow and red screens slowed down the reaction almost immediately and to a considerable degree; on replacing the blue screen, however, the reaction was at once accelerated. It was found that it made little difference whether chlorine or natural gas was being run into the apparatus, except that the character of the product varied accordingly. Further experiments showed that the blue end of the spectrum is the active agent for the reaction of chlorine and natural gas. It was found that screening is of little use, since the inactive red, yellow and green rays are hardly of an interfering character. The primarily important condition was found to be a source of light rich in the rays of the visible blue spectrum—that is, the spectrum from the bluish green through the visible violet. We have found that the invisible spectrum (the ultra-violet) does not induce the desired activity and that it plays little part in the reaction.

As it was not always convenient to fuse the large glass tubes in making connections, it may be of interest to give the method resorted to for making tight junctions through which such corrosive gases as chlorine and hydrogen chloride may be passed. The glass tubes were first cut smooth and closely fitted to each other. The junction was then wrapped with wet, thin sheets of asbestos paper. After drying, the asbestos was given several coats of Bakelite varnish No. 4. The next day this was tightly wrapped with electric adhesive tape and thoroughly coated again several times with the Bakelite varnish.

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APPLICATIONS OF DUCTILE TUNGSTEN¹

By C. G. FINK

Less than ten years ago tungsten was universally conceded to be a very brittle metal. Since the introduction of ductile tungsten,² however, large quantities of drawn wire, flexible and strong, are being daily produced for the manufacture of incandescent lamps.

We have studied the physical and chemical properties of this new tungsten, and have obtained a number of very interesting results.

The ductile metal is practically insoluble in all of the common acids,³ its melting point is higher than that of any other metal,⁴ its tensile strength exceeds that of iron and nickel, it is non-magnetic, it can be drawn down to smaller sizes than any other metal, and its specific gravity is 70 per cent. higher than that of lead.

It was natural that a metal with such striking properties as these should soon find applications other than that for incandescent lamps.

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

² C. G. Fink, *Trans. Am. Electrochem. Soc.*, **17**, 229; W. D. Coolidge, *Trans. Am. Elec. Inst. Eng.*, **29**, 961.

³ W. E. Ruder, *Jour. Am. Chem. Soc.*, **1912**, 387.

⁴ I. Langmuir, *Trans. Am. Electrochem. Soc.*, **20**, 237.

ELECTRICAL CONTACTS

Wrought tungsten has been substituted with success for platinum and platinum-iridium as contact points in spark coils, voltage regulators, telegraph relays, etc.¹ The service far exceeds that for platinum and platinum-iridium contacts due to the greater hardness, higher heat conductivity and lower vapor pressure of tungsten as compared with platinum.

TUNGSTEN FURNACES

These furnaces are of two types. The type recently described by Winne and Dantsizen² consists of an alundum tube wound with tungsten (or molybdenum) wire. To prevent oxidation the tube is encased in an air-tight box with an inlet and outlet for hydrogen. This furnace is admirably well suited for laboratory experiments. Temperatures of 1600°–1800° C. can be easily maintained for hours, whereas platinum at these temperatures would rapidly disintegrate.

A second type of tungsten furnace³ is constructed on lines similar to those of the Arsem vacuum furnace. A tungsten metal tube takes the place of the helical carbon resistor. The tube is surrounded by a screen and the whole enclosed in an air-tight compartment almost identical to that used by Arsem. The compartment is either evacuated or a small quantity of gas, such as hydrogen, is introduced. This furnace lends itself admirably for the study of reactions at very high temperatures, such as the production of artificial gems.

TUNGSTEN GAUZE

We have used this gauze successfully for separating solids from acid liquors. We performed these experiments on a laboratory scale. However, this gauze could well be used on a commercial scale. For example, for the removal of sludge from copper refining baths, and for centrifugal apparatus, in general, whenever acid liquids or acid gases are dealt with.

Furthermore, it might be used in apparatus such as described by Cottrell⁴ for the removal of sulfuric mist from gases. The Cottrell electrodes consist of three concentric cylindrical screens of iron wire, the inner and outer ones acting as discharge electrodes while the intermediate screen and the outer leaded glass containing vessel act as collecting electrodes from which the deposited acid drains into a leaden pan below. Tungsten gauze is not attacked by sulfuric acid and would consequently give a much longer life than iron gauze.

WROUGHT TUNGSTEN TARGETS FOR ROËNTGEN TUBES

This application has proved to be one of the most interesting. Tungsten is very well suited for targets or anticathodes and the realms of application and efficiency of the Roëntgen tube have been thereby greatly increased.

As has been shown by Coolidge, the high specific gravity, high melting point, high heat conductivity and low vapor pressure make tungsten a far more efficient target than any other metal.

¹ W. D. Coolidge, *Trans. Am. Inst. Elec. Eng.*, **31**, 870; *THIS JOURNAL*, **4**, 2.

² *Trans. Am. Electrochem. Soc.*, **20**, 287.

³ U. S. Pat., 1,006,620.

⁴ *THIS JOURNAL*, **3**, 542.