

CHLORINATION OF NATURAL GAS

by

CARL ALFRED DORF

B. S. Bethany College, 1920



A THESIS

submitted in partial fulfillment of the  
requirements for the degree of

MASTER OF SCIENCE

KANSAS STATE COLLEGE  
OF AGRICULTURE AND APPLIED SCIENCE

1932

## TABLE OF CONTENTS

	page
INTRODUCTION .....	2
LITERATURE .....	4
EXPERIMENTAL .....	10
Apparatus .....	10
METHODS AND PROCEDURE .....	12
NOTES .....	16
DISCUSSION OF EXPERIMENT .....	19
CONCLUSIONS .....	23
ACKNOWLEDGMENT .....	24
LITERATURE CITED .....	25

## INTRODUCTION

The United States possesses an abundance of natural gas and efforts have been made to utilize it in ways other than as fuel. Among the things investigated has been the production of chlorine substituted products.

Many natural gas fields of the United States yield gas in which methane is the only combustible constituent. This gas is especially suitable for making chlorinated products. The natural gas from several of these fields, where the wells are too remote from industrial centers and large cities to warrant the expense of piping, could profitably be made into chlorinated products. All four of the chlorine substitution products have commercial value if they can be made cheaply. And undoubtedly other markets would be created with the cheap manufacture of these products, particularly methyl chloride, chloroform, and carbon tetrachloride.

Our problem was a study of the chlorination of natural gas. The investigations were confined to a study of the effect of various ratios of natural gas to chlorine, rates of flow of the gases, the effect of various reaction temperatures, of water vapor upon the reaction, of various catalyzers and of using a catalyzer for several inter-

mittent runs.

It was found that by using the two gases in the ratio of 1:1 some uncombined chlorine passed through the apparatus, but when they were used in the ratio of two volumes of natural gas to one volume of chlorine, there was very little if any free chlorine passed through. When the ratio of natural gas to chlorine was 3:1 or more, it was necessary to use charcoal absorbers.

The rate of flow which gave the greatest yield was found to be not in excess of 16 inches per minute. With a greater rate of flow, the mixture passed through the reaction chamber in such a short time that chlorination was not complete.

In studying the effect of reaction temperatures, there was evidence that chlorination began as low as about 250°C. Very little of the higher chlorides were formed at this temperature. No run of any length was made at temperatures below 325°C. At temperatures from 325° to 400°C. high yields were obtained, and temperatures from 350° to 375°C. gave the best yield with a smooth reaction. At 400°C. there were slight explosions with the deposition of carbon, and, with one catalyzer, explosions occurred at a temperature as low as 370°C.

On making repeated runs with the same catalyzer, no variation in yield was observed.

Among the catalyzers used, activated wood charcoal, charcoal treated with nickel chloride, and with nickel chloride and sodium hydroxide gave good yields. Charcoal treated with ferric chloride and with ferric chloride and sodium hydroxide gave fair yields but explosions occurred at about  $370^{\circ}\text{C}$ . Gas carbon gave slightly lower yields, and in using red phosphorous as catalyst, very poor yields were obtained. Phorous pentachloride volatilized and condensed on the walls of the cooler.

#### LITERATURE

Among the first investigators to work on chlorination of natural gas was Berthollet (1), who, in 1858, found that unless the reaction between chlorine and methane was carried out very slowly, explosions occurred and separation of carbon resulted. Phillips (4), in 1893, tried to avoid explosions by chlorinating methane, without the access of light, in a tube heated to  $300^{\circ}$  to  $400^{\circ}\text{C}$ . and finding that only the first and last chlorides of the series were formed in appreciable quantities. He questioned the successful chlorination to intermediate products. Tolloczko (7), in 1912, also working in hot tubes, obtained results similar to Phillips. Walter (5), in 1909, states that water vapor cuts down the speed of chlorination considerably and if the chlorine is added gradually that it reacts more readily

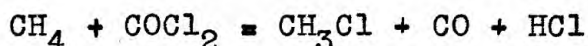
with the partially chlorinated methane than with the original hydrocarbon, the result being the highest chlorine substitution possible. Baskerville and Riederer (8) cite the work of Walter and Phillips and seek to obtain chloroform indirectly by chlorinating methane to the tetrachloride and reducing. They also show that the blue end of the visible spectrum is more suitable for use in chlorination than ultraviolet rays. Graul and Hanschke (6), in 1912, state that chlorination of ethane in diffused daylight, as carried out by Schorlemma in 1869 is impractical, since at low temperatures, the halogen reacts very slowly.

Phillips (4) found that when a mixture of natural gas with chlorine was passed over red-hot lamp black, methyl chloride and carbon tetrachloride were formed in abundance. Methylene chloride and chloroform were found in only small quantities.

Baskerville and Riederer (8) discovered that the primarily important condition for the chlorination was the source of light, rich in the rays of the visible blue spectrum, that is, the spectrum from the bluish green through the visible violet. They stated that the ultraviolet part of the spectrum played little part in the reaction, and that apparently the necessary source of light could be obtained by an arc, between iron electrodes, in the circuit. In some experiments a 20-25 per cent yield, based on

natural gas, of a mixture of carbon tetrachloride and chloroform was obtained.

Hochstetter (7) obtained methyl chloride from methane by the action of carbonyl chloride at a high temperature according to the equation:



The reaction was brought about by leading the gases, containing a slight excess of methane, over a catalyst capable of acting as a chlorine carrier or of accelerating the reaction by surface condensation.

Lacy (11) found that a high yield of methyl chloride with a little methylene chloride was formed when a cold mixture of 1 volume of chlorine and 5 volumes of methane were mixed with 10 volumes of methane, heated to 370°C. and then allowed to enter a reaction chamber at about 250°C. The reaction progressed smoothly and was free from carbonization. A temperature from 400° to 500°C. was maintained by the reaction. The temperature was easily controlled by the amount of methane passing through the furnace. The result was less than 0.01 per cent uncombined chlorine.

Garner and Clayton (12) produced a mixture of the chlorine substitution products by mixing natural gas and chlorine in a body of charcoal at a low temperature, and then passing the mixture through a body of charcoal heated to about 300°C.

Yoneyama and Ban (14) stated that methyl chloride was easily prepared without explosion by passing dry methane and chlorine over a catalyst composed of a mixture of animal charcoal and finely divided calcium oxide at 250°C. at the rate of 3 and 5.5 liters per minute respectively.

Jones, Allison, and Meighan (15) found that by passing a mixture of methane and chlorine through an electrically heated tube with different catalyzers, various percentages of the four chlorides of methane were obtained.

Schleede and Luckow (17) discovered that when a mixture of methane and chlorine in mole proportions were passed through electrically heated tubes, inflammation occurred, but the flame gradually died out. It was permanent when an excess of chlorine was used. If an excess of methane was used, ignition was not observed. The phenomena were not greatly affected by the presence of catalysts or by an increase of temperature of 100° above the minimum.

Leiser and Ziffer (18) found that when a mixture containing 1 volume of chlorine to 6 volumes of methane and also hydrogen chloride gas was exposed to actinic light, methyl chloride was produced. The mixture was heated to start the reaction. With this proportion of gases, methyl chloride was the main product.

Gault and Benlain (20) found that the chlorination of natural gas at temperatures of 245° to 415°C., with a



methane to chlorine ratio of one to one and gas flow of four liters per hour, in presence of ferric chloride and absence of light, always gave a mixture of the four chlorides of methane. Over this range of temperature, iron exerted no limiting action.

Roka (22) discovered that natural gas was chlorinated to methyl chloride in the presence of steam as a diluent at a temperature of 400° to 500°C.  $\text{CaCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{MgCl}_2$ , and  $\text{FeCl}_3$ , were used as catalysts.

Boswell and McLaughlin (23) found that complete chlorination of methane to methyl chloride was obtained when partially reduced  $\text{CuCl}_2$  was used as a catalyst. They used a ratio of nitrogen to methane of 10 to 1, and of methane to chlorine of 8 to 1 in the presence of water vapor and a temperature of reaction of 450°C. A yield of 80 to 90 per cent was obtained. Chlorination of methane to carbon tetrachloride with 90 per cent yield was also obtained with the same catalyst.

The fact that natural gas can be chlorinated quite readily to yield the four chlorides of methane is generally accepted, but the effect of ratios of the two gases, the reaction temperature, the presence of water vapor and the effect of different catalyzers brings out considerable difference of opinion.

Tollozcko and Kling (7) used an excess of either

methane or chlorine to avoid explosions but found that a poor yield was obtained when an excess of natural gas was used. Lacy (11) used a ratio of methane to chlorine of 15 to 1 with a result of less than 0.01 per cent of uncombined chlorine.

Jones, Allison and Meighan (15) state that the best results were obtained at temperatures from 300° to 400°C. Gault and Benlain (20) used temperatures from 245° to 415°C. Boswell and McLaughlin (23) found that the best results were obtained at 450°C. Lacy (11) maintained temperatures from 400° to 500°C.

Walter (5) states that water vapor cuts down the speed of reaction considerably. Jones, Allison, and Meighan (15) state that the presence of water vapor tends to help the reaction. Boswell and McLaughlin (23) found that the presence of water vapor was an aid to the reaction.

Schleede and Luckow (17) state that the phenomena were not greatly affected by the presence of a catalyst. Hochstetter (9) states that the reaction was brought about over a catalyst capable of acting as a chlorine carrier. Jones, Allison, and Meighan (15) state that the chlorination system, in order to work successfully, requires the presence of a catalyzer such that the reaction will proceed smoothly without explosions or the deposition of carbon.

## EXPERIMENTAL

The gas used in the experiment was taken from the mains at the college, supplied by the Kansas Gas and Pipe Line Company from the McPherson field in Kansas.

An analysis of the gas, furnished by the gas company, gave the composition as:

Methane .....	78.20 per cent
Ethane .....	14.20 per cent
Carbon dioxide .	0.72 per cent
Oxygen .....	0.50 per cent
Residue .....	6.38 per cent

## Apparatus

The general plan of the apparatus used is shown in figure 1. The rates of flow of the natural gas and chlorine were regulated by flow meters. The flow meters were calibrated by passing gas from a calibrated container through them. From the data thus obtained, the rates were determined and a scale was made for reading the rate directly.

The reaction chamber consisted of a silica tube 24 inches long and three-fourths inch in diameter and was heated electrically. Nichrome wire was wrapped about the tube, cemented with a magnesia-sodium silicate cement and

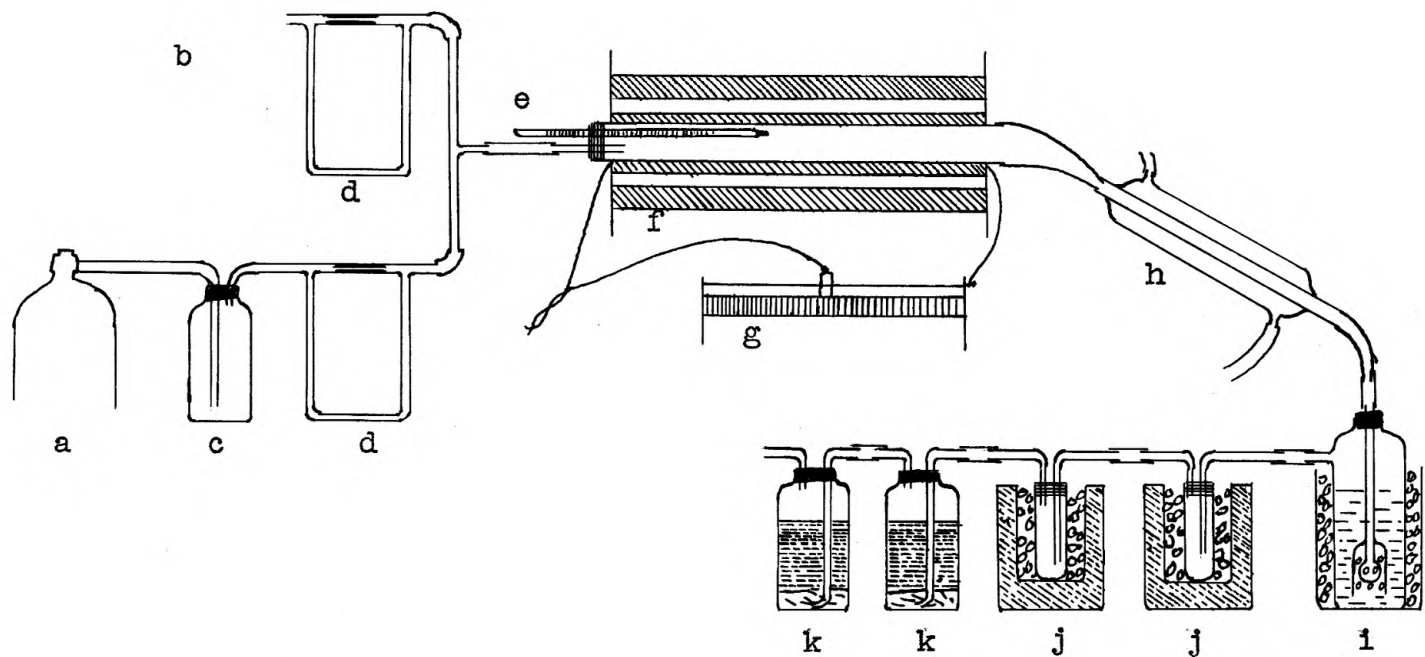


Fig. 1. Diagram of Apparatus.

a - chlorine tank  
 b - gas inlet  
 c - trap  
 d - flow meters  
 e - thermometer  
 f - furnace

g - slide wire resistance  
 h - cooler  
 i - scrubber  
 j - brine cooled condenser  
 k - charcoal absorbers

covered with asbestos paper. The tube was centered in a sheet metal pipe which was itself wrapped with asbestos. The temperature was read on a thermometer inserted into the tube through a stopper, or on a millivolt meter with a thermocouple.

The collection system consisted of a small water cooled condenser followed by a scrubber filled with a strong sodium hydroxide solution, then two brine cooled condensers and finally two charcoal absorbers.

#### METHODS AND PROCEDURE

The mixed gases were usually passed into the reaction chamber directly. In some of the runs, however, the gas was bubbled through water first. The hot gases upon leaving the reaction tube passed through the collecting system. Carbon tetrachloride and some chloroform condensed in the sodium hydroxide scrubber, and at the end of the run, were separated by a separatory funnel. Some of the liquid collected in the brine cooled condensers and the rest of the products were absorbed in the charcoal absorbers.

At the end of the run, the absorbers were heated, the absorbed products condensed in a receiver cooled with acetone and carbon dioxide ice. This distillate contained the methyl chloride as well as small portions of the other

chlorides. This was measured and the methyl chloride allowed to boil off at  $0^{\circ}\text{C}$ . The rest of the liquid was then added to those from the scrubbers and condensers. It was then treated with calcium chloride to remove the water and with solid sodium hydroxide to remove any dissolved chlorine.

The liquid was then filtered into a 50 cubic centimeter distilling flask and distilled at the rate of about 10 cubic centimeters per hour. Cuts were made of the distillates coming over at  $50^{\circ}\text{C}$ ., from  $50^{\circ}$  to  $70^{\circ}$  and from  $70^{\circ}$  to  $85^{\circ}\text{C}$ . Each cut was carefully measured, weighed and the specific gravity calculated.

In the first few runs, activated charcoal was used as the catalyzer. Several runs were made with this catalyzer under different conditions to determine the effect of various reaction temperatures. Runs were made at temperatures of  $325^{\circ}$ ,  $350^{\circ}$ ,  $375^{\circ}$ , and  $400^{\circ}\text{C}$ . The effect of water vapor upon the reaction was studied. In the first runs, the mixed gases were allowed to pass directly into the reaction chamber. In later runs, it was bubbled through water before entering the reaction chamber.

The effect of various ratios of natural gas to chlorine was next studied. A series of runs were made with different rates of flow to determine the effect on the reaction, and finally with the same catalyzer a series of runs were made

under the same conditions to determine the poisoning effect upon the catalyzer. The conditions used were those which had been found to give the best results.

Various catalyzers were used to determine their effect on the reaction, among which were:

1. Gas carbon, obtained from the carbon deposit in the reaction chamber used in the experimental work on pyrolysis.

2. Activated charcoal prepared by heating 10-20 mesh wood charcoal in a retort.

3. Charcoal treated with ferric chloride. The charcoal was placed in a 10 per cent solution of ferric chloride and allowed to stand over night, then filtered on a suction filter, and dried at 200°C.

4. Charcoal boiled in a 10 per cent nickel chloride solution for 30 minutes, filtered on a suction funnel, boiled in a 10 per cent solution of sodium hydroxide for 30 minutes, filtered and dried at 200°C.

5. Charcoal boiled in a 10 per cent solution of nickel chloride for 30 minutes, filtered and dried at 200°C.

6. Red phosphorous.

Table 1 shows yields of the different products under various conditions.

Table 1. Showing Yields of the Chlorides of Methane Under Various Conditions

Runs:	Catalyst	Temperature	Ratio gas to chlorine	Rate of flow (liters per hour)	Water vapor	Product based on weight of chlorine used (per cent)					Total
						Methyl chloride	Meth- ylene chloride	Chloro- form	Carbon tetra- chloride	Residue	
1	Activated charcoal	350°C.	1:1	10	No	16.40	7.20	25.63	14.70	3.90	67.83
2	Activated charcoal	350°C.	1:1	10	Yes	20.05	6.77	26.80	18.05	4.26	75.93
3	Activated charcoal	400°C.	1:1	10	Yes	11.70	9.25	25.20	18.70	5.22	70.20
4	Activated charcoal	350°C.	2:1	6	Yes	18.30	9.85	30.10	17.45	7.50	83.20
5	Gas carbon	350°C.	1:1	6	Yes	4.14	8.21	24.30	10.02	7.30	53.97
6	Gas carbon	350°C.	2:1	6	Yes	7.65	5.69	25.40	14.20	10.80	63.74
7	Charcoal FeCl <sub>3</sub> + NaOH	350°C.	2:1	6	Yes	11.24	8.01	26.00	19.70	11.43	76.70
8	Charcoal NiCl <sub>2</sub> + NaOH	350°C.	2:1	6	Yes	18.80	6.75	26.20	21.70	13.40	86.85
9	Charcoal NiCl <sub>2</sub>	350°C.	2:1	6	Yes	27.20	8.62	24.37	20.40	12.40	92.99



Figure 2 is a curve showing the relative yield of the products.

#### NOTES

In the study of the effect of various reaction temperatures, it was found that at 325°C. an appreciable amount of free chlorine was passing through the apparatus, as shown by a test with starch-potassium iodide paper at a point just before entering the scrubbers. At temperatures of 350° to 375° very little if any free chlorine passed through. At 400° slight explosions occurred, and some free carbon was obtained.

Runs made in the presence of water vapor were found to proceed with a smoother reaction as well as to give a higher yield, so all the subsequent runs were made in the presence of moisture. The water used was always saturated with the gases by running the mixed gases through for some time before starting the run. The catalyzers were saturated at the same time at the temperature at which the run was to be made.

In studying the effect of various ratios of natural gas to chlorine on the reaction, it was found that a ratio of about 2 to 1 gave the best results. If a higher ratio of chlorine was used, an appreciable amount of chlorine passed through the apparatus, and if a larger amount of natural gas was used, a considerable amount of vaporized

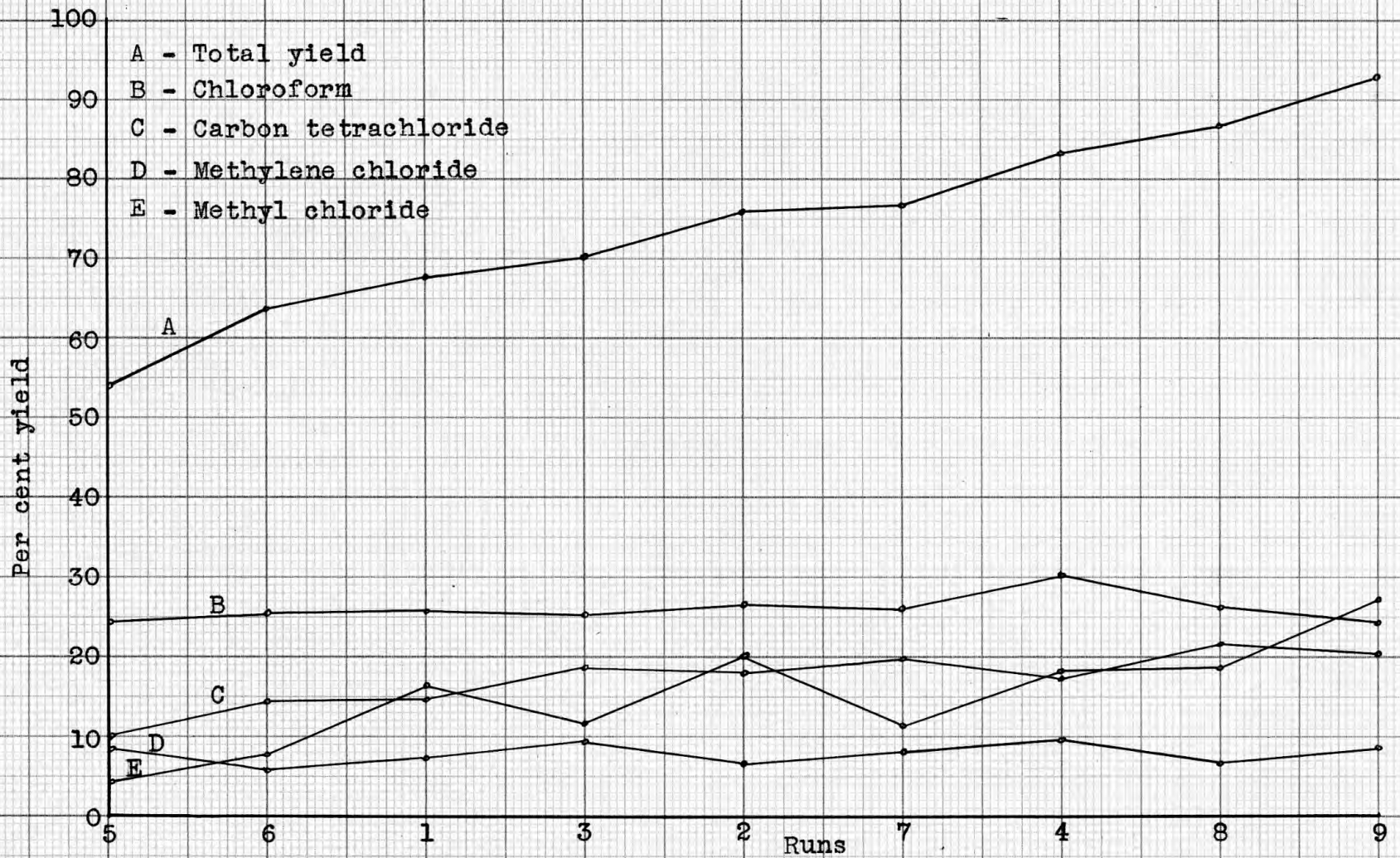


Fig. 2. Showing yields of various products.

products was carried over. These vapors were absorbed in the charcoal absorbers, but for a run of several hours, it was necessary to use more absorbers to insure the removal of all the vapors from the excess gas.

The rate of flow giving the best results was found to be close to 7 liters of chlorine per hour, which in the size of apparatus used represented a velocity of about 16 inches per minute or about one and one-half minutes for the gas to pass through the reaction tube. When the velocity was greater than this, the gases passed through the reaction tube so rapidly that complete chlorination was not obtained.

In the study of the effect of various catalyzers, it was found that yields varying from about 50 per cent to more than 90 per cent based on the weight of chlorine used were obtained. The per cent of each of the four chlorides of methane also varied considerably with different catalyzers. In almost every instance, methylene chloride was obtained in the smallest quantity, then methyl chloride, carbon tetrachloride, and chloroform in the order named.

What appeared to be hexachlorethane crystallized on the walls of the cooler. These were collected and added to the liquid products before distilling.

It was found to be very difficult to collect the methyl chloride. Having a boiling point of  $-23.7^{\circ}\text{C}$ . it could not be condensed in the brine cooled condensers. At

0°C. powdered charcoal will hold practically all the methyl chloride formed, therefore, the absorbers were placed in an ice bath and at the end of the run the absorbed products were distilled off and condensed in an acetone-carbon dioxide ice bath. Even with the carbon dioxide ice, all the methyl chloride did not condense, some of the vapor escaping.

#### DISCUSSION OF EXPERIMENT

The chlorine substitution products of methane are all more or less volatile, making it difficult to collect them without loss unless an elaborate collecting system is used.

At the average room temperature, which was about 23°C., the vapor pressure of carbon tetrachloride is 104 millimeters, that of chloroform 183.5 millimeters, and for methylene chloride 397.6 millimeters. The average atmospheric pressure was 740 millimeters. Thus when an excess of natural gas was used, the gas would have to contain  $\frac{104}{740} \times 100$  or 14 per cent carbon tetrachloride,  $\frac{183}{740} \times 100$  or 24.8 per cent chloroform, and  $\frac{397.6}{740} \times 100$  or 53 per cent methylene chloride before any of these products would condense.

Because of the volatile nature of the products, the scrubbers were surrounded with ice so as to keep the vapor tension down as low as possible. The brine cooled baths

were kept at about  $-15^{\circ}\text{C}$ . at which temperature the carbon tetrachloride reaches saturation at 1.82 per cent, and the chloroform at 2.45 per cent.

The analysis of the products of the reaction, under the conditions under which the work was carried out, could be only approximate. To get a complete separation of the three liquid chlorides of methane would be impossible without the use of a fractionating column or similar method. However, the results are sufficiently accurate to give comparative results for the chlorination of methane under the various conditions used.

Electricity was used as a source of heat because of the greater ease of controlling the conditions. Other sources of heat could be used, such as gas burners. Gas burners were used in one run and found to be practical although they required closer attention.

In the mixing of the natural gas and chlorine, no special type of mixer was used. The two gases were led into the delivery tube through a T-tube, then bubbled together through the water, entering the reaction tube through a glass wool plug.

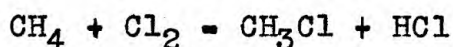
Schleede and Luckow (17) showed that either gas could be used in excess, but they found that when an excess of chlorine was used, inflammation occurred. For this reason, and from an economical point of view as well as in a desire

to keep an excess of chlorine out of the laboratory as much as possible, chlorine was not used in excess.

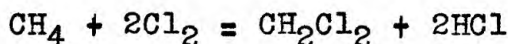
The chlorination system, in order to work successfully, apparently requires the presence of a catalyzer such that the reaction will proceed smoothly without explosions or the deposition of carbon, and will result in the formation of the substitution products desired and not in the production of carbon and hydrochloric acid. There are many catalyzers which will cause chlorine and methane to react when heated to 300° to 400°C. In fact, no catalyzer at all is needed at temperatures of about 400°C., but the reaction takes place rapidly and, being exothermic in character, causes an explosion, with the result that very little, if any, products are formed other than carbon and hydrochloric acid.

The reactions of chlorine with methane are as follows:

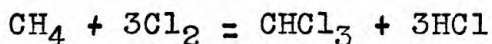
For the formation of methyl chloride:



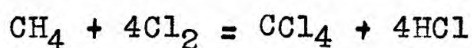
For the formation of methylene chloride:



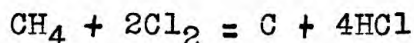
For the formation of chloroform:



For the formation of carbon tetrachloride (Tetrachloromethane):



For the deposition of free carbon:



One would expect, when a given volume of chlorine reacts with an equal volume of methane that methyl chloride and hydrochloric acid would be formed. This reaction is not realized experimentally. Not only is methyl chloride formed but other substitution products as well. Similar results are obtained for reactions for the other substitution products.

Temperatures between 300° and 400°C. have been found the most suitable for the reaction and still give a wide margin below the temperature at which carbon deposits. The reaction is exothermic and from a theoretical standpoint gives a calculated temperature of about 1820°C. when one volume of methane reacts with one volume of chlorine, to form methyl chloride. Two volumes of chlorine should produce a temperature of about 2290°C. when caused to react completely with one volume of methane to produce one volume of dichlormethane. Likewise three and four volumes of chlorine should produce temperatures of about 2760° and 3270°C. when reacting with one volume of methane to form chloroform and carbon tetrachloride, respectively.

These calculated temperatures are only approximate, for no accurate data are available on the specific heats of

chloroform and carbon tetrachloride at high temperatures. The system does not attain these high temperatures because the heat lost by radiation and by conduction through the apparatus, and that required to heat up the inflowing gases, slightly more than account for the heat of reaction.

### CONCLUSIONS

1. Natural gas can be completely chlorinated in one operation.
2. It is possible to obtain yields of more than 90 per cent of the calculated amount based on the weight of gas used.
3. The best temperature range for chlorination in the presence of a catalyzer extends from about 325° to 400°C.
4. The presence of a small amount of water vapor tends to aid the reaction.
5. Very absorbent catalyzers, such as activated charcoal and gas carbon, give a low yield of methyl chloride but a high yield of chloroform and carbon tetrachloride.
6. Some metal impregnated charcoals give a high yield of methyl chloride.
7. No poisoning of the catalyzing material was found on continued use.



## ACKNOWLEDGMENT

The writer wishes to express his hearty thanks and sincere appreciation to Dr. Wilson F. Brown for suggesting this problem, making it possible to be carried out and for his kindly interest shown throughout the work.

## LITERATURE CITED

- (1) Berthollet  
1858. Synthese de l' esprit-de-bois. Ann. Chim. Phys., 52, [3], 98.
- (2) Henry  
1884. Chloro Derivatives of Methane. Journal of the Chemical Society, 46, A 718.
- (3) Losnaitzsch  
1884. Chlorine Derivatives of Methane. Journal of the Chemical Society, 46, A 1107.
- (4) Phillips  
1894. Action of Chlorine on Methane. Journal of the Chemical Society, 66, A 393.
- (5) Walter  
1910. Chlorinating Methane under Action of Light. Chemical Abstracts, 4, [2], 2866.
- (6) Graul and Hanschke  
1912. Forming Halogen Derivatives of Paraffin Hydrocarbons by the Action of Light. Chemical Abstract, 6, [2], 2686.
- (7) Tolloczko and Kling  
1913. Chlorination of Natural Gas. Journal of the Society of Chemical Industry, 32, 742.
- (8) Baskerville and Riederer  
1913. Chlorination of Methane from Natural Gas. Journal of the Chemical Society, 104, A 242.
- (9) Hochstetter  
1916. Methyl Chloride from Methane. Journal of the Chemical Society, 110, 625.
- (10) Bedford  
1916. The Production of the Lower Chlorides of Methane from Natural Gas. Journal of Industrial and Engineering Chemistry, 8, 1090.
- (11) Lacy  
1918. Apparatus for Manufacturing Chlormethane. Chemical and Metallurgical Engineering, 19, [3], 152.

- (12) Garner and Clayton  
1918. Chlorinating Natural Gas. U.S. Patent  
1,262,769.
- (13) Pfeifer, Mauthner, and Reitlinger  
1919. Chlorination of Methane. Journal of the  
Chemical Society, 116, A 565.
- (14) Yoneyama and Ban  
1921. Preparation of Methyl Chloride. Journal of  
the Chemical Society, 120, A 3.
- (15) Jones, Allison, and Meighan  
1921. Chlorination of Natural Gas. Bureau of  
Mines Technical Paper No. 255.
- (16) Whitson  
1920. Action of Methane under Influence of Light.  
Journal of the Chemical Society, 123, T 183.
- (17) Schleede and Luckow  
1923. Chlorination of Methane. Chemical Abstract,  
17, 2864.
- (18) Leiser and Ziffer  
1923. Chlorinating Methane. Chemical Abstract,  
17, 2886.
- (19) Riesenfeld  
1923. Chlorinating Methane. Chemical Abstract,  
17, 2290.
- (20) Gault and Benlain  
1924. Chlorination of Natural Gas. Chemie et  
industrie, Special Number 272.
- (21) Krause  
1928. Chlorinating Methane by Use of Antimony  
Pentachloride. Chemical Abstract, 22, 3171.
- (22) Roka  
1929. Chlorination of Methane. U. S. Patent  
1,723,442.
- (23) Boswell and McLaughlin  
1930. Chlorinating Methane. Chemical Abstract,  
24, [1], 53.