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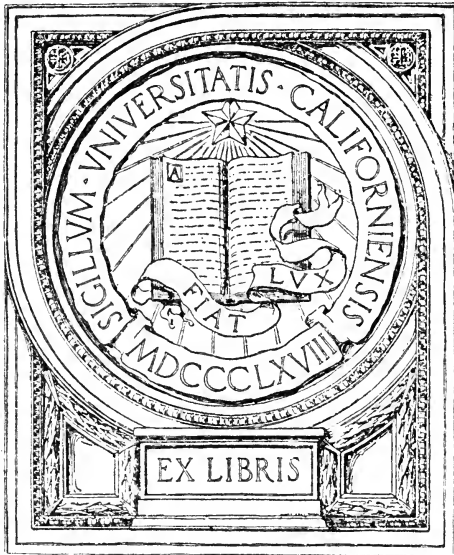
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# **Thermal Reactions in Carbureting Water Gas**

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## **DISSERTATION**

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS  
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY  
IN THE FACULTY OF PURE SCIENCE  
COLUMBIA UNIVERSITY

BY

**Walter Frank Rittman, M.A., M.E.**



**NEW YORK CITY  
1914**



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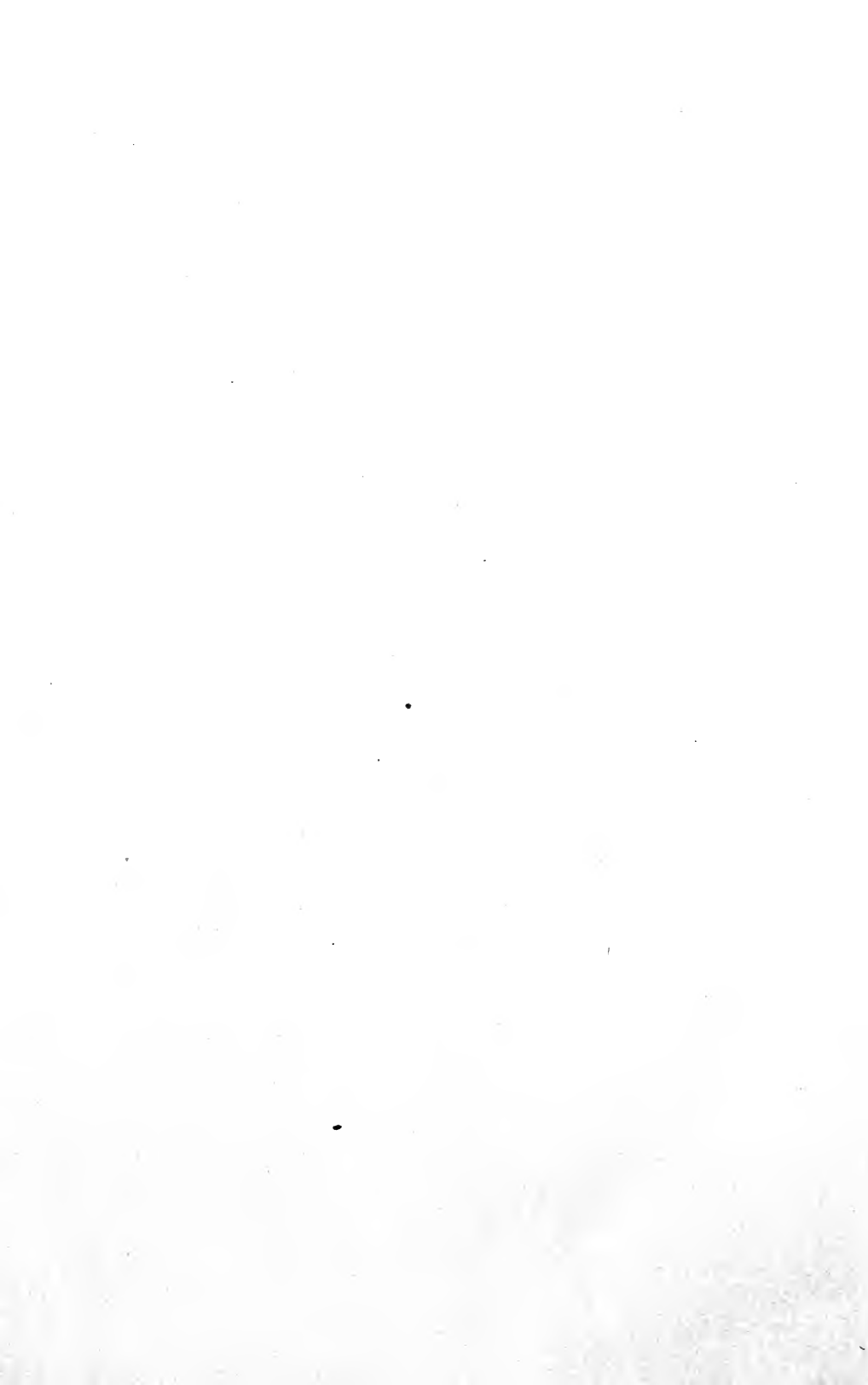
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PROFESSOR OF CHEMISTRY  
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### ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to Professor Milton C. Whitaker, at whose suggestion and under whose direct supervision this work was carried out; his practical advice and active cooperation have been essential factors in the progress and development of this research.

Thanks are due to Professor J. L. R. Morgan for assistance in the development of the theoretical discussion; to Professor F. J. Metzger for suggestions as to methods of gas analysis and experimental procedure; and to the other members of the chemical faculty for time given to informal discussions of the principles involved in the problem.

W. F. RITTMAN

CHEMICAL ENGINEERING LABORATORY  
COLUMBIA UNIVERSITY, NEW YORK  
May, 1914



## THERMAL REACTIONS IN CARBURETING WATER GAS

### PART I—THEORETICAL

Much careful scientific work has been done on the equilibria involved in the manufacture of uncarbureted blue water gas. In the combined processes of manufacturing and carbureting blue water gas according to present practice, few experiments have been made on the equilibria of the constituents to find out the effect of varying pressure, temperature and concentration conditions. In the technical literature of gas manufacture, one rarely finds a reference to the relationship which may exist between the spheres of reaction in the process. The natural conclusion has been that the water gas and oil gas reactions are separate and influence each other but little.

It is proposed to consider some of the factors in which the  $H_2$ ,  $CO$ ,  $CO_2$  and  $H_2O$  of the blue water gas may affect the proportions of  $CH_4$ ,  $C_2H_6$ ,  $C_2H_4$ ,  $H_2$ , etc., resulting from the cracking of the gas oil which is added. Likewise the influence of the gases coming from the oil on the percentage composition of the final gas mixture will be considered.

When the blue water gas or oil gas are manufactured in separate operations, hydrogen is the only gas which is found in the free state, in any quantity. But if the two gases, separately made, should be brought together at high temperature in a container such as a gas plant superheater, would there not be new equilibria to be satisfied? For example, might not the  $CO$  and  $H_2$  of one become  $CH_4$  and  $H_2O$  of the other, or *vice versa*? In case of these new equilibria, of course, there would be vital reactions between the gases of the two processes. In actual manufacturing practice, all the gases produced are in intimate contact at high temperature for the greater part of the manufacturing period, *i. e.*, while passing through the carbureter and superheater. Is it then correct to regard carbureted water gas as the result of two distinct reactions?

Equilibrium conditions tend to establish themselves both during the periods of initial cracking of the oil and the subsequent passage of the mixture through the carbureter and superheater. Gas oil itself can be "cracked" in a short distance, as has

been shown in practically all laboratory experiments; in the laboratory the length of the cracking tube is usually a question of inches. It would seem on *a priori* grounds that the only important reason for the existence of the superheater is to enable the various gases present to interact ("fix") and reach a favorable equilibrium.

This laboratory has begun a comprehensive study of the reactions and equilibria involved in water gas manufacture. While unable to cover the field in two years, it has come to a full realization of the importance of the investigation. The present paper will be confined to a theoretical consideration of the problem. Further papers will take up experimental data.

The problem has been attacked entirely from the point of view of physical chemistry, and from the standpoint of mass action and thermodynamics. In so doing, the mechanism of the reactions involved has not been seriously considered. The materials at the start, the final products desired, the energy transformations essential to bring the latter from the former, the temperature, the pressure and the concentration conditions favorable to the changes have had primary consideration.

Basing an experimental investigation upon the theoretical considerations evolved, it has been possible, among other things, to establish the following results:

(1) Increase the yield of illuminants over the best results recorded in the literature by more than 100 per cent.

(2) Decrease the carbon deposited to less than 1 per cent, by weight, of the oil used.

(3) Make an oil gas in which 56 per cent of the fixed gases are illuminants.

These figures result from the application of conditions which the theory shows would favor such results more than do those at present used in water gas manufacture. Conversely by applying conditions, which, according to theory would give less favorable results to the theory involved, and by comparing the maximum yield under these conditions with a maximum yield obtained under ordinary conditions, it has been found possible to:

(4) Decrease the yield of illuminants by 25 per cent.

(5) Increase the carbon deposited to 51.5 per cent, by weight, of the oil used.

(6) Make an oil gas containing only 5 per cent total illuminants.

Further, it has been found possible to produce:

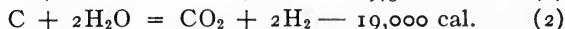
(7) A viscous tar of relatively high specific gravity containing naphthalene and anthracene; or

(8) A liquid "tar" of relatively low specific gravity resembling petroleum oil, and containing no naphthalene and anthracene.

In the examination of the problem, no single reaction can be considered exclusively by itself. All the reactions are vitally interrelated, though any single reaction, or set of reactions, may be extremely important as indicating a tendency. The experiments are designed to obtain the largest yield of hydrocarbons, and to eliminate, as much as possible, CO<sub>2</sub>, water vapor, deposited carbon, and tar vapors. The goal is to increase the yield of illuminants.

#### MANUFACTURE OF UNCARBURETED BLUE WATER GAS

The manufacture of blue water gas may be represented by the equations:



The two equations are combined by subtracting (2) from (1) in order to eliminate the carbon:



Equilibrium is established between these gases when

$$K = \frac{p_{CO} p_{H_2O}}{p_{CO_2} p_{H_2}}$$

where  $K$  represents the usual equilibrium constant; *i. e.*, the value of the product of the partial pressures of CO and H<sub>2</sub>O divided by the product of the partial pressures of CO<sub>2</sub> and H<sub>2</sub>.  $K$  has a definite value for each definite absolute temperature.

For a practical illustration of the significance of equilibrium conditions in the manufacture of blue water gas, assume a theoretically ideal mixture consisting of 50 per cent H<sub>2</sub> and 50 per cent CO. Pass the two gases through a chamber heated to 715° C. (1319° F.) until they reach the equilibrium of this temperature; what are the resulting gases?  $K$  at this temperature is in the neighborhood of 0.30.



Under equilibrium conditions at atmospheric pressure

$$\begin{array}{l} \text{Let } X = \text{volume } CO_2 \\ \text{then } X = \text{volume } H_2O \\ 0.5 - X = \text{volume } H_2 \\ 0.5 - 3X = \text{volume } CO \\ \hline \therefore 1 - 2X = \text{total final volume} \end{array}$$

(3)

$$\left(\frac{X}{1-2X}\right)_1 = \text{partial pressure CO}_2 \quad \left(\frac{0.5-X}{1-2X}\right)_1 = \text{partial pressure H}_2$$

$$\left(\frac{X}{1-2X}\right)_1 = \text{partial pressure H}_2\text{O} \quad \left(\frac{0.5-3X}{1-2X}\right)_1 = \text{partial pressure CO}$$

$$K = 0.30 = \frac{p_{\text{CO}_2} p_{\text{H}_2\text{O}}}{p_{\text{CO}}^2 p_{\text{H}_2}} = \frac{\left(\frac{X}{1-2X}\right)\left(\frac{X}{1-2X}\right)}{\left(\frac{0.5-3X}{1-2X}\right)^2 \left(\frac{0.5-X}{1-2X}\right)} = \frac{2X^2(1-2X)}{(0.5-3X)^3}$$

Solving,  $X = 0.069 = 6.9$  per cent

$2X =$  gas lost in reaction  $= 13.8$  per cent

$$\left(\frac{X}{1-2X}\right)_1 = \frac{0.069}{0.862} = 8 \text{ per cent CO}_2$$

$$\left(\frac{X}{1-2X}\right)_1 = \frac{0.069}{0.862} = 8 \text{ per cent H}_2\text{O}$$

$$\left(\frac{0.5-3X}{1-2X}\right)_1 = \frac{0.293}{0.862} = 34 \text{ per cent CO}$$

$$\left(\frac{0.5-X}{1-2X}\right)_1 = \frac{0.431}{0.862} = 50 \text{ per cent H}_2$$

Applying the above calculations to a mixture of 1,000 cu. ft. each of carbon monoxide and hydrogen, and assuming that no hydrocarbons are formed, there would be a net loss of 13.8 per cent (276 cu. ft.) due to the reaction, leaving 1,724 cu. ft. of mixed gases, as follows:

$$1724 \times 0.08 = 138 \text{ cu. ft. CO}_2$$

$$1724 \times 0.08 = 138 \text{ cu. ft. H}_2\text{O}$$

$$1724 \times 0.34 = 586 \text{ cu. ft. CO}$$

$$1724 \times 0.50 = 862 \text{ cu. ft. H}_2$$

The water in condensing leaves a net volume of permanent gases equal to  $1724 - 138 = 1586$  cu. ft. This permanent gas is composed of 8.7 per cent  $\text{CO}_2$ , 37 per cent CO and 54.3 per cent  $\text{H}_2$ . There would be also a deposit of 9.25 pounds of carbon. In other words, there are only  $1586 - 138 = 1448$  cu. ft. of the original  $\text{H}_2$  and CO remaining.

Different temperature conditions would obviously give different results. A numerical problem of this nature shows how vitally equilibria conditions influence gas manufacture, and indicates the commercial importance of an understanding of such equilibria conditions. Just as the equilibria conditions here are of importance, it can be shown that they are no less important when the reactions are between CO,  $\text{H}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  coming from the blue water gas on one hand, and  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ , and tar vapors, etc., coming from the gas oil on the other hand.

The blue water gas reactions and equilibria have been investigated<sup>1</sup> and are well understood, so that we know

<sup>1</sup> Bureau of Mines, *Bulletin* 7, 1911; Jüptner, *Chem. Ztg.*, 1904, p. 902; K. Neuman, *Stahl und Eisen*, 1913, p. 394; O. Hahn, *Z. physik. Chem.*, 44, 513-547; C. LeChatelier and K. Neuman, *Stahl und Eisen*, 1913, p. 1485; E. A. Allcut, *Engineering*, 1911, p. 601.

what conditions are favorable and what are unfavorable; *i. e.*, degree of temperature, quantity of steam, depth of fuel bed, etc.

#### MANUFACTURE OF STRAIGHT OIL GAS

The manufacture of an oil gas as carried out by the Pintsch or Blau Gas companies is an old process, but is not as well understood as the blue water gas equilibrium. Few experimental equilibria of the various components of oil gas have been worked out, as have been the  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{O}$  and  $\text{H}_2$  relations of blue water gas. Here, one at once faces the fact that in the oil cracking process, instead of the four gases of the blue water gas reaction, there are all the members of the methane, ethylene and acetylene series, as well as those hydrocarbons which constitute the tars produced in pyrogenetic decomposition.

Synthetic methane has been made from carbon and hydrogen,<sup>1</sup> where equilibrium exists when

$$K = \frac{p_{\text{CH}_4}}{p_{\text{H}_2}^2}$$

Similarly, we may conclude that equilibrium exists between  $\text{H}_2$  and all of the other hydrocarbons.

By combining the ethane and ethylene equations through the elimination of carbon, one gets  $\text{C}_2\text{H}_6 = \text{C}_2\text{H}_4 + \text{H}_2$ , where equilibrium conditions prevail when

$$K = \frac{p_{\text{C}_2\text{H}_4} p_{\text{H}_2}}{p_{\text{C}_2\text{H}_6}}$$

For a practical illustration of the meaning of this expression, take the effect of heat on a known volume of  $\text{C}_2\text{H}_6$ . Eliminating other reactions than the one between ethane and ethylene, consider the resultant relative quantities of  $\text{H}_2$ ,  $\text{C}_2\text{H}_6$  and  $\text{C}_2\text{H}_4$  at a temperature of  $900^\circ \text{C}$ ., taking the value of  $K$  equal to 1.28.



Let  $X$  = volume  $\text{H}_2$

then  $X$  = volume  $\text{C}_2\text{H}_4$

$1 - X$  = volume  $\text{C}_2\text{H}_6$

$\therefore 1 + X$  = total final volume

$$\frac{X}{1 + X} = \text{partial pressure } \text{C}_2\text{H}_4$$

$$\frac{X}{1 + X} = \text{partial pressure } \text{H}_2$$

$$\frac{1 - X}{1 + X} = \text{partial pressure } \text{C}_2\text{H}_6$$

<sup>1</sup> Pring and Fairlie, Report of Eighth International Congress; Ipatiew, *Jour. prakt. Chem.*, **1913**, pp. 479-487; Pring and Fairlie, *Jour. Chem. Soc.*, **1906** p. 1591; *Ibid.*, **1911**, p. 1796; *Ibid.*, **1912**, pp. 91-103; Bone and Coward, *J. Chem. Soc.*, **1908**, p. 1975. *Proc. Chem. Soc.*, **1910**, p. 146.

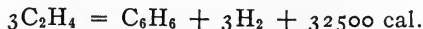
$$K = 1.28 = \frac{\left(\frac{X}{1+X}\right)\left(\frac{X}{1+X}\right)}{\left(\frac{1-X}{1+X}\right)} = \frac{X^2}{1-X^2}$$

Solving,  $X = 0.75$

$$\frac{0.75}{1.75} = 42.85 \text{ per cent } C_2H_4, \quad \frac{0.75}{1.75} = 42.85 \text{ per cent } H_2$$

$$\text{and } \frac{0.25}{1.75} = 14.30 \text{ per cent } C_2H_6.$$

In dealing with any of these equilibria expressions, one must be careful to remember that no single equilibrium can be considered by itself. In the ethane-hydrogen-ethylene equilibrium at  $900^\circ C.$ , for instance, there is a pronounced tendency for the ethane to go to ethylene; and in practice one should expect, therefore, a high ethylene yield, but by referring to the ethylene-benzene system one finds that at  $900^\circ C.$  there is an even greater tendency for the ethylene to be removed by polymerization to benzene. Assuming a volume of  $C_2H_4$  and bringing it to equilibrium at  $900^\circ C.$ , observe the resultant relative quantities of  $C_2H_4$  and  $C_6H_6$ :



Under equilibrium conditions at atmospheric pressure

$$\begin{aligned} X &= \text{volume } C_6H_6 \\ 3X &= \text{volume } H_2 \\ 1 - 3X &= \text{volume } C_2H_4 \\ \hline \therefore 1 + X &= \text{total final volume} \end{aligned}$$

$$\begin{aligned} \frac{X}{1+X} &= \text{partial pressure of } C_6H_6 & \frac{1-3X}{1+X} &= \text{partial pressure } C_2H_4 \\ \frac{3X}{1+X} &= \text{partial pressure of } H_2 \end{aligned}$$

$$K = \frac{p_{C_6H_6} p_{H_2}^3}{p_{C_2H_4}^3} = 68 \times 10^9 = \frac{\left(\frac{X}{1+X}\right)\left(\frac{3X}{1+X}\right)^3}{\left(\frac{1-3X}{1+X}\right)^3} = \frac{27X^4}{(1+X)(1-3X)^3}$$

Solving,  $X = 0.33$

$$\frac{0.33}{1.33} = 24.8 \text{ per cent } C_6H_6, \quad \frac{0.99}{1.33} = 74.4 \text{ per cent } H_2$$

$$\text{and } \frac{0.01}{1.33} = 0.8 \text{ per cent } C_2H_4.$$

Thus an experimental test, with the yield calculated according to the first equilibrium without a consideration of the second, would result in disappointment. Further, not only must the ethane-hydrogen-ethylene-benzene equilibrium be satisfied, but each of these constituents, in turn, must be in equilibrium with methane, acetylene, propane, naphthalene, etc. In short, there will be a grand symphony of equilibria between all components of the system.



Equilibria expressions, such as the ones just given, are therefore of value when properly understood and used as a basis for experimental proof. First of all, the time element is very important to insure final equilibrium; and secondly, their mathematical derivations involve integration factors based on physical properties such as specific heat, vapor pressure, heat of reaction, etc., under conditions which have not been experimentally determined. Experimental demonstration based upon a few selected and isolated equilibria is almost certain to result in failure, due to overlooking other equally important equilibria which might modify or even reverse the direction of final reactions.

Sufficient experimental and commercial work has been done on the making of all oil gas under atmospheric conditions<sup>1</sup> to give empirical data indicating that as the temperature goes above 800° C. the yield of hydrocarbons rapidly decreases; on the other hand, the hydrogen and carbon rapidly increase.

#### CARBURETED WATER GAS PROCESS

In the carbureted water gas practice, as carried out to-day, there is a combination of the blue water gas and the oil gas process. Much is known about the blue gas; it is also known that this blue gas is carbureted by spraying in and cracking oil which furnishes the hydrocarbons and illuminants. There is little scientific information, however, regarding the interactions and equilibria which are reached when the two processes are combined. The formation of hydrocarbons and water from CO and H<sub>2</sub> or from CO<sub>2</sub> and H<sub>2</sub> is not theoretical speculation;<sup>2</sup> likewise the destruction of hydrocarbons with water to form CO and H<sub>2</sub> or CO<sub>2</sub> and H<sub>2</sub>, as carried out in the all oil water gas process, is not theoretical speculation. Whichever course prevails depends entirely upon conditions. Consequently, one is justified in concluding that the present composi-

<sup>1</sup> Haber and co-workers, *Jour. Gasb.*, **1896**, pp. 377, 395, 435, 452; Hempel, Dissertation, *Jour. Gasb.*, **1910**, pp. 53, 77, 101, 137, 155.

<sup>2</sup> Mayer, Henseling and Altmayer, *J. f. Gasb.*, **1909**, pp. 166, 194, 238, 326; P. Sabatier, *Chem. Ztg.*, **1913**, p. 148; P. Sabatier, Fr. Patent 355,325, **1905**; *Ibid.*, 355,900, **1905**; *Ibid.*, 361,616; *Ibid.*, 400,656; Eng. Patent 14,971, **1908**; *Ibid.*, 27,045; L. Vignon, Fr. Patent 416,699, **1909**; *Compt. rend.*, **1913**, pp. 131-134; Gautier, *Ibid.*, **1910**, p. 1565; Elsworth and Williamson, Eng. Patent 12,461, **1902**; Bedford and Williams, Eng. Patents 17,017, 22,219, **1909**; H. J. Coleman, *Jour. Gas Lighting*, **1908**, p. 683; E. Erdman, *Jour. f. Gasb.*, **1911**, pp. 737-743; E. Orlow, *Jour. Russ. Phys. Chem.*, **1908**, p. 1588; P. Jockum, *Jour. f. Gasb.*, **1914**, pp. 73, 103, 124, 149; T. Holgate, *Gas World*, **1914**, p. 90; German Patents 183,412, 190,201, 191,026, 237,499, 226,942, 177,703, 174,343 and 250,909.

tion of carbureted water gas is not the result of additive processes. Instead there is a mixture of blue water gas and cracked oil gas passing through the carbureter and superheater which constitute a single unbalanced system of gases; naturally, there is a tendency to establish equilibrium between the constituents just as surely as there is a tendency to establish an equilibrium between the constituents of either the blue gas or the all oil gas when made individually. This equilibrium at the usual temperature of the superheater has fortunately favored the formation, or at least the preservation, of hydrocarbons. This fact, however, does not prove that the process is working under conditions of, or approaching maximum efficiency. Nor does it prove that the present method of carbureting water gas is the most economical from the side of the quantity of gas oil consumed.

Many questions arise at this point. It might be possible to alter conditions in such a way as to solve, or assist in solving, the naphthalene and carbon problems of the gas manufacturer. It might still further be worth while to question the soundness of the natural tendency of the American manufacturer to combine processes; it may appear that the attempt to do everything in a single vat rather than carry it out in stages is not the most economical method in the end.

#### EQUATIONS AND THEORETICAL EQUILIBRIA INVOLVED

The formation of methane from carbon monoxide and hydrogen, or from carbon dioxide and hydrogen is an exothermic reaction and consequently is favored by low temperatures, although at these low temperatures a greater amount of time is required for complete reaction. The rate of the reaction may be greatly stimulated by catalytic agents such as nickel and cobalt. In view of the fact that there is a decrease in volume, one should expect pressure to be favorable to hydrocarbon formation. Equilibrium exists between CO and H<sub>2</sub> or CO<sub>2</sub> and H<sub>2</sub> on the one side and CH<sub>4</sub> and H<sub>2</sub>O on the other.



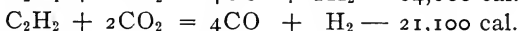
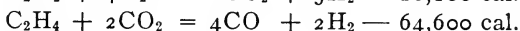
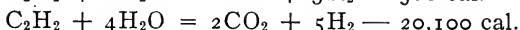
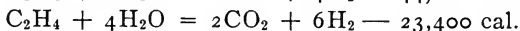
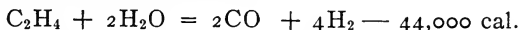
with equilibrium established when

$$K = \frac{p_{\text{CO}} p_{\text{H}_2}^3}{p_{\text{CH}_4} p_{\text{H}_2\text{O}}} \text{ and } K' = \frac{p_{\text{CO}_2} p_{\text{H}_2}^4}{p_{\text{CH}_4} p_{\text{H}_2\text{O}}^2}$$

Combining the two equations with elimination of  $\text{H}_2\text{O}$ ,  
 $2\text{CO} + 2\text{H}_2 = \text{CH}_4 + \text{CO}_2 + 58,500 \text{ cal.}$

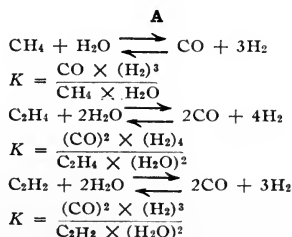
$$K'' = \frac{p_{\text{CO}}^2 p_{\text{H}_2}^2}{p_{\text{CH}_4} p_{\text{CO}_2}}$$

In like manner the equilibria between  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ , on the one side, and  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$  and  $\text{H}_2\text{O}$  on the other, are considered below:

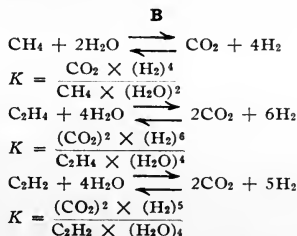


With these there is sufficient data to determine in a *qualitative* way the concentration conditions favorable to the methane, ethylene and acetylene desired in the resultant gas.

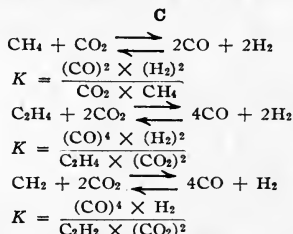
TABLE I—QUALITATIVE STUDY OF EQUILIBRIA



FAVORABLE WHEN CO AND H<sub>2</sub> ARE LARGE AND H<sub>2</sub>O IS SMALL



FAVORABLE WHEN CO<sub>2</sub> AND H<sub>2</sub> ARE LARGE AND H<sub>2</sub>O IS SMALL



FAVORABLE WHEN CO AND H<sub>2</sub> ARE LARGE AND CO<sub>2</sub> IS SMALL

The original complex state of affairs is thus partially simplified. One sees that conditions favorable to the formation of hydrocarbons, or at least unfavorable to the decomposition of hydrocarbons, exist when in

- A, B and C there is an excess of H<sub>2</sub>,
- A and C, there is an excess of CO,
- A and B, there is a minimum of water vapor,
- B, there is an excess of CO<sub>2</sub>,
- C, there is a minimum of CO<sub>2</sub>.

An excess of hydrogen is favorable under any conditions; a minimum of water vapor is favorable under any conditions; an excess of CO appears to be favorable under any conditions; in the case of CO<sub>2</sub>, however, one condition indicates an excess as favorable whereas another indicates an excess as unfavorable.

#### INFLUENCE OF TEMPERATURE ON EQUILIBRIUM CONDITIONS

While these qualitative relations are extremely valuable in the consideration of favorable conditions, they do not give a sufficiently concrete idea of the conditions which prevail at different temperatures. Each equilibrium constant has a definite value for a definite temperature. If this value of  $K$  is considered for 500° C. the reaction may proceed in one direction; whereas on considering the value of  $K'$  for the same reacting agents at 900° C., the reaction may proceed in the opposite direction. Qualitative expressions point merely in general directions and give no ideas as to maxima or minima in the curve of favorable conditions. As an example, consider the equilibrium

$$K = \frac{p_{\text{CO}} p_{\text{H}_2}^3}{p_{\text{CH}_4} p_{\text{H}_2\text{O}}}$$

where  $K$  equals approximately 0.001 for 500° C.; at 900° C. the equilibrium constant for the same relationship has the approximate value  $K'$  346, or 346,000 times as great. This illustrates the importance of getting numerical values for the constants expressing equilibrium conditions for the various gases, even though they be approximate.

From a consideration of the CO, H<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>O equilibrium, it appears that excesses of H<sub>2</sub> and CO would be favorable to the formation or preservation of hydrocarbons both at 500° C. and 900° C. It will further appear, however, that at 900° C. the excess of H<sub>2</sub> and CO to stimulate the reaction towards hydrocarbons will have to be enormous, while at 500° C.

it need be only moderate. This can be seen from a mathematical study of the equilibrium, purely aside from the chemistry involved. At 500° C. the denominator is obviously the predominant factor. At 900° C. the numerator has become the predominant factor. In fact the situation is so different that it would take many times as much H<sub>2</sub> and CO at 900° C. as it would at 500° C. Taking the two equilibrium constants and calculating theoretical mixtures one obtains the following contrasting results:



$$\begin{aligned} X &= \text{final volume CO} & \frac{1}{2}(1-4X) &= \text{final volume CH}_4 \\ 3X &= \text{final volume H}_2 & \frac{1}{2}(1-4X) &= \text{final volume H}_2\text{O} \end{aligned}$$

$$K = \frac{p_{\text{CO}} p_{\text{H}_2}^3}{p_{\text{CH}_4} p_{\text{H}_2\text{O}}} = \frac{108 X^4}{16 X^2 - 8 X + 1}$$

Temp. ° C.	Percentages				
	K <sub>calc.</sub>	CO	H <sub>2</sub>	CH <sub>4</sub>	H <sub>2</sub> O
500.....	0.001	5	15	40	40
900.....	346	24.3	72.9	1.4	1.4

The water vapor of these equilibria is usually not considered in practice because it never appears in either the gas of the tank holder or in the gas sampling tube and resulting analysis. This does not prove its absence in the machine. Also equal pressures of hydrogen and CO in a given system are not necessarily of the same influence. This is shown in equilibrium conditions for the CH<sub>4</sub>, H<sub>2</sub>O, CO and H<sub>2</sub> system, where for instance the concentration of H<sub>2</sub> is raised to the third power, while that of CO is of the first power. In manufacturing practice the total pressure is approximately one atmosphere, the partial pressures are expressed by such decimals as 0.5. The third power of 0.5, or 0.125, is much less than the first power, 0.5.

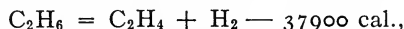
Examples to show the effect of temperature on the state of equilibrium can be found in straight hydrocarbon reactions. The equilibrium between acetylene and benzene shows the following results:

$$K = \frac{\text{C}_6\text{H}_6}{(\text{C}_2\text{H}_2)^3} \quad \begin{array}{ccc} 600^\circ \text{C} & 900^\circ \text{C} & 2000^\circ \text{C} \\ 9 \times 10^{23} & 1.2 \times 10^{13} & 6 \times 10^{-4} \end{array}$$

It appears that the value of  $K'$  at 2000° C. is 1.5 × 10<sup>27</sup> times as great as the value of  $K$  at 600° C. This leads to the expectation that while at 600° C. all the acetylene tends to polymerize to benzene,

at 2000° C., under proper conditions of pressure, benzene tends to depolymerize to acetylene.

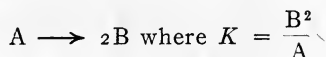
In the equilibrium existing between ethane and ethylene,



the value of  $K'$  at 900° is approximately 1.28, whereas the value of  $K$  at 150° is approximately 0.0000000000000007. Ethane at 900° C. has a pronounced tendency to go to ethylene; the tendency for the ethylene to combine with hydrogen at 150° C. to form ethane is even more pronounced. The relatively small amount of ethane in oil gas made at 900° C. would seem to verify the first equilibrium constant; the large yield of ethane through the reduction of ethylene with hydrogen in the presence of palladium at 150° C. indicates the second constant.

#### EFFECT OF PRESSURE ON GASEOUS REACTIONS

In passing from ethane to acetylene,  $\text{C}_2\text{H}_6 = \text{C}_2\text{H}_2 + 2\text{H}_2$ , there is an increase in volume; on the other hand, when acetylene polymerizes to benzene,  $3\text{C}_2\text{H}_2 \longrightarrow \text{C}_6\text{H}_6$ , there is a decrease in volume. According to the principle of LeChatelier one would not expect the same pressure conditions to be favorable to both. Again, the information is qualitative and gives no concrete idea of the relative influence of one-third atmosphere when added to one atmosphere pressure absolute as compared to adding the same one-third atmosphere to ten atmospheres pressure absolute. As a type reaction consider



For numerical illustration, assume the value of  $K$  to be equal to 1 (any other value serving equally well). From this, one finds for partial pressures, when  $\text{A} = 100$ ,  $\text{B} = 10$  or when  $\text{A} = 0.01$ ,  $\text{B} = 0.1$ . In the first case the partial pressure of A is ten times as great as that of B; in the second case the partial pressure of A is only one-tenth as large as the partial pressure of B. In other words, by simply changing the total pressure on the system and keeping all other conditions constant, the ratio of A to B for the pressures shown has been divided by 100. By taking the first differential of the relationship, and equating it to 0,

$$K = \frac{\text{B}^2}{\text{A}} \quad \text{A} = \frac{\text{B}^2}{K} \quad \frac{d\text{A}}{d\text{B}} = \frac{2\text{B}}{K} = 0 \quad \therefore \text{B} = 0$$

one sees there is a maximum or minimum in the ratio of A to B as zero pressure is approached. By taking the second differential

$$\frac{d^2A}{dB^2} = + \frac{2}{K}$$

one finds the sign to be positive, indicating that the partial pressure of A as compared with the partial pressure of B approaches a minimum as the pressure approaches the absolute zero; or conversely there would be a maximum relative yield of B the closer one approached zero pressure absolute. The rate of change can best be seen by determining points for the parabola,  $B^2 = KA$ , and plotting the resulting curve.<sup>1</sup>

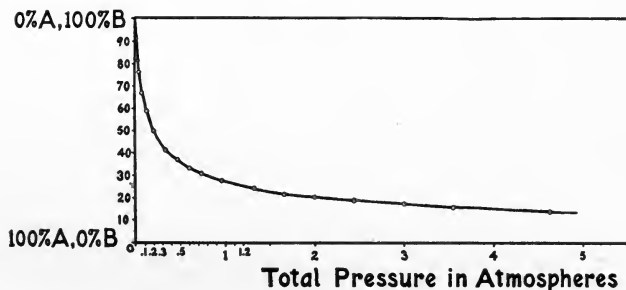
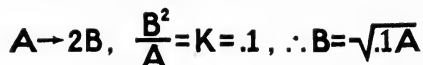


FIG. I—REACTION ISOTHERM

The general relationship of B to A changes only in degree the greater the change in the number of volumes, as can be seen by considering the curve for

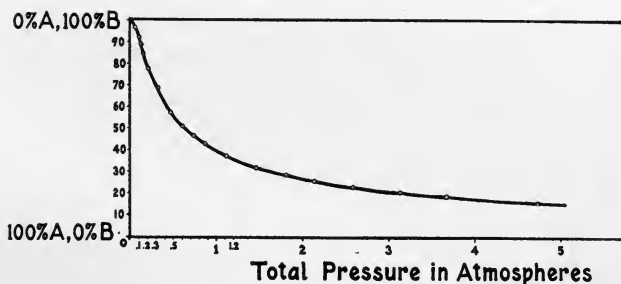
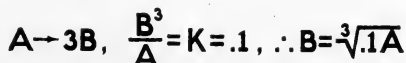


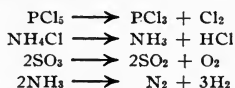
FIG. II—REACTION ISOTHERM

<sup>1</sup> Since most of the values of  $K$  encountered in the practical study of the problem were represented by decimals, Curves I and II were plotted on the basis of  $K = 0.1$ .

From the curves shown, one can readily see that the effect of reducing pressure from one atmosphere to two-thirds of an atmosphere gives an advantage which is of little practical consequence when compared with the advantage gained by the same reductions when nearer the absolute zero of pressure. One-thirtieth of an atmosphere added to one-thirtieth atmosphere pressure doubles the total pressure on a system just as effectually as an increase from 100 to 200 atmospheres.

#### EFFECT OF CONCENTRATION IN GASEOUS REACTIONS

The addition of an end product in any decomposition or dissociation process, such as



checks the decomposition or dissociation. In other words, less  $\text{PCl}_5$  will dissociate in an atmosphere of chlorine than in an atmosphere of nitrogen or air. Ammonium chloride when heated in an atmosphere of ammonia will not dissociate to the same extent as in a vacuum or in an atmosphere containing neither ammonia nor hydrochloric acid gas. Likewise it would be expected that ethylene would not decompose to the same degree when subjected to a high temperature in the presence of hydrogen as when subjected to the same temperature in an atmosphere of nitrogen. Further, if the ethylene were subjected to the same high temperature in the presence of both hydrogen and methane, these two constituents in the ethylene-methane-hydrogen equilibrium could be in excess; as a result, less of the ethylene should be decomposed in the formation of methane and hydrogen. In the same way if petroleum is cracked in an atmosphere containing all the hydrocarbon gases with the exception of ethylene, one would expect all the fixed gas coming from the petroleum to be ethylene, at least until the ethylene content of the system is sufficient to conform to the equilibrium conditions. The consideration of these principles seems to question the necessity of using valuable gas oil in continually generating new end products, such as tar and hydrogen; if they could be artificially supplied the equilibrium conditions would be satisfied without producing new decomposition and polymerization end products.

#### COMBINED INFLUENCE OF PRESSURE AND CONCENTRATION ON GASEOUS REACTIONS

Theoretical consideration of the effect of pressure



on gaseous reactions indicates that an increased yield of gaseous hydrocarbons will be obtained as the total pressure on the system approaches zero; also an increased yield of illuminants will be obtained by cracking the oil in an atmosphere of end products such as hydrogen and methane. On combination the logical conclusion is that one should obtain the maximum yield of illuminants by cracking the petroleum at low pressures and in an atmosphere of end products. Upon first consideration one might reasonably question the idea of adding hydrogen or methane to a vacuum, but this investigation deals with relative partial pressures, regardless of whether the total pressure equals fifty atmospheres or one-fiftieth of one atmosphere absolute.

#### INFLUENCE OF CATALYSTS ON GASEOUS REACTIONS

Catalytic agents such as platinum, palladium, cobalt and nickel do not, in any way, influence final conditions of equilibrium; they merely hasten the rate at which the system reaches its final equilibrium. Whereas ethylene and hydrogen do not combine to an appreciable degree when heated to  $100^{\circ}$  C. in the absence of a catalyzer, the same mixture passed over colloidal palladium heated to  $100^{\circ}$  C. unites to form a considerable percentage of ethane. Likewise CO and  $H_2$  or  $CO_2$  and  $H_2$  can be in intimate contact at  $200^{\circ}$  to  $300^{\circ}$  without appreciable reaction in the formation of methane, but when the same proportions are brought together in the presence of a catalytic agent such as nickel or cobalt there is a very large yield of methane and water.<sup>1</sup> Vignon<sup>2</sup> finds that lime has much the same effect on the combination of CO and  $H_2$ .

#### THE VAN'T HOFF DIFFERENTIAL EQUATION SHOWING THE RELATION OF $K$ TO $K'$

To all students of physical chemistry the proposition of Berthelot and Thomson that "every chemical change gives rise to the production of those substances which occasion the greatest development of heat" is familiar. Were this true, it would be easy to predict which of two given reactions would take place at a given temperature. Chemists today recognize

<sup>1</sup> Mayer, Henseling and Altmayer, *Jour. f. Gasb.*, **1909**, pp. 166, 194; Jockum, *Ibid.*, **1914**, pp. 73, 103, 124, 149; Orlow, *Jour. Russ. Phys. Chem.*, **1908**, p. 1588.

<sup>2</sup> Vignon, L., *Compt. rend.*, **1913**, pp. 131-134.

the fallacy of the statement because in all chemical reactions one deals with the additional so-called "latent energy." Berthelot's principle disregards this molecular energy, and assumes the free energy, termed maximum work, to be equal to the total energy change. Nernst maintains that this is true only at the absolute zero, *i. e.*, the entropy of liquids and solids at absolute zero temperature equals zero.

The van't Hoff equation showing the relation between  $K$  and  $K'$  is expressed by

$$\frac{d}{dT} (\log_e K_p) = \frac{-q_p}{RT^2} \quad \text{or} \quad d (\log_e K_p) = \frac{-q_p}{R} \frac{dT}{T^2}$$

Upon integration this becomes

$$\log_e K_p = \frac{q_p}{RT} + \text{constant}$$

Were it a simple matter to determine the value of this constant of integration, as well as the value of  $q$  at the different temperatures (in other words integrate the expression to absolute units) this would constitute a mathematical expression for what many consider a third law of thermodynamics. As yet there is no such accepted integration, and the best solution is to use approximate expressions, remembering at all times that the expressions are approximate, and making intelligent use of them as such. It is possible to avoid the constant of integration, however, by integrating between limits  $p'$  and  $p$  to

$$\log_e K_{p'} - \log_e K_p = \frac{q_p}{R} \left( \frac{1}{T^1} - \frac{1}{T} \right)$$

This integrated expression is extremely important in determining the value of  $K'$  for any desired temperature after the value of  $K$  for any other temperature has been experimentally determined. It is also valuable in showing relationships between  $K$  and  $K'$  for two different temperatures, where neither has been determined, but in this case it expresses relationships and not direct values. For instance, assume that one wished to find the relationship between  $K$  and  $K'$  for the reaction



at the temperatures 600° and 900° C.

$$\log_e K_{p'} - \log_e K_p = \frac{-58100}{2} \left( \frac{1}{1173} - \frac{1}{873} \right) = 8.49$$

$$\log_e \frac{K_{p'}}{K_p} = 8.49 \quad \text{or,} \quad \log_{10} \frac{K_{p'}}{K_p} = 3.69$$

whence 
$$K_{800} = \frac{K_{900}}{4900}$$

THE NERNST APPROXIMATION FORMULA FOR  $K$

Even though correct,  $K$  is a value based on the assumption that sufficient time elapses to allow the system to reach complete equilibrium. When dealing with hydrocarbons at different temperatures, this must not be overlooked. In fact the time element is of such primary moment that numerically correct values for  $K$  would be of little more practical use in gas manufacture than approximate values. In the case of reacting gases one does not have the speed conditions that ordinarily exist in solutions. On the other hand, gases brought together at sufficiently high temperatures do reach equilibrium practically instantly. It is important to bring out these limitations despite the value of approximate quantitative expressions such as the Nernst formula; the latter is of immense value in predicting the tendency of a reaction. In this paper Nernst's formula is merely used; its derivation with comments can be found in the seventh German edition of Nernst's "Theoretical Chemistry," Jellinek's "Physikalische Chemie der Gasreaktionen," or Sackur's "Thermochemie und Thermodynamik."

$$\log K = \frac{q}{4.571T} + \Sigma v \cdot 1.75 \log T + \Sigma vC$$

where  $q$  is the heat developed at ordinary temperatures and under constant pressure, as taken from thermochemical tables;  $\Sigma v$  represents the volume changes, and  $\Sigma vC$  represents a summation of constants. These constants are given as follows:

H <sub>2</sub>	1.6	C <sub>2</sub> H <sub>6</sub>	2.6	C <sub>2</sub> H <sub>2</sub>	3.2	CO	3.5	H <sub>2</sub> O	3.6
CH <sub>4</sub>	2.5	C <sub>2</sub> H <sub>4</sub>	2.8	C <sub>2</sub> H <sub>6</sub>	3.0	CO <sub>2</sub>	3.2	O <sub>2</sub>	2.8

To use Nernst's words, the equation gives a "fairly accurate" idea of the state of equilibrium in a system.

The approximation is applied in this fashion:



$$\log K_{800} = \frac{+18900}{4.571 \times 873} - 1.75 \log 873 - 0.7 = -1.11 = \bar{2}.89(a)$$

$$\log K_{750} = \frac{+18900}{4.571 \times 1023} - 1.75 \log 1023 - 0.7 = -1.93 = \bar{2}.07$$

$$\log K_{900} = \frac{+18900}{4.571 \times 1173} - 1.75 \log 1173 - 0.7 = -2.55 = \bar{3}.45$$

whence,

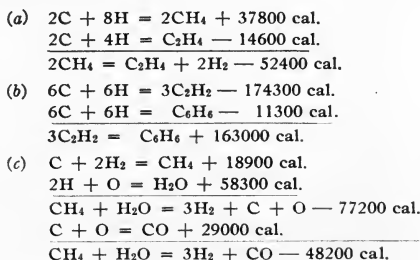
$$K_{800} = 0.077 \quad K_{750} = 0.012 \quad K_{900} = 0.003$$

(a) Negative logarithms must be converted into logarithms with positive mantissa.

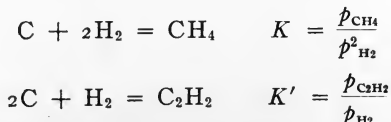
In similar manner, the values of  $K$ ,  $K'$ , and  $K''$  for Equations 1, 2, 3, 4, 5, 6, 7, 13, 16, 17, 18, and 22 in Table II have been calculated. In those reactions involving CO and CO<sub>2</sub>, as 19, 23, and 26, use has been made of the approximation formulas for the same as worked out by Mayer and co-workers,<sup>1</sup> but substituting the values of  $q$  shown in the table.

#### CALCULATION OF HEATS OF REACTIONS FOR DIFFERENT EQUILIBRIA

The heat absorbed or emitted in a given reaction was determined by means of the ordinary thermochemical methods of addition and subtraction, as in the following typical examples:



It is likewise possible to combine the values of  $K$  for one reaction with  $K'$  for a second reaction in order to determine  $K''$  for the resultant reaction.



Dividing the square of the methane equilibrium by the acetylene equilibrium, one gets

$$K'' = \frac{(K')}{(K)^2} = \frac{p_{C_2H_2} p_{H_2}^4}{p_{H_2}^2 p_{CH_4}^2} = \frac{p_{C_2H_2} p_{H_2}^3}{p_{CH_4}^2}$$

This operation can be represented by the equation



In this work the values of  $K$  and  $K'$  have been combined in the manner just shown in order to determine values for equations 8, 9, 10, 11, 12, 14 and 15. The Nernst approximation formula could be applied directly to each of these equations with the same results. All reactions indicated in Table II may go in either direction. Attention is called again to the fact that the reactions given must be used with a consideration of all factors involved; no equation by itself repre-

<sup>1</sup> Mayer, Henseling and Altmayer, *Jour. Gasb.*, 1909, pp. 166, 194, 238.

sents a complete system. All the gases mentioned, together with many others, are tending to reach equilibrium with one another. Tar compounds were not listed. Benzene,  $C_6H_6$ , has been used as typical of all tar formations. In technical practice one gets benzene and other tar compounds from methane hydrocarbons; from experimental evidence, it is known that from ethylene<sup>1</sup> or acetylene<sup>2</sup> the same results are reached. Throughout the literature one finds questions as to whether methane goes to acetylene, or acetylene to methane, ethane to ethylene, ethylene to ethane, etc. Considered in the light of this study it appears that regardless of which hydrocarbon is used initially there is a pronounced tendency for the system to reach a common equilibrium dependent upon the existing temperature. With hydrocarbons the result seems to depend more upon conditions of temperature, pressure and concentration than upon the initial hydrocarbons. In other words, with proper conditions of temperature, pressure and concentration, and with sufficient time for complete reaction, the final equilibrium will be that of the mentioned hydrocarbons and their reaction products, regardless of whether decane, hexane, ethane, methane, ethylene or acetylene,<sup>3</sup> singly or in mixtures, are used in the beginning.

Table II furnishes the basis for the experimental work of this research. Its interpretation serves as a guide in determining the direction of experiments. Taking Equation 9 as typical, where  $K_{600} = 0.0000001$  and  $K_{900} = 0.0004$ , it seems advisable to exceed  $900^\circ$  C. in temperature. However, referring to  $K_{600} = 0.077$  and  $K_{900} = 0.003$  for Equation 3, it is evident that the rate at which methane would decompose to carbon and hydrogen, in accordance with Equation 3, easily might be sufficient to offset all  $C_2H_4$  formation, in accordance with Equation 9.

Considering Equations 16 and 19, two of the most vital in present carbureted water gas manufacture, one finds

		$K_{600}$	$K_{750}$	$K_{900}$
16	$C + H_2O \rightleftharpoons CO + H_2 \dots$	0.2	3.1	25.0
19	$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \dots$	0.06	8.7	346.0

<sup>1</sup> Ipatiew, *Ber.*, **1911**, p. 2978; Ipatiew and Rontala, *Ibid.*, **1913**, p. 1748.

<sup>2</sup> R. Meyer, *Ibid.*, **1912**, p. 1609; Meyer and Tanzen, *Ibid.*, **1913**, p. 3183.

<sup>3</sup> W. A. Bone, *Jour. f. Gasb.*, **1908**, p. 803; D. T. Day, *Am. Chem. Jour.*, **1886**, p. 153; V. Lewes, *Proc. Roy. Soc.*, **1894**, p. 90; Worstall and Burwell, *Am. Chem. Jour.*, **1897**, p. 815; Bone and Coward, *Jour. Chem. Soc.*, **1908**, p. 1197; Sabatier and Senderens, *Compt. rend.*, **130**, 1559; C. Paal, *Chem. Zig.*, **1912**, p. 60; Ipatiew, *Ber.*, **44**, 2987.

TABLE II—QUANTITATIVE STUDY OF EQUILIBRIA

NO.	REACTIONS	HEATS OF REACTION	VOLUME CHANGES	FORMULAS REFER TO PARTIAL PRESSURES	APPROXIMATE		
					K <sub>600</sub>	K <sub>750</sub>	K <sub>900</sub>
1.	$C + O_2 \rightleftharpoons CO_2$	+97650	1 to 1	$K = \frac{CO_2}{O_2}$	$6.9 \times 10^{24}$	$1.9 \times 10^{21}$	$4 \times 10^{13}$
2.	$CO_2 + C \rightleftharpoons 2CO$	-39650	1 to 2	$K = \frac{(CO)_2}{CO_2}$	0.1	3.9	59.0
3.	$C + 2H_2 \rightleftharpoons CH_4$	+18900	2 to 1	$K = \frac{CH_4}{(H_2)_2}$	0.077	0.012	0.003
4.	$2C + 3H_2 \rightleftharpoons C_2H_6$	+23300	3 to 1	$K = \frac{C_2H_6}{(H_2)_3}$	$2.2 \times 10^{-7}$	$1.7 \times 10^{-8}$	$2.5 \times 10^{-9}$
5.	$2C + 2H_2 \rightleftharpoons C_2H_4$	-14600	2 to 1	$K = \frac{C_2H_4}{(H_2)_2}$	$6.0 \times 10^{-10}$	$1.6 \times 10^{-9}$	$3.2 \times 10^{-9}$
6.	$2C + H_2 \rightleftharpoons C_2H_2$	-58100	1 to 1	$K = \frac{C_2H_2}{H_2}$	$1.1 \times 10^{-12}$	$1.5 \times 10^{-11}$	$5.7 \times 10^{-10}$
7.	$6C + 3H_2 \rightleftharpoons C_6H_6$	-11300	3 to 1	$K = \frac{C_6H_6}{(H_2)_3}$	$1.2 \times 10^{-15}$	$1.7 \times 10^{-15}$	$2.2 \times 10^{-15}$
8.	$C_2H_6 \rightleftharpoons C_2H_4 + H_2$	-37900	1 to 2	$K = \frac{C_2H_4 \times H_2}{C_2H_6}$	0.0027	0.094	1.28
9.	$2CH_4 \rightleftharpoons C_2H_4 + 2H_2$	-52400	2 to 3	$K = \frac{C_2H_4 \times (H_2)_2}{(CH_4)_2}$	0.0000001	0.00001	0.0004
10.	$2CH_4 \rightleftharpoons C_2H_2 + 3H_2$	-95900	2 to 4	$K = \frac{C_2H_2 \times (H_2)_3}{(CH_4)_2}$	$1.86 \times 10^{-11}$	0.0000001	0.00006
11.	$C_2H_4 \rightleftharpoons C_2H_2 + H_2$	-43500	1 to 2	$K = \frac{C_2H_2 \times H_2}{C_2H_4}$	0.00018	0.0093	0.178
12.	$C_2H_6 \rightleftharpoons C_2H_2 + 2H_2$	-81400	1 to 3	$K = \frac{C_2H_2 \times (H_2)_2}{C_2H_6}$	0.0000005	0.00089	0.228
13.	$C_4H_8 \rightleftharpoons 2C_2H_4$	-31800	1 to 2	$K = \frac{(C_2H_4)_2}{C_4H_8}$	1.41	31.6	258.0
14.	$3C_2H_2 \rightleftharpoons C_6H_6$	+163000	3 to 1	$K = \frac{C_6H_6}{(C_2H_2)_3}$	$9 \times 10^{23}$	$5 \times 10^{17}$	$1.2 \times 10^{13}$

15.	$3\text{C}_2\text{H}_4 \rightleftharpoons \text{C}_3\text{H}_6 + 3\text{H}_2, \dots, \dots + 32500$	3 to 4	$K = \frac{\text{C}_3\text{H}_6 \times (\text{H}_2)^3}{(\text{C}_2\text{H}_4)^3}$	$5.5 \times 10^{12}$	$4.1 \times 10^{11}$	$6.7 \times 10^{10}$
16.	$\text{C} + \text{H}_2\text{O} \rightleftharpoons \text{CO} + \text{H}_2, \dots, \dots - 29300$	1 to 2	$K = \frac{\text{CO} \times \text{H}_2}{\text{H}_2\text{O}}$	0.2	3.1	25
17.	$\text{C} + 2\text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + 2\text{H}_2, \dots, \dots - 19000$	2 to 3	$K = \frac{\text{CO}_2 \times (\text{H}_2)^2}{(\text{H}_2\text{O})^2}$	0.4	2.5	11
18.	$\text{H}_2\text{O} + \text{CO} \rightleftharpoons \text{CO}_2 + \text{H}_2, \dots, \dots + 10350$	2 to 2	$K = \frac{\text{CO}_2 \times \text{H}_2}{\text{H}_2\text{O} \times \text{CO}}$	1.95	0.81	0.42
19.	$\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2, \dots, \dots - 48200$	2 to 4	$K = \frac{\text{CO} \times (\text{H}_2)^3}{\text{CH}_4 \times \text{H}_2\text{O}}$	0.06	8.7	346.0
20.	$\text{C}_2\text{H}_4 + 2\text{H}_2\text{O} \rightleftharpoons 2\text{CO} + 4\text{H}_2, \dots, \dots - 44000$	3 to 6	$K = \frac{(\text{CO})^2 \times (\text{H}_2)^4}{(\text{C}_2\text{H}_4 \times \text{H}_2\text{O})^2}$	...	...	...
21.	$\text{C}_2\text{H}_2 + 2\text{H}_2\text{O} \rightleftharpoons 2\text{CO} + 3\text{H}_2, \dots, \dots - 500$	3 to 5	$K = \frac{(\text{CO})^2 \times (\text{H}_2)^3}{\text{C}_2\text{H}_2 \times (\text{H}_2\text{O})^2}$	...	...	...
22.	$\text{C}_2\text{H}_6 + 6\text{H}_2\text{O} \rightleftharpoons 6\text{CO} + 9\text{H}_2, \dots, \dots - 164500$	7 to 15	$K = \frac{(\text{CO})^6 \times (\text{H}_2)^9}{\text{C}_2\text{H}_6 \times (\text{H}_2\text{O})^6}$	$1.2 \times 10^{-7}$	0.49	48000
23.	$\text{CH}_4 + 2\text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + 4\text{H}_2, \dots, \dots - 37900$	3 to 5	$K = \frac{\text{CO}_2 \times (\text{H}_2)^4}{\text{CH}_4 \times (\text{H}_2\text{O})^2}$	0.3	16	280
24.	$\text{C}_2\text{H}_6 + 4\text{H}_2\text{O} \rightleftharpoons 2\text{CO}_2 + 6\text{H}_2, \dots, \dots + 23400$	5 to 8	$K = \frac{(\text{CO}_2)^2 \times (\text{H}_2)^6}{\text{C}_2\text{H}_6 \times (\text{H}_2\text{O})^4}$	...	...	...
25.	$\text{C}_2\text{H}_2 + 4\text{H}_2\text{O} \rightleftharpoons 2\text{CO}_2 + 5\text{H}_2, \dots, \dots + 20100$	5 to 7	$K = \frac{(\text{CO}_2)^2 \times (\text{H}_2)^4}{\text{C}_2\text{H}_2 \times (\text{H}_2\text{O})^4}$	...	...	...
26.	$\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2, \dots, \dots - 58500$	2 to 4	$K = \frac{(\text{CO})^2 \times (\text{H}_2)^2}{\text{CH}_4 \times \text{CO}_2}$	0.017	5	354
27.	$\text{C}_2\text{H}_4 + 2\text{CO}_2 \rightleftharpoons 4\text{CO} + 2\text{H}_2, \dots, \dots - 64600$	3 to 6	$K = \frac{(\text{CO})^4 \times (\text{H}_2)^2}{\text{C}_2\text{H}_4 \times (\text{CO}_2)^2}$	...	...	...
28.	$\text{C}_2\text{H}_2 + 2\text{CO}_2 \rightleftharpoons 4\text{CO} + \text{H}_2, \dots, \dots - 21100$	3 to 5	$K = \frac{(\text{CO})^4 \times \text{H}_2}{\text{C}_2\text{H}_2 \times (\text{CO}_2)^2}$	...	...	...

and that a temperature of  $900^{\circ}$  C. is favorable to the CO and  $H_2$  formation of 16, but unfavorable to the methane preservation in Equation 19. On the other hand, a temperature of  $600^{\circ}$  C. is unfavorable to preservation of CO and  $H_2$  in Equation 16 but is more favorable than  $900^{\circ}$  to hydrocarbon formation or preservation. Also it is more favorable to formation of  $CO_2$  as shown by Equation 17. These temperature effects can be more clearly understood by reference to the first numerical problem cited, and to the theoretical mixtures given for Equation 19 at temperatures of  $600^{\circ}$  and  $900^{\circ}$  C. It appears impossible to find a temperature favorable to both when the two reactions are simultaneously carried out. In order to preserve the hydrocarbons it becomes necessary to form  $H_2O$ ,  $CO_2$  and deposit carbon; or in order to avoid forming water vapor,  $CO_2$  and deposit carbon, it becomes necessary to destroy hydrocarbons. The two cannot be reconciled.

#### SUMMARY

On theoretical grounds, therefore, it appears:

I—Possible to create such conditions that the oil cracking process can be carried out at a higher temperature than is now used in oil gas processes, and thereby greatly increase the yield of valuable hydrocarbons.

II—Possible to "crack" oil without depositing carbon, and without the formation of water vapor and  $CO_2$ .

III—Possible to partially control the quantity and composition of "tar" produced in gas manufacture.

IV—Impossible to preserve hydrocarbons and at the same time avoid  $CO_2$ , water vapor, and deposited carbon, when oil is "cracked" as in the present carbureted water gas process.







## THERMAL REACTIONS IN CARBURETING WATER GAS

### PART II—EXPERIMENTAL

In the design of an experimental apparatus for cracking oil in accordance with the theory set forth in Part I, it is necessary to provide accurate control over the three variables: temperature, pressure, and concentration. The plan of research has been: (1) To keep pressure and concentration constant until the effect of changing temperature is understood; (2) to keep the temperature constant and change the total pressure on the system; (3) to hold both temperature and pressure constant and crack the oil in the presence of other gases in order to vary the concentrations.

Considerable time was spent in designing and building an apparatus which would be stable, durable, easy of access and replaceable in all its parts, as well as under complete control with respect to temperature, pressure and concentration. The machine was further designed to be of such dimensions and capacity as would indicate results which might be expected in the commercial application of the principles involved. In its completed form the apparatus covers a floor space sixteen feet by four feet and the oil feed cup at the top of the machine is nine feet from the floor. With this equipment it is possible to maintain any temperature up to  $1000^{\circ}$  C. within five degrees, and any pressure ranging from one-thirtieth of one atmosphere absolute to three atmospheres absolute.

#### FURNACE BODY

The furnace body is made from  $1\frac{1}{2}$  in. "Reading" brand wrought iron pipe, 32 in. long. For a length of 18 in. the pipe is wrapped with No. 15 Nichrome resistance wire, seven turns to the inch. Between the wrought iron pipe and resistance wire five layers of asbestos paper serve as insulation. In series with the nichrome wire of the furnace is a large rheostat, with graduated steps between  $2\frac{1}{2}$  and 9 amperes. An incandescent tell-tale lamp is connected across the binding posts of the furnace, to indicate when the current is on as well as to give a rough idea of the

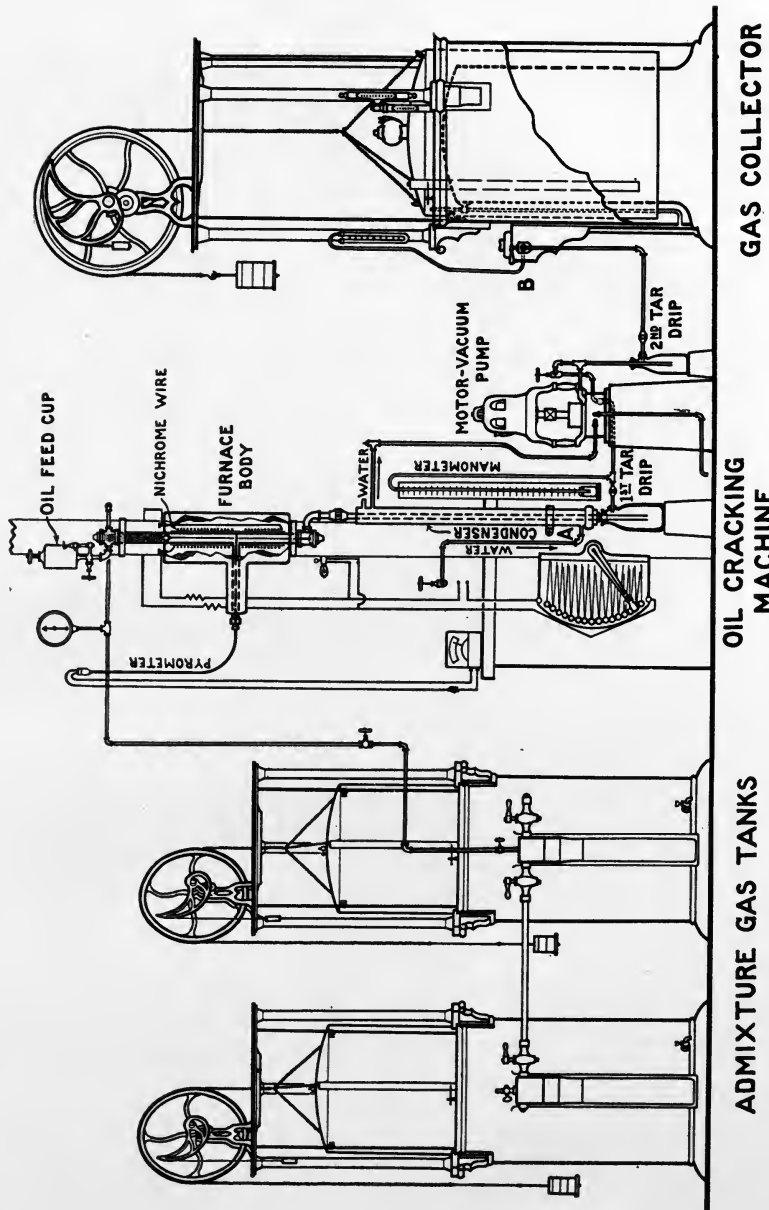


FIG. III—APPARATUS FOR OIL CRACKING AND GAS MAKING

wattage in use. Both voltmeter and ammeter are connected in the circuit. (See Fig. III.)

The nichrome wire windings are enclosed in a five-inch insulation of magnesia-asbestos pipe covering to minimize radiation. A  $\frac{3}{4}$  in. wrought iron pipe is welded at right angles into the  $1\frac{1}{2}$  in. wrought iron furnace body to serve as a container for the pyrometer point. This side tube is likewise insulated with asbestos and is fitted with a stuffing box surrounding the pyrometer rod. With this side tube it is possible to keep the pyrometer point directly in the furnace body at all times. The pyrometer couple is of the iron-nickel type connected with a millivoltmeter calibrated in degrees Centigrade.

After continued use at the higher temperatures the furnace body warps or the nichrome wire burns out. Duplicates for all parts are kept on hand, and the apparatus is so designed that any part may be replaced within a few minutes.

In order to vaporize the oil before it reaches the cracking zone, the upper part of the furnace tube is filled with  $\frac{5}{8}$  in. steel balls. These are held in place by a thin post which runs vertically through the furnace supporting a perforated plate. The vertical rod is bent to permit the centering required for the pyrometer. The object of the steel balls is to spread the oil in thin films and facilitate vaporization, but not to serve as cracking surface; in order to accomplish this they are kept at a safe height above the cracking zone. Lowering them into the cracking zone has a marked influence on the products obtained from the cracking process. The furnace, together with condenser, oil feed, pressure gauge and admixture gas-inlet pipe are vertically supported by iron clamps attached to an upright 3 in.  $\times$  6 in. yellow pine timber. The assembled apparatus was tested at 100 lbs. hydraulic pressure.

#### OIL FEED

A Powell sight feed oil cup of one quart capacity is joined by a  $\frac{3}{4}$  in. elbow and nipple to a  $1\frac{1}{2} \times 1\frac{1}{2} \times \frac{3}{4} \times \frac{3}{4}$  in. cross which forms the upper end of the furnace body. The pressure in the oil cup is equalized through a small internal pipe which communicates with the furnace body below the point of oil discharge. As a result of this equalizing tube, regardless of whether the apparatus is under increased or reduced pressure, the oil supply is always under a

supply pressure equal to its own head. As this head decreases the rate of flow may be regulated by the needle valve controlling the feed inlet. The rate of supply may be determined by counting the drops for a given time.

#### PRESSURE GAUGES

For all vacuum work the apparatus is connected with a mercury manometer calibrated in inches. A mechanical vacuum gauge is also placed at the top of the apparatus to indicate a free path in the cracking tube. In the course of the experiments under certain conditions, sufficient carbon was deposited to clog up the apparatus and show a considerable difference in the pressure between the two gauges. Such a condition, however, is limited to experiments involving high temperatures and pressures (atmospheric or greater), where the deposition of carbon is at its maximum. There is never any clogging under reduced pressures. For pressure work, the mercury column is disconnected and a mechanical pressure gauge is substituted.

#### CONDENSER

At the lower end, the generating tube or furnace body discharges through a Liebig type condenser into a tar drip for the collection of liquid condensates. The cooling water enters at the bottom of the condenser and on leaving continues through the jacket of the vacuum pump. The condenser pipe is offset from the furnace body rather than placed directly under it so that the furnace may be cleaned by simply removing the lower plug and withdrawing the contents. It is thus possible to remove and weigh the deposited carbon from the furnace body after each run.

#### TAR DRIPS

For vacuum work the tar drips are of glass, as this facilitates observation of the gas, as well as the nature and the rate of tar formation. In vacuum work it was soon found that the lighter condensates would continue through the vacuum pump because of the low pressure in the first tar drip. To collect the liquids drawn through, a second tar drip was placed beyond the vacuum pump. Upon reaching the second drip these lighter hydrocarbons condense, as the pressure is then approximately atmospheric. When working under one-thirtieth of an atmosphere it was found that only a small percentage of the hydrocarbons would

collect in the first tar drip. For pressure work a steel tar collector was substituted.

#### VACUUM PUMP

Vacuum in the system is maintained by a May-Nelson two-ring vacuum pump. By means of a bypass connection joining the outlet and inlet of the pump, it is possible so to regulate the valve as to maintain any desired vacuum down to one-thirtieth of an atmosphere.

#### CONNECTION FOR PRESSURE WORK

The vacuum pump is mounted on a movable concrete foundation and by disconnecting a few couplings the vacuum attachments may be removed. For pressure work there is substituted an all metal tar collector, connecting pipe, and release pressure valve, as shown in Fig. IV. The apparatus may be changed from vacuum to pressure, or *vice versa*, in twenty minutes. When working under pressure, the gas

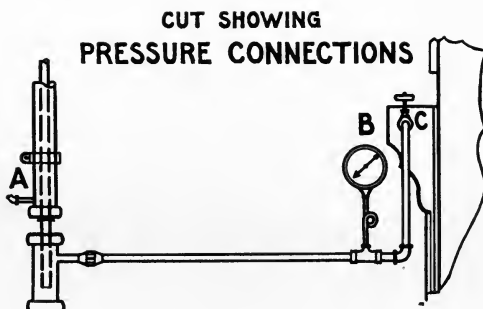


FIG. IV

generated in the furnace body creates its own pressure. This pressure is controlled by an ordinary release valve placed at the inlet to the gas collector. By regulating the release of this valve, the apparatus may be set to work under any pressure from atmospheric to 30 lbs. per square inch above atmospheric, which seemed to be the upper safe working limit of the furnace under the conditions of operation. A pressure gauge is placed in the discharge line and used as a check on the pressure gauge near the oil feed.

#### GAS COLLECTOR AND ADMIXTURE GAS TANKS

The gas generated is collected in a 12 cu. ft. capacity gas holder, made by the American Meter Company. The tank is graduated in tenths of a cubic foot. By multiplying the number of cubic feet by 28.32 the

volume is reported in liters. To avoid relying upon natural diffusion for mixing the gases, the bell of the holder is fitted with an internal mechanical stirrer directly connected through a stuffing box to an electric motor located on top of the bell. Perfect mixing of the gases may be attained in two minutes with this equipment whereas natural diffusion would require from one to two hours.

The equipment also contains two 6 cu. ft. capacity admixture tanks of the same design as the large holder. These serve as gas supply tanks when cracking oil in the presence of other gases such as  $H_2$ , CO, or mixtures of the two. A  $1/4$  in. steel pipe, fitted with needle control valves, connects these two tanks with the inlet end of the furnace body. The piping is so arranged as to connect any two of the three tanks.

#### METHOD OF MAKING A RUN

When the apparatus is operated under vacuum the furnace body is first heated by the resistance coils to the desired temperature for cracking the oil into fixed gases. The oil is permitted to enter the upper part of the generating tube where it spreads over the steel balls and is vaporized. In the meantime, the vacuum pump has been set in operation and draws the oil vapors downward into the cracking zone of the furnace body, whereupon these vapors are immediately cracked into fixed gases and other products. These products, before opportunity is offered for polymerization or decomposition of the hydrocarbon gases, are withdrawn by the vacuum pump from the cracking zone and their place is taken by a quantity of oil vapor from the vaporizing zone above. In this manner the hydrocarbon gases are withdrawn continuously and as quickly as they form. After they pass through the condenser and receiver for the removal of the condensable vapors, they are forwarded by way of the pump to the gas holder.

#### GAS SAMPLING AND ANALYSIS

After the gas in the holder is thoroughly mixed by the mechanical stirrer, three or four sampling tubes are filled for analysis. As a guide for all methods of gas analysis, Dennis' 1913 edition of "Gas Analysis," using the Hempel equipment, is followed. To determine the hydrogen in a mixture of hydrogen, methane and ethane, Hempel's fractional combus-



tion method<sup>1</sup> is used. All analyses are made in duplicate.

#### DATA OBTAINED FROM A RUN

In this work all conditions outside of temperature, pressure, and concentration were maintained as uniform as possible. Four hundred cc. of oil were used per run, fed at the rate of about 3 cc. per minute. The oil used is technically known as "150° (F) water white oil;" its specific gravity at 15° C. is 0.7984; boiling point between 150° and 290° C. Oil from the same tank was used throughout the experiments. All runs were made in duplicate.

TABLE I—TYPICAL VACUUM RUN RECORD

Time	Temp. ° C.	Vacuum Inches	Barometer, 756 mm.	
			Oil used, 400 cc.	Oil feed Drops in 10 sec.
11.43	900	29.00	..	....
12.00	903	28.50	24	....
12.15	905	28.00	26	2.16
12.30	895	28.75	23	3.01
12.45	895	28.75	21	3.76
1.00	895	28.50	24	4.86
1.30	895	28.50	26	6.86
1.45	895	28.50	25	7.76
2.00	895	28.75	17	8.36
2.07	Run ended			8.75

Corrected to standard conditions as follows:

$$8.75 \times \frac{273}{288} \times \frac{756}{760} \times 28.32 = 234 \text{ liters}$$

#### ANALYSIS OF PRODUCTS FROM TABLE I—GAS ANALYSIS

	Per cent by vol.	Liters at std. cond.
CO <sub>2</sub> .....	0.1	....
H <sub>2</sub> .....	52.1	122.0
O <sub>2</sub> .....	0.9	....
CO.....	0.4	....
CH <sub>4</sub> .....	24.0	56.0
C <sub>2</sub> H <sub>6</sub> .....	1.3	3.0
H <sub>2</sub> .....	17.3	40.0
N <sub>2</sub> (difference).....	3.9	....
	100.0	....

Carbon, 3 grams.

"Tar" 60 cc. Sp. gr. 20° Bé.

#### EFFECT OF TEMPERATURE CHANGES

The experimental data on changes in temperature in the cracking of the oil, with pressure and concentration maintained constant, agree with the data recorded in the literature from the experiments by Haber,<sup>2</sup>

<sup>1</sup> *Zeitsch. angew. Chem.*, **1912**, 1841.

<sup>2</sup> *Journal f. Gasb.*, **1896**, 799, 813, 830.

Hempel,<sup>1</sup> Ross and Leather,<sup>2</sup> Lewes,<sup>3</sup> Fulweiler,<sup>4</sup> and others. It is difficult to make accurate comparisons of two experiments conducted in different apparatus on account of the great variety of conditions involved. Subjecting a gas to a temperature of 900° C. for five seconds is quite different from subjecting it to the same temperature for five minutes.<sup>5</sup> Leading the gases through a 1/8 in. pipe heated to 900° C. would give different results from those obtained by leading the same gases through a 2 in. pipe heated to 900° C. While the difference due to experimental apparatus would not be so great as the examples cited, there is sufficient difference to affect the value of direct comparison.

However, the general results obtained at different temperatures by different experimenters are comparable. As the temperature increases, the quantity of valuable gas from a given amount of oil increases to a maximum, after which the gaseous hydrocarbons rapidly decrease and the deposited carbon increases. The quantity of tar decreases, but this is due to a dissociation of the hydrocarbons and cannot be construed favorably. Upon subjecting the oil to temperatures of 650°, 750° and 900° C., under atmospheric pressure, the results are as follows:

TABLE II  
Oil used, 400 cc.

Temp. ° C.	Press.	Gas liters	Carbon	Tar
		Standard conditions	Grams	Cc.
650	atmos.	135	3	163
750	atmos.	206	18	80
900	atmos.	382	115	11

Analysis of Gas from Table II

Temp. ° C.	C <sub>2</sub> H <sub>6</sub> Per cent	CH <sub>4</sub> Per cent	H <sub>2</sub> Per cent	Ill Per cent
650	10.2	33.7	9.1	43.6
750	4.9	41.1	19.2	30.6
900	None	46.7	38.6	13.1

#### EFFECT OF INCREASED PRESSURE ON GASEOUS REACTIONS

It seems reasonable to expect that a high pressure will assist materially in condensing three volumes of acetylene into one volume of benzene:  $3\text{C}_2\text{H}_2 \rightleftharpoons \text{C}_6\text{H}_6$ .

<sup>1</sup> *Journal f. Gasb.*, **1910**, 53.

<sup>2</sup> *Journal of Gas Lighting*, **1906**, 825.

<sup>3</sup> *Jour. Soc. Chem. Ind.*, **1892**, 584.

<sup>4</sup> Rogers' "Industrial Chemistry."

<sup>5</sup> Lewes, *Proceedings of Royal Soc.*, **1894**, 90; W. A. Bone, *Jour. f. Gasb.*, **1908**, 803; Bone and Coward, *Jour. Chem. Soc.*, **1908**, 1197.

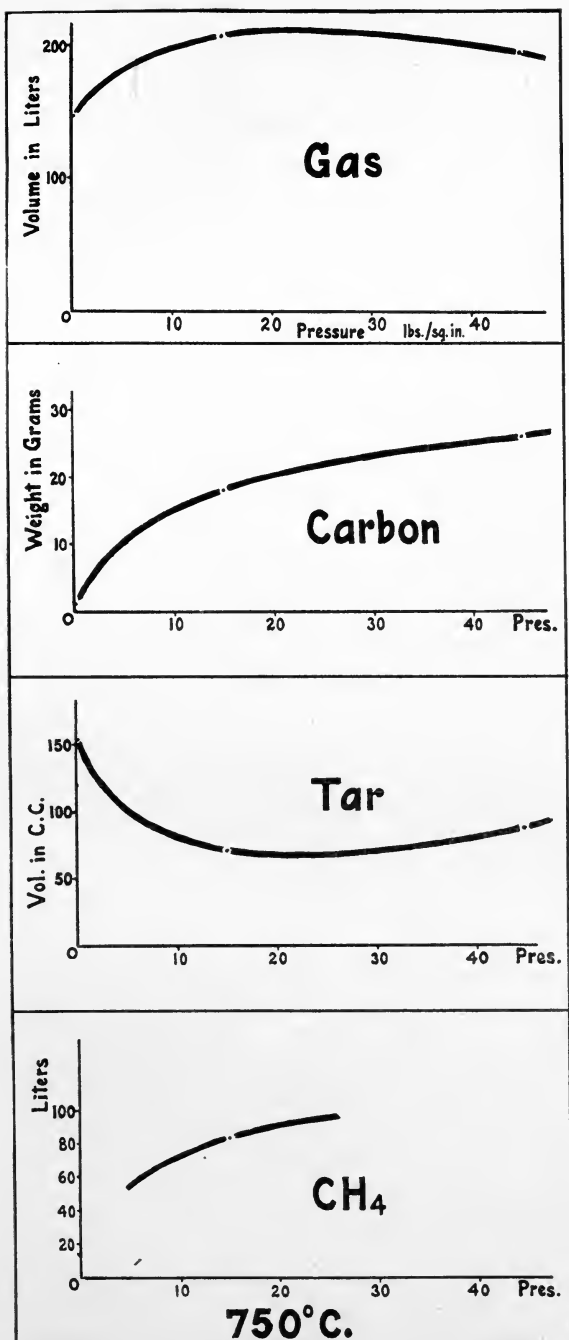


FIG. V.—VARIATIONS IN YIELDS OF PRODUCTS AT 750° C., UNDER VARYING PRESSURES. (TABLES II, III, IV AND VI)

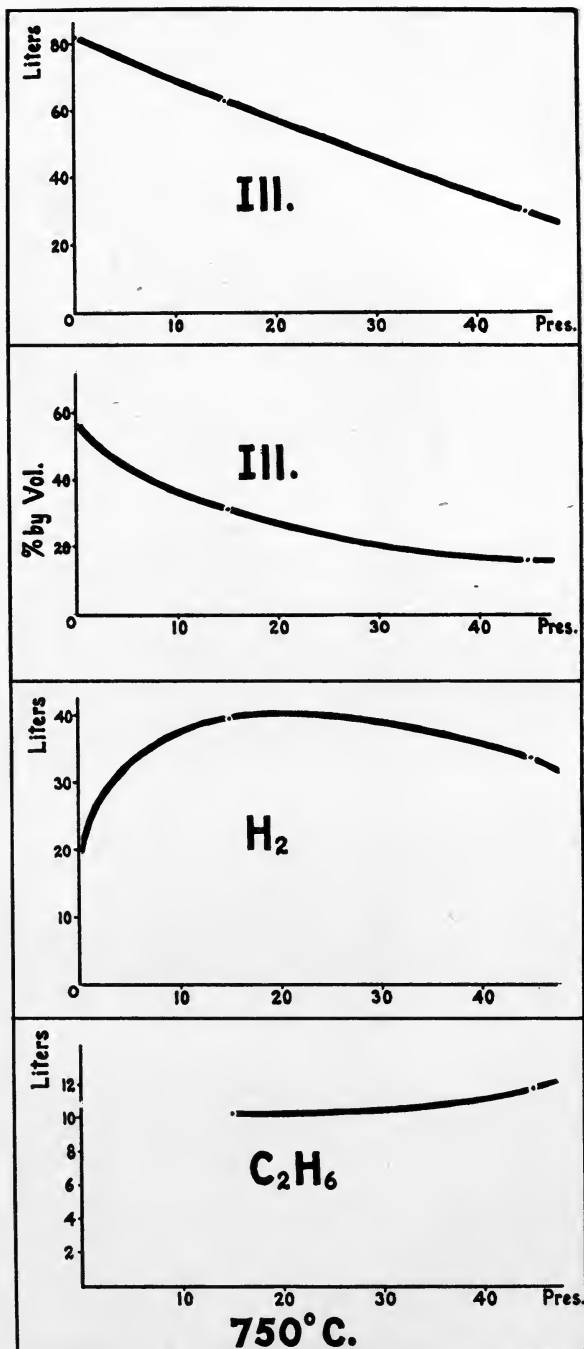


FIG. VI—VARIATIONS IN YIELDS OF PRODUCTS AT 750° C., UNDER VARYING PRESSURES. (TABLES II, III, IV AND VI)

On the other hand, it seems reasonable to expect that, under a high pressure, it will be considerably more difficult for one volume of oil vapor to break up or expand to many volumes of gas than under reduced pressure.

In the system



one would expect that the application of high pressures would increase the difficulty of generating gas, and after the gas is generated it would make easier the condensation reactions which proceed to the tar stage. Since the unsaturated hydrocarbons, ethylene and acetylene, polymerize most readily, increased pressure should preferably condense them with the formation of tar compounds. In addition to the direct influence of pressure, it may be assumed that when working under increased pressure the gaseous hydrocarbons are subjected to the influence of heat for a longer time, which further tends towards the formation of heavy condensation products at the expense of the illuminants. The following series of experimental results appears to justify these conclusions:

TABLE III  
Oil used, 400 cc.

Temp. ° C.	Pressure	Gas Liters	Carbon Grams	Tar Cc.
	Absolute Lbs.			
650	45	145	8	133
750	45	194	26	87
900	45	310	165	9

Analysis of Gas from Table III

Temp. ° C.	C <sub>2</sub> H <sub>6</sub>	CH <sub>4</sub>	H <sub>2</sub>	Ill
	Per cent	Per cent	Per cent	Per cent
650	11.5	45.1	9.3	30.5
750	6.1	56.6	17.5	15.5
900	None	41.6	50.0	5.0

The yields of gaseous hydrocarbons are lower than those shown in Table II, which were obtained at the same temperatures, and likewise the maximum yield is lower than the maximum obtained under atmospheric pressure.

EFFECT OF DIMINISHED PRESSURE ON GASEOUS REACTIONS

By referring to the OIL-GAS-TAR system cited above, it becomes evident that a high vacuum would favor the increase in volume due to cracking the oil into gas and at the same time withdraw the gas from

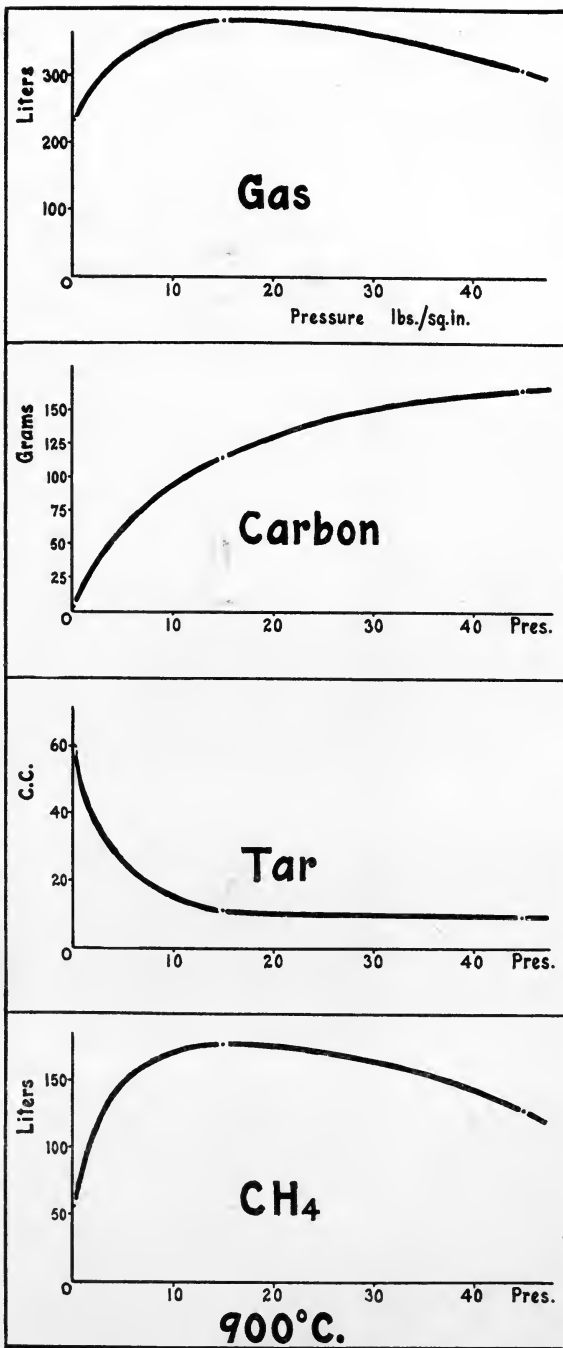


FIG. VII—VARIATIONS IN YIELDS OF PRODUCTS AT 900° C., UNDER VARYING PRESSURES. (TABLES II, III, IV AND VI)

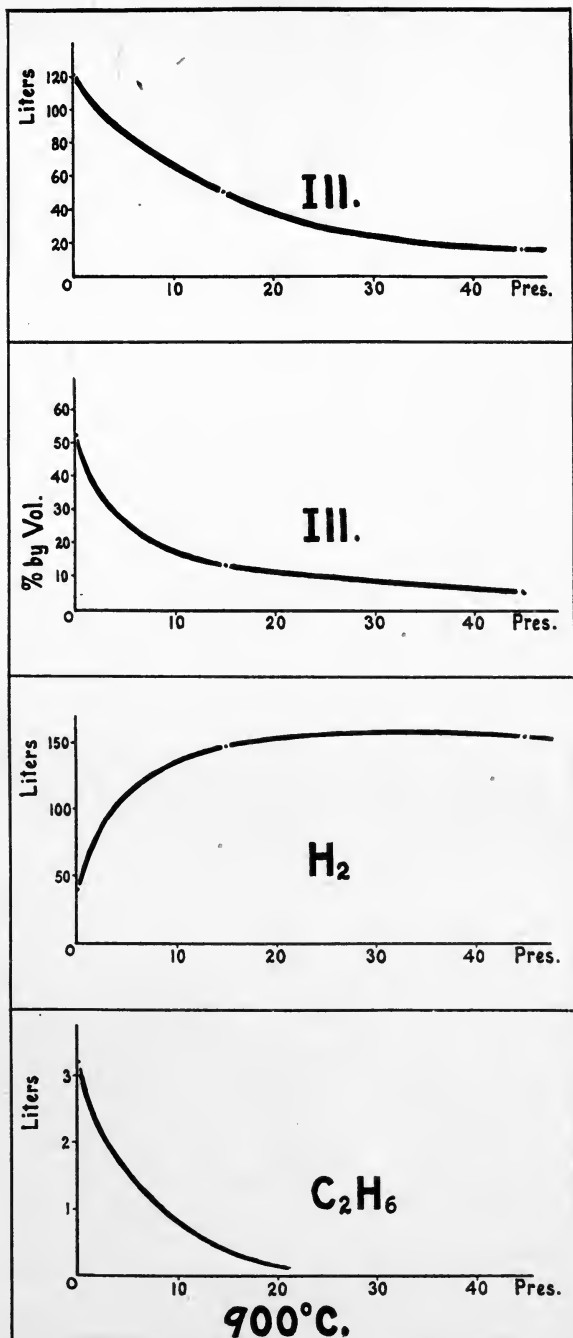


FIG. VIII—VARIATIONS IN YIELDS OF PRODUCTS AT 900° C., UNDER VARYING PRESSURES. (TABLES II, III, IV AND VI)

the heat zone before it could form tar. The effects of this reduced pressure can best be observed from the results of the following experiments:

TABLE IV  
Oil used, 400 cc.

Temp. ° C.	Pressure Absolute	Gas Liters	Carbon Grams	"Tar" Cc.
750	1/20 to 1/30 atmos.	146	1	153
850	1/20 to 1/30 atmos.	211	3	100
900	1/20 to 1/30 atmos.	234	3	60
950	1/20 to 1/30 atmos.	235	12	58

Analysis of Gas from Table IV

Temp. ° C.	C <sub>2</sub> H <sub>6</sub> Per cent	CH <sub>4</sub> Per cent	H <sub>2</sub> Per cent	Ill Per cent
750	...	...	12.5	56.1
850	3.4	20.5	15.6	52.9
900	1.3	24.0	17.3	52.1
950	Trace	27.0	20.8	46.9

This striking difference in end products due to diminished pressure seems to have been overlooked, perhaps because for the first few pounds per square inch vacuum the increase is not marked.

#### INFLUENCE OF CONCENTRATION CHANGES ON GASEOUS REACTIONS

The present investigation has merely opened this field. It has been established that oil cracked in an atmosphere of a gas, such as hydrogen, which reacts chemically with the end products of the cracking process, will yield products which are not analogous to those resulting from a physical mixture of the two gases. Not only does the mere presence of the admixed gas influence the end products, but as is to be expected from the theoretical consideration, the quantity of the admixed gas is influential.

To study the various gases and their quantitative relation will require much further experimental work. The results of preliminary study indicate that there is a vital relationship between the resulting gases in a cracking process and the atmosphere in which the oil is cracked. This relationship is likely to be of commercial significance in practical water gas carburization. The quantity of CO and H<sub>2</sub> admixed per gallon of oil cracked is an important factor, just as the temperature and the pressure have been shown to be important factors. Jones,<sup>1</sup> in his improved all oil water gas process, recognizes the importance of adding an "active gas" to the cracking zone, but considers

<sup>1</sup> *The Gas Age*, 1913, p. 369; *American Gas Light Journal*, 1913, p. 272; *Gas World*, 1913, 916.



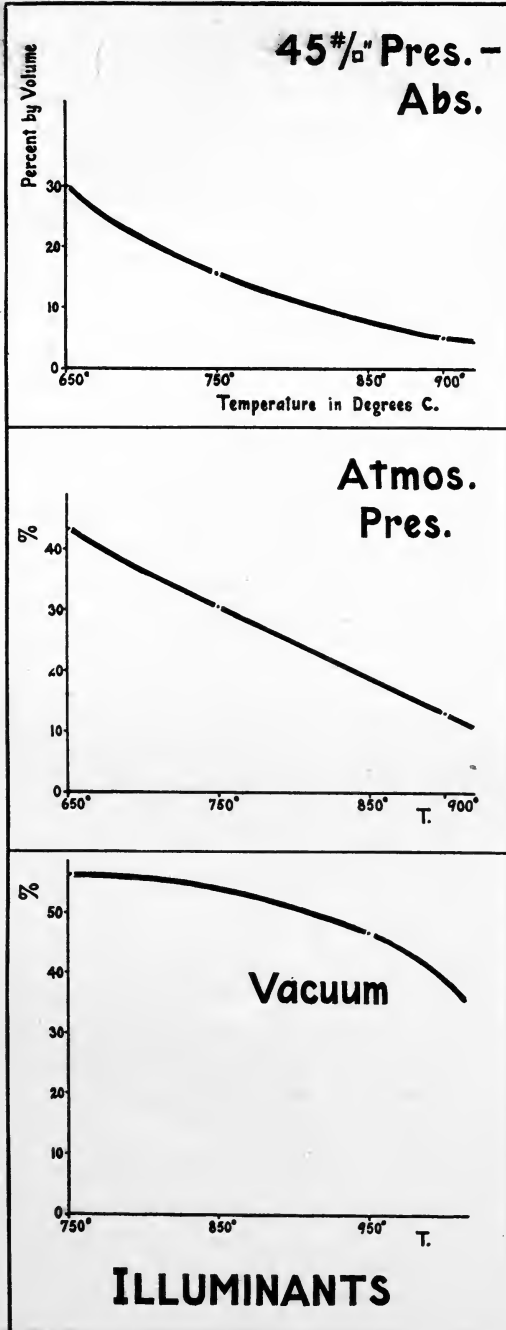


FIG. IX—PERCENTAGES OF ILLUMINANTS UNDER VARYING TEMPERATURES AND PRESSURES. COMPILED FROM TABLES II, III AND IV

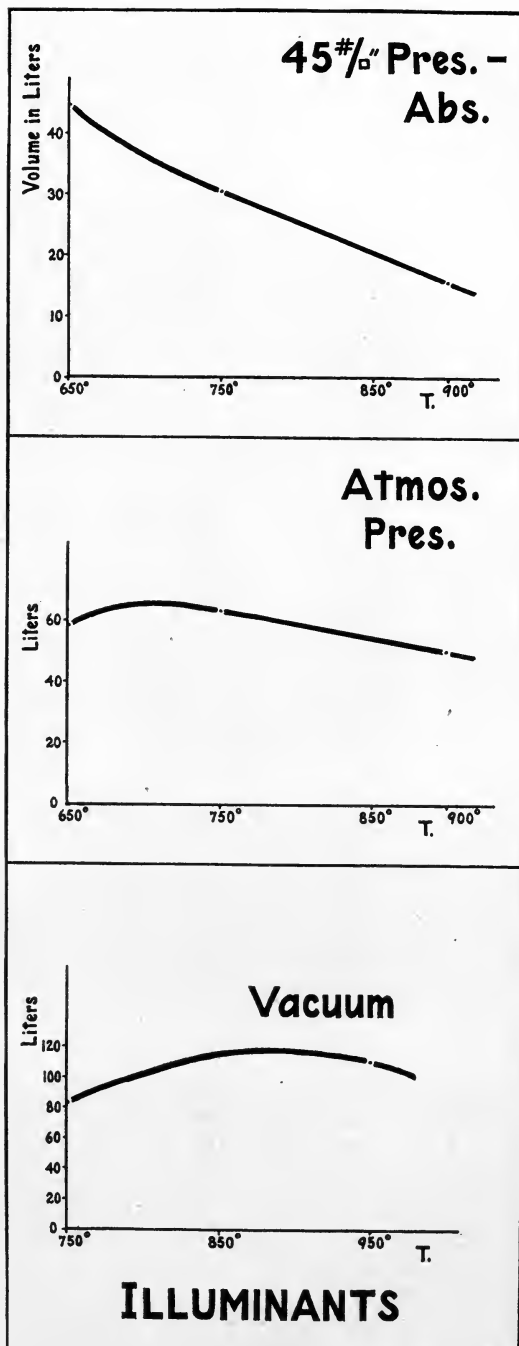


FIG. X—LITERS OF ILLUMINANTS UNDER VARYING TEMPERATURES AND PRESSURES. COMPILED FROM TABLE VI

the effect of the presence of the admixed gas to be catalytic. Hempel<sup>1</sup> found that by cracking oil in the presence of hydrogen not only did none of the hydrogen split off from the hydrocarbons, but part of the admixed hydrogen actually combined for the formation and preservation of hydrocarbons. On the other hand, on the basis of a single experiment reported, he maintains that the presence of CO in the cracking zone is similar to the presence of a neutral gas and is without material influence on the end products obtained from the oil. As to the hydrogen, the results of this research agree with the observations of both Hempel and Jones. The quantity and quality of gas per cc. of oil increase, and qualitative results show that the tar and deposited carbon decrease.

TABLE V

Temp. ° C.	Pressure	H <sub>2</sub> admixed. L.	Liters			Shrinkage in H <sub>2</sub> . Liters	
	Absolute Lbs.		C <sub>2</sub> H <sub>6</sub>	CH <sub>4</sub>	Ill	H <sub>2</sub>	
750	15.0	358	15.4	125.0	70.6	308	50
800	15.0	412	18.0	116.0	83.2	335	77
750	0.75	400	9.5	52.0	112.0	381	19
810	0.75	413		86.5	140.0	378	35
860	0.75	388		99.5	133.0	350	38
900	0.75	292		92.0	120.0	272	20
960	0.75	382		95.0	113.0	348	34

From these results it appears that a greater percentage of the admixed hydrogen enters into combination to form saturated hydrocarbons when the cracking process is carried out under atmospheric pressure, than is the case under greatly reduced pressure. The percentage increase in yield of the illuminants when the cracking process is carried out under reduced pressure in the presence of hydrogen is about as great, however, as is the percentage increase in illuminants when the reaction is carried out under atmospheric pressure.

INFLUENCE OF TEMPERATURE, PRESSURE AND CONCENTRATION CHANGES ON COMPOSITION OF RESULTANT TARS

If changing temperature and pressure have a marked influence on the quantity and quality of gaseous hydrocarbons obtained from cracking petroleum oil, one should expect simultaneous changes in the condensable hydrocarbons, which differ from the permanent gaseous hydrocarbons only in that they are liquid or solid at ordinary temperatures. There should be equilibrium between all hydrocarbons of a series at the

<sup>1</sup> *Jour. f. Gasb.*, 1910, p. 53, et al.

high temperatures prevailing in the furnace where practically all the hydrocarbons are gaseous. That the end products should contain ethylene and then suddenly jump to hexene is not to be expected, any more than that the hydrocarbons in coal tar would jump from benzene to naphthalene or anthracene. In industrial practice the "illuminants" are usually said to consist of 75 per cent ethylene and 25 per cent benzene vapor.

When the gas made by cracking oil in the apparatus under one-thirtieth of an atmosphere pressure absolute is passed over palladium in the presence of an excess of hydrogen, over 90 per cent of the illuminants are converted into saturated hydrocarbons, principally ethane, indicating that the illuminants contain but little, if any, benzene vapor. If the gas contains no benzene, it is only logical to believe that the condensable hydrocarbons contain no aromatic hydrocarbons. It is further found that the vacuum tar will combine with 1.82 sp. gr. sulfuric acid. It has a low specific gravity, and on permitting the higher boiling point fractions to stand, no naphthalene or anthracene separate out. Tars resulting from cracking oil in carbureting blue water gas under atmospheric pressure contain quantities of benzene, toluene and other aromatic hydrocarbons in sufficient amounts to be of commercial importance. In view of these facts, there is justification for the statement that tars which result from cracking petroleum under low pressures are different from those which result from cracking under atmospheric or higher pressure. Instead of benzene, toluene and other aromatic hydrocarbons, the vacuum tar contains members of the more unsaturated hydrocarbon series. The composition of these tars is now the subject of a further investigation.

#### SUMMARY

In the theoretical discussion on the influence of diminished pressure on oil gas manufacture, it was pointed out that one should expect an increase in the yield of gaseous hydrocarbons from a given amount of oil by reducing the pressure below atmospheric. This increase should reach a maximum as the absolute zero of pressure is approached. The correctness of this is shown by results recorded in Tables IV and VI. Not only are the gaseous hydrocarbons yields greatly increased, but the deposited carbon is practically eliminated,

and there is much less gaseous hydrogen produced than in the product obtained at the same temperatures under higher pressure.

It was pointed out that increasing the total pressure under which the oil is cracked to several atmospheres will decrease the gaseous hydrocarbon yields from a given amount of oil. Experimental results, shown in Table III, have proven this correct.

It was pointed out that varying the pressure on the system would enable one to better control the quantity and quality of "tar" obtained than at present where all tar is made under atmospheric pressure. Experimental results indicate considerable flexibility.

It has further been established that the end products resulting from cracking oil in an atmosphere of a gas, such as  $H_2$ , which reacts chemically with the end products of the cracking, are a function of both the composition and the quantity of the gas admixed, per Table V.

Experiments, Table IV, have proven that it is possible to "crack" oil at a temperature of  $900^\circ C.$  without depositing more carbon than 1% by weight of the oil used.

TABLE VI—SUMMARY OF GAS TABLES

(All based on 400 cc. oil and calculated to  $0^\circ C.$ , and 760 mm. pressure)

Temp. $^\circ C.$	Pressure		Gas L.	Carbon G.	Tar Cc.	$C_2H_6$ L.	$CH_4$ L.	$H_2$ L.	III L.
	Lbs. per sq. in.	sq. in.							
Atmospheric Pressure Group (See Table II)									
650	15.0		135	3	163	13.8	45.5	12.1	58.8
750	15.0		206	18	80	10.15	84.5	39.6	63.0
900	15.0		382	115	11	Trace	178.1	148.2	50.0
High Pressure Group (See Table III)									
650	45.0		145	8	133	16.7	65.2	13.1	44.3
750	45.0		194	26	87	11.8	110.0	33.9	30.1
900	45.0		310	165	9	None	128.9	155.0	15.5
Low Pressure Group (See Tables I and IV)									
750	0.75		146	1	153	..	..	18.3	82.0
850	0.75		211	3	100	7.16	43.2	32.9	111.5
900	0.75		234	3	60	3.0	56.0	40.0	122.0
950	0.75		235	12	58	Trace	63.4	48.8	110.0
Admixed Gas Group (See Table V)									
			Hydrogen admixed L.		Hydrogen shrinkage L.				
750	15.0		358		50	15.4	125.0	308.0	70.6
800	15.0		412		77	18.0	116.0	335.0	83.2
750	1.0		400		19	9.5	52.0	381.0	112.0
810	1.0		413		35	..	86.5	378.0	140.0
860	1.0		388		38	..	99.5	350.0	133.0
900	1.0		292		20	..	92.0	272.0	120.0
950	1.0		382		34	..	95.0	348.0	113.0

Through a proper consideration of equilibrium and mass action conditions under various degrees of temperature and pressure, much can be expected in gaseous reactions. It soon becomes evident that the single stage method wherein endothermic and exothermic, expansion and contraction reactions are combined in a single apparatus, is open to question.

## VITA

Walter Frank Rittman was born in Sandusky, Ohio, on December 2, 1883. Before entering college he spent four years in the shops and drawing rooms of steel and machine manufacturers in Cleveland, Ohio. He received the degrees of A.B. from Swarthmore College in 1908, M.A. in 1909, and M.E. in 1911. During 1909 he served as chemist in the laboratory of the United Gas Improvement Company, of Philadelphia. From 1909 to 1912 he was engaged in professional chemical engineering work in and about Philadelphia, and at the same time held the position of lecturer and laboratory instructor in Industrial Chemistry at Swarthmore College. From 1912 to 1914 he was engaged in graduate study in Columbia University. He was special lecturer on Industrial Chemistry at Columbia University in the Summer School of 1913.







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