METHANE

BY WILLIAM MALISOFF AND GUSTAV EGLOFF

Introductory

The systematic study of methane, looked upon as the parent substance of organic compounds, the simplest and at the same time the most baffling of the hydrides of carbon, has now well passed the century mark. The aims of the men who pursued investigations on the subject have been as varied as the results have been restricted, and consequently a mass of data has accumulated, which perhaps is fairly complete but entirely uncoördinated. The aim of the present communication is to formulate the result of research on methane up to date, to indicate thereby the future of research on methane both theoretical and practical, and to introduce the necessary data and theoretical discussion leading to a series of papers on the researches of the authors.

The Scope of Past Research

The theoretical and practical aims of the various investigators on methane were mixed at the outset. Hence, for clarity we may classify the researches up to the present along the following lines:

A. Physical Characteristics of Methane.
    1. Physical Constants.
    2. Specific Properties.
    3. Gas Properties.
    4. Application of Physical Characteristics Industrially.
B. Chemical Characteristics of Methane.
    1. Combustion and Explosion of Methane.
    2. Solubility of Methane in Various Solvents.
    3. Occlusion of Methane.
    4. Miscellaneous Physico-Chemical Properties.
    5. Industrial Reactions of Methane.
        Oxidations.
        Halogenation of Methane.
        Formation of Carbides.
        Cyanides from Methane.

- C. Synthesis and Decomposition of Methane.
    1. Direct Union of Carbon and Hydrogen.
    2. Synthesis not Directly from the Elements.
    3. Catalytic Production Indirectly.
    4. Electrosyntheses from Methane.
    5. Formation of Methane Electrically.
- D. Miscellaneous on Methane.
    1. Biological Data.
    2. Sources and Supply of Methane.
- E. Research Possibilities on Methane.

A. PHYSICAL CHARACTERISTICS OF METHANE

1. Physical Constants

The work of Guye[1] and of Baumé and Perrot[2] on methane, made from CH_3MgI, and carefully cleared of all traces of air, gave as an average of a series of determinations the values of 0.7168 g as the weight of 1 liter of methane at 0° C, 760 mm, sea level, 45° parallel. Up to the present no other check upon this value by any other method has been made. The value is an important one in view of the fact that it is used in a large number of thermodynamic calculations on the gas.

Baumé and Perrot[3] also determined the melting point, 184° C, at which temperature methane becomes a colorless, mobile liquid.

Wahl,[4] in his optical investigation of crystalline nitrogen, etc., found that methane (solidifying at —186° C) forms crystals in the regular system, usually setting in from many centers, forming beautiful spherulites.

Similar values are given by Moissan and Chavanne,[5] who set the freezing point at —185.8° C and the boiling point at —164° C at 760 mm pressure. Olszewski[6] gives the melting point as —184° C.

Some interesting theoretical deductions may be drawn from the work of the above investigators, especially from that of Wahl. Indeed the latter's work may be of important application to theories dealing with the configuration of the atoms in the molecule of methane. Though all the four hydrogens have to be considered as chemically the same, yet the molecular valencies may be such that the carbon could display a valence of six. The world may well be grateful to one who will show the vital relation between its structure and reactivity, beyond the usual, merely qualitative explanation.

2. Specific Properties

Further details on methane are given by Cardoso,[7] who gives the critical temperature as —82.85° C, critical pressure as 45.60 atmospheres, critical density as 0.1623. His method is a very accurate one and would indicate that the value given by Goldhammer[8] for critical density, 0.1519, is incorrect. Goldhammer's method, however, gave a precision of within 1 percent.

The formula for critical density was as follows:

$$\frac{(q_1 - q_2)^3}{q_1 + q_2 - 2q_K} = 27\, q^2_K\, q_K = \text{critical density}$$

The triple point of methane has been determined by Crommelin,[9] who puts it as —183.15° C and 70 mm of mercury pressure. Olszewski[10] gave —185.8° C and 80 mm pressure.

The study of the critical constants and even of the coefficients is likely to be of great use in the determination of the scientific reasons for the stability of methane. The hydrogen in methane is located very close to the carbon atom. The substitution of a heavier atom for a hydrogen as in the case of the halogen derivatives, increases greatly the *electrochemical field of the molecule.* Such a consideration would also help one to understand the formation of the higher substituted halogen derivatives from the lower substituted ones rather than from methane itself. If the above data on the critical constants of methane could be supplemented by a set on the critical constants of the halogen derivatives, the mathematical chemist might readily fall into his stride.

3. Gas Properties

In his work on the coefficients of expansion of gases, Leduc[11] included methane. He gives the true coefficients times 10^6 as $\alpha = 3687$, and $\beta = 3681$. The average coefficients $\alpha_{0° - 100° C} = 3681$ and $\beta_{0° - 100° C} = 3679$. These values, again, are significant in the thermodynamic calculations on methane.

Friendly physicists have produced some rather important data on methane which might at any time prove of unexpected value when applied to the consideration of the reactions of methane.

W. H. Bragg and W. T. Cooke[12] have worked out the ionization curve of methane. It is a gas more suitable for such research than air because it shows the four ionization steps more definitely. Similarly, the particles of high velocity are inhibited less by methane than low velocity particles, compared to air. The deductions therefrom are not altogether clear. Further data may throw some light on the subject. However, an explanation may be volunteered for the fact that the rapidly moving particles are less stopped by methane than the slow ones, by considering, in view of the work of Wahl, Bragg, and others, that the structure of the methane molecule must be very compact (work of Wahl). In such a case the probability of impact by fast-moving particles would be less, hardly any time being given for the linking of the fields indicating impact because of the smallness of the field of relatively inactive substance.

Himstedt and Dechend,[13] in trying to obtain the spectrum of methane, found that its decomposition gave hydrogen ions and the Swan spectrum. To all appearances, it seems, they did not speculate as to the nature of the hydrocarbons giving the Swan spectrum.

Noteworthy is the work on the dispersion of light in gases by Loria.[14] Values were obtained for several wave-lengths and the constants in Cauchy's formula determined:

Wave-Length $\lambda \times 10^{-5}$ =
6.585 6.375 5.9355 5.718

In Cauchy's formula $n - 1 = a(1 - b/\lambda^2)$, $a = 0.00042607$, $b = 1.441 \times 10^{-10}$.

Von Bahr[15] investigated the effect of pressure on absorption of ultra-red rays by gases. Great effect was shown and gases were proved to have a maximum absorption for certain pressures. It should be pointed out that this observation is of exceeding importance in determining the optimum pressure for chemical reactions of methane which are furthered by ultra-red rays.

E. Parr Metcalfe[16] found an additive law showing the effect of molecular grouping on the ionizations of methane, ethane, etc.

The results obtained by Soddy and Berry[17] on the heat conductivity of rarefied gases indicates a better conductivity for methane than for hydrogen. The number of calories which are conducted at 0.01 mm pressure through a cubic centimeter for 1° C temperature difference between surfaces is as 2.7 in the case of methane to 2.29 in the case of hydrogen. For higher pressures hardly any data are available. Such would be of use in the theoretical treatment, at least, of the velocity of flame propagation, and ignition of methane.

4. Application of Physical Characteristics Industrially

The data concerning the boiling point and freezing point of methane will assume greater importance, as a commercial process is developed, for the liquefaction of methane. There are further possibilities for the use of methane as a constant temperature liquid bath for reactions and investigation at low temperatures. A process may indeed be developed for the purpose of obtaining low temperatures by the expansion of the liquid methane to a gas. It comes in conveniently between the ranges covered commonly in low temperature work. Whether the liquefaction of methane for such purposes would be a commercial proposition would be more easily seen after some development. Considering the volume relations for a methane explosion, and the limits of explosibility, the transportation of the liquefied gas is likely to be attended with no greater danger, and probably with less danger, than that of any other highly compressed gas. There is therefore considerable room for exploiting the physical properties of methane to a greater extent commercially.

B. CHEMICAL CHARACTERISTICS OF METHANE

1. Combustion and Explosion of Methane

The burning and explosion of methane has always been a serious problem. Aside from the natural interest taken in the prevention of mine accidents, other useful practical applications have been sought for.

The study of the lower and upper limits of inflammability of methane with mixture of nitrogen or oxygen or air by Parker,[18] Taffanel and LeFlock,[19] Coward and Brinsley,[20] LePrince-Ringuet,[21] Burgess and Wheeler,[22] Wheeler,[23] Burrell and Robertson,[24] produced a mass of rather contradictory data on the subject. The results may, however, be summarized as follows: According to Prof. Enrique Hauser in his Leçons sur le Grisou (Madrid, 1908) one gets different limits of inflammability depending on the direction in which the flame has to travel. The variations arising therefrom are enough to change values 5.4 percent to 6.0 percent or 13.4 percent to 14.8 percent equivalent to a 10 percent variation. With this in view the data of the various workers may be consulted more intelligently. Some other generalizations are possible, as, that the lowering of the temperature of the gas raises the lower limit of inflammability. The condition necessary for the ignition of explosive mixtures is that the temperature of the constituents should be raised, at least locally, to a degree at which the mass of the gas self-heats by combination until it bursts into flame, *i. e.*, until chemical action becomes autogenous or self-propelling.

Dixon and Coward[25] (1909) state that the temperature at which ignition occurs lies within a very narrow range in cases where the mechanism of combustion is probably simple, for example hydrogen and carbon monoxide, and within the limits of experimental error they are the same for air as for oxygen (Hydrogen 580°–590° C; Carbon monoxide 640°–658° C). However, if the mechanism of combustion is very complex, as in the case of hydrocarbons, the ignition range is either fairly large or materially lower in oxygen than in air (for methane in air, 650°–750° C; in oxygen, 556°–700° C). An explanation for this is to be found in the fact that the combustion is not simple, because of the fairly rapid interaction between the inflammable gas and the oxygen before the ignition point is reached. If such interaction were to be suppressed somehow, or made very rapid, as it is in the case of ethylene, the ignition range would become smaller (ethylene 542°–547° C in air; 500°–519° C in oxygen).

Besides the method of ignition by heating the constituents separately and then mixing, or by heating some one spot in the mixture, two other methods have been used: ignition by adiabatic compression and more commonly, by sparking. Nernst recommended the first of the two alternative methods, provided (1) the ignition is not produced merely locally, and (2) the piston of the apparatus does not move appreciably after the gas has been raised to the ignition temperature. This method is a rather difficult one because of the last proviso mentioned. Consequently considerable doubt has been cast on the results obtained by this method, as the work, for instance, of Falk in America showing that hydrogen peroxide is first formed in the combustion of hydrogen and oxygen.

The mathematical relation for estimating the temperature of ignition from the initial temperature and the initial and final volumes is

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{j-1} \quad j = 1.41$$

Dixon's photographic analysis of the flame in hydrocarbon combustions showed that it took time for the flame to spread. This indicated that even more refined precautions for stopping the piston were necessary in the method discussed above, because the real ignition point is not synchronous with the appearance of the flame. The pre-flame period is negligible only in the fastest burning mixtures.

That ignition may not be a thermal problem purely is indicated from results obtained by Dixon, Bradshaw and Campbell.[26] The addition of hydrogen and nitrogen raised the ignition temperature of various mixtures. This can be explained by considerations of dilution and the fact that hydrogen has a high thermal conductivity. The addition of oxygen, however, lowered the ignition point. A possible explanation would be that perhaps some polymeride of oxygen is formed. This is difficult of proof, but the fact in itself seems to warrant the conclusion given above.

The pressure and temperature may vary over a rather wide range without affecting explosibility. Variations are introduced in the results by the method of ignition, nature of the source of ignition, size and shape of the containing vessel. Inaccuracies in the mixing and analyzing of the gases may be avoided. The largest range of inflammability has been obtained by Burrell and Oberfell[27] (making spark at the bottom of a box by pulling two wires apart, carrying 7 amperes at 220 volts) with a minimum of 4.9 percent of methane to a maximum percentage of 15–15.4 percent.

The above studies dealt principally with the explosibilities of mine mixtures. A further application would lie in the development of a motor not to run on methane (natural gas) but on a mixture of methane and other hydrocarbons and air. With the certain development of alcohol motors, the introduction of a percentage of methane (dissolved or under some pressure in the alcohol) is sure to be of aid. Of somewhat greater importance perhaps would become the work on the velocity and mode of propagation of the methane flame; by Parker and Rhead[28] who found a maximum flame velocity of 70 cm per second; by Burgess and Wheeler,[29,30] Parker;[31] and the work on ignition temperatures of gases by Dixon and Coward,[32] who found the value for methane in air to be from 650° C to 750° C, with 10° C variation, depending on the rate of flow of the gas, and independent of the form, material, or surface of the apparatus; or the work of Bucher[33] showing the negative influence of hydrogen on the velocity of ignition of methane; or that of Thornton[34] on the ignition of coal gas and methane by momentary electric arcs, showing that at 20 volts no ignition occurs and hence electrical signalling is safe.

2. Solubility of Methane in Various Solvents

A field, which is very promising and has not as yet been covered as it should, before being dropped, is the investigation of the solubility of methane in various solvents. A. S. McDaniell[35] gives the solubilities of methane in methyl, ethyl and other alcohols, benzene, toluene, *m*-xylene, hexane, heptane, and pinene. McDaniel's determinations were very carefully made in a specially designed apparatus, making certain of the saturation of the liquid with methane, and with a certainty that air was excluded from the experiment. The figures for the ratio of the volume of gas to liquid in these cases are:

Solvent	$\frac{\text{cc gas}}{\text{cc solvent}} = A_{25°}$ C.
CH_3OH (99%)	0.4437
C_2H_5OH (99.8%)	0.4581
(Iso) $C_3H_7OHCH_3OH$	0.4584
$C_5H_{11}OH$	0.4500
C_6H_6	0.4844
$C_6H_5CH_3$	0.4852
(*m*) $C_6H_4(CH_3)_2$	0.5096
C_6H_{14}	0.5918
C_7H_{16}	0.7116
Pinene	0.4623

The values of $\frac{dA}{dt}$ vary greatly for the same liquid in many instances, and therefore predictions as to the solubility at other than observed temperatures are unsafe. In general, however, absorption increases as the temperature decreases. The solubilities, of course, have a negative temperature coefficient.

A good many solvents have as yet to be tried out. In particular the authors would recommend mixtures of various solvents. Some values precisely obtained are:

1 volume of water at $t°$ absorbs
$0.05449 - 0.001807t - 0.00001028t^2$ volumes of methane
1 volume of alcohol at $t°$ absorbs
$0.522586 - 0.00286550t - 0.0000142t^2$ volumes of methane

It may be of some importance to point out that substances of high molecular weight, saturated and unsaturated, would probably give higher coefficients of absorption (e. g., oleic acid, linoleic acid). There is also likelihood of a relation existing between the index of refraction, the viscosity, and the critical constants, on the one hand, and the absorption coefficient on the other. This likely relationship would show up on further research of an experimental character on the above physical constants.

The solubility of methane in various solvents may have tremendous industrial application. A solution of methane in pentane, heptane, benzene, or ethyl alcohol under pressure may be an ideal motor fuel for aeroplane engines which are subjected to sudden temperature changes of 60° C or more in a relatively short interval of time.

The reseaches merge into more strictly chemical lines when we find the work by Worstall[36] on the absorption of methane by fuming sulphuric acid. He was interested in showing that the absorption was within the limit of error in analysis. However, there is a very small absorption, which hardly can be explained as a chemical reaction and must be explained on the grounds of solubility.

The effect of oxidizing agents, as nitric and chromic acids, has been studied but little. Though the action may be very slight ordinarily, there seems to be no reason why it could not be accelerated catalytically. There is a total lack of data on this field.

There is no essential reason in the opinion of the authors why methane should not be capable of nitration and sulphonation directly. It is a known fact that even the lower aliphatics may be sulphonated, by the use of oleum. The conditions required are

1. Sufficient concentrations of the reacting substances.
2. Very intimate mixing.
3. Proper temperature.
4. Catalyst.

In case of gaseous constituents the effect of pressure is obvious. The syntheses which could be carried out with such a process as a starting point would produce valuable products like formaldehyde simply and more complex compounds by coupling.

3. Occlusion of Methane

A property of physico-chemical interest is the occlusion of methane by metals. B. Delanchal[37] has studied the occlusion of methane by some common metals.

From 1,000 grams of tin he obtained on heating:

	Cc
Methane	2.80
Hydrogen	3.25
Carbon monoxide	2.05
Carbon dioxide	1.44
Nitrogen	1.56

From 144 grams of commercial platinum:

	Cc
Methane	3.67
Hydrogen	0.47
Carbon monoxide	4.05
Carbon dioxide	0.70
Nitrogen	1.31

The gases were obtained from commercial specimens and very little was done to check occlusion by *pure* metals. However, it is possible that the methane is not occluded by the metals, but forms during the heating from hydrogen and carbon monoxide previously occluded. Since the equilibrium between hydrogen, carbon monoxide and methane differs with the temperature, further work along this line will aid in discovering the truth of the matter, if various temperatures were to be tried in the expulsion of the occluded gases. The bearing a further research on the occlusion of methane would have on the catalytic ignition, burning and oxidation of methane, is likely to have significance industrially.

The ideas on occlusion may have a rather important bearing on the choice of material for methane reactions. It seems that occlusion by palladium and other catalyst metals has not been investigated. In the search for catalysts, of course, the numerous oxides and organo-metallic compounds which have found such wide application elsewhere should be tested.

Among the non-metallic substances which occlude methane is coal. The latest discussion of the matter may be found in a pamphlet by S. H. Katz.[39] For further information as to earlier experiments, the reader is asked to refer to Richters,[40] Thiessen,[41] Le Prince-Ringuet,[42] Graham,[43] Porter and Ovitz,[44] Mahler,[45] Porter and Ralston[46] and Winmill.[47]

Katz reports a series of experiments on the absorption of gases from the various mixtures of Pittsburgh bituminous coal:

1. At ordinary temperatures newly mined coal quickly absorbed methane from an atmosphere of air containing about 5 percent of admixed methane, the absorption being about 0.08 cc per gram of coal. Equilibrium was obtained after 4 hours.

2. Under the same conditions, coal that had been exposed to the action of room air for 5 weeks, with resulting loss of methane, absorbed 0.16 cc or twice as much methane. Equilibrium attained in 4 hours.

3. The coal in equilibrium with nitrogen absorbed methane in amounts that increased with increase in the partial pressure of the methane.

4. With absorption of the methane there was an evolu-

tion of nitrogen in amounts somewhat less than the amount of methane.

5. Coal in equilibrium with a mixture of nitrogen with methane absorbs gas with a fall in temperature and evolves gas with a rise in temperature.

6. If the temperature is held constant at a certain point, then allowed to vary and again held constant at that point, a definite equilibrium between coal and gas is repeatedly established. The author claims that the absorption of gas by coal is closely analogous to the absorption of gases by charcoal.

It would be desirable that such investigations should be conducted with a somewhat different point of view. Coal, gram for gram, is a better "solvent" for methane than the usual liquid solvents. And besides, why not try coal as a catalyst in methane reactions?

4. Miscellaneous Physico-Chemical Properties

L. T. Wright[48] has investigated the luminosity of methane and found about 5.2 candles per 5 cubic feet per hour.

Some little work on the catalytic ignition of methane of practical application has been done by Dixon and Lowe[49] on the effect of incombustible dust on the ignition of methane.

Even the radioactivity of methane has been investigated. J. Satterly[50] gives some interesting results. It is marsh gas, however, that is radioactive rather than methane.

5. Industrial Reactions of Methane

Oxidations

Only a few chemical reactions of methane have been utilized commercially. Some are, however, of great promise.

Lance,[51] English patentee, deals with the making of methyl alcohol from methane. He uses hydrogen peroxide, with or without ferrous sulphate or monopersulphuric acid, or with monopersulphuric acid alone.

An important patent of the Sauerstoff und Stickstoff Industrie Hausmann und Co.[52] deals with the production of formaldehyde, and eventually methyl alcohol and formic acid from methane mixtures of air or oxygen. The gases are passed over granulated copper at 600° C. If fatty substances are used as contact masses, as for example, tan bark, the process may be carried on at 30°–50° C.

A patent by von Unruh[53] deals with the oxidation of methane by tan bark and similar materials.

Halogenation of Methane

Halogenation of methane in various stages has offered and still offers a fruitful field of research. Patents[54-65] on the formation of chloroform and of carbon tetrachloride have been taken out in numbers. Methyl alcohol may also be made from methyl chloride which comes from methane. To complete the series one may mention the work of F. Swarts[66] on fluorine derivatives of methane and that of A. Byden[67] and G. Guerin[68] on bromine and iodine derivatives of the gas.

A review of the work on the lower chlorides of methane from natural gas is given by various writers, notably C. W. Bedford,[69] Baskerville and Riederer.[70] The evolution of the subject and its present state are as follows: Berthelot, in 1858, found that unless chlorine and methane were made to interact very slowly explosions took place with a separation of carbon. This was not very encouraging and practically nothing of consequence was done till 1893 by Phillips, who chlorinated methane without light at 300°–400° C, obtaining only the first and last chlorides. Walter[71] bases his patent on the fact that water retards the reaction, and the fact that if the chlorine is added gradually it reacts selectively with the already chlorinated product rather than methane to form carbon tetrachloride.

Baskerville and Riederer[70] found that the blue end of the spectrum was more suitable than the ultraviolet in chlorination reactions. They have a process of making carbon tetrachloride and then reducing to chloroform. The reason why decomposition occurs is found in the fact that according to thermochemical calculations there would be a rise of 2000° C if all the heat of the reaction were to go toward the raising of the temperature of the mixture. As the temperature rises, of course, the methane begins to decompose. If thin tubes are used the radiation takes care of the rise of temperature and decomposition is avoided. In reactions involving the making of chloroform, the temperature must be low enough to condense out the chloroform. This is equivalent to getting it out of the sphere of action and thus avoiding chlorination to carbon tetrachloride. C. W. Bedford[69] found that the less chlorine used, the stronger the light necessary. Very good results may be obtained by using ice cooling and strong light, as the white flame arc. According to his patent, methane and chlorine are caused to react in a chamber filled with pieces of ice and having a window and curtain for regulated admission of actinic light. Various other halogenation reactions may be similarly carried out with gaseous materials, starting with methylene chloride to make chloroform or with methane to make carbon tetrachloride, or with ethane or methyl chloride and chlorine and using either ice or a shower of water to control the temperatures of the reacting materials and thus regulate the degree of chlorinations. By keeping the temperature and supply of chlorine low in chlorinating methane, methyl chloride nearly free of higher chlorination products of methane may be obtained.

Carbides Formed from Methane

Various carbides have been prepared from methane. J. Novak[72] notes that the decomposition of methane begins at 600° C in presence of magnesium. MgC_2 forms in traces at 733° C. A maximum formation of Mg_2C_3 occurs at 760° C. S. Helpert and J. Paunesen[73] prepared the carbides by manganese by heating the metal in the presence of a current of methane. Five percent of the carbon in methane is absorbed at 600° C. At 700° C the carbon content of the product is 25 to 28 percent. At 900° C a 50 percent mixture of hydrogen and methane is 15 percent reacted upon by the metal. When the products containing up to 8 percent are put in dilute hydrochloric acid, methane is obtained and a small percent of ethylene. The products containing more than 8 percent carbon gave a carbon slime and fatty substance and a very small percent of unsaturated hydrocarbons.

An observation which may turn out to be of some importance in the production of lamp-black from methane is that during the formation of magnesium carbides, carbon separates out very strongly at 20° C.

Of interest may be then the carbides of magnesium. MgC_2 has its limit of existence at 600° C. It can, however, be shown to be present in traces up to 1030° C. Its decomposition starts at 490° C. No suitable solvent has been found for MgC_2 up to the present. It is decomposed energetically by water. Magnesium carbide (Mg_2C_3) is also not stable at high temperatures. The decomposition starts at 700° C and at 780° C it is found present only in traces. In spite of this it can be shown to be present up to 1200° C; and both carbides can also be produced by the action of magnesium upon alcohols, ketones, aldehydes, acetylene, ethane, etc., by heating carbon and magnesium at 530° to 740° C.

The decomposition of manganese carbides might lead to similar results. The reaction of making carbon from methane may therefore take place in two steps, or the metals, manganese and magnesium, may be introduced in such a manner as to bring this about in one so-called catalytic reaction.

The above investigation should be pushed by all means since it has apparently an important bearing on the possible catalytic transformation of methane into fatty substances, the metal acting as a condensing agent.

The types of reaction occurring in the electric arc or under varying temperature and pressure conditions will be taken up in the subsequent portions of the paper.

Cyanides from Methane

The processes for making cyanides from methane are varied in that in some cases nitrogen alone is used, in other cases air, in others hydrogen is added to the nitrogen, and in still others ammonia is used.

Some representative processes follow: Gow (U. S. Pat. 801,728) mixes natural gas (95 percent methane) with nitrogen or air and passes the mixture through an arc, a sputtering arc giving the best results. Sinding-Larsen (U. S. Pat. 1,042,723), passes nitrogen and the vapors of hydrocarbons through the system. He obtained thereby nitrides of aluminium and silicon and in the volatile constituents ammonia and hydrocyanic acid. Moscicki and Jablczynski, U. S. Pat. 1,050,978, manufactured hydrocyanic acid from a repeatedly used gas mixture containing nitrogen, hydrogen and hydrocarbon at high temperature and subsequent cooling, preventing increase of the hydrogen by removing the same from time to time. The heating is done in an electric furnace having a revolving high tension flame, the temperature reaching 2500 to 3500° C.

Attempts have been made to use catalysts, such as copper. Commerical results are claimed to be obtainable at 500° C. (Beindl, U. S. Pat. 1,144,457.)

Liebknecht (U. S. Pat. 1,235,342) has a process for the production of hydrocyanic acid from nitrogen, hydrogen, and hydrocarbons in an electric furnace containing a high voltage arc at a pressure of approximately 1.6 atmospheres. 50 grams of hydrocyanic acid per kilowatt hour were produced from a mixture of 5.3 percent carbon monoxide, 8.3 percent methane, 33.7 percent hydrogen and 42.7 percent nitrogen.

Amongst foreign processes, the Lipinski process has received the most consideration. Lipinski reports that on passing an electric discharge through a mixture of nitrogen, hydrogen and methane, the last mentioned may be changed to hydrocyanic acid entirely. A favorable mixture is 10 percent of hydrogen, 20 percent of methane, and 70 percent of nitrogen. The yield of hydrocyanic acid is equivalent to 19 percent of the mixture. The large excess of nitrogen is necessary to prevent the separation of free carbon. Evidently ordinary coal gas can form a basis for the preparation of such a mixture.

Roessler reports that 4 liters of a gas mixture of nitrogen and marsh gas passed through a flame of 1000 volts; 0.8 ampere gave 0.75 gram of hydrocyanic acid.

An experimental apparatus is described by Muthmann and Schaidauf which consisted of a 1500 cc glass alembic containing 4 tubes, of which only two carry electrodes, while the other two serve as inlet and outlet tubes. In the reaction vessel an excess pressure of 40 cm is maintained during the operation. The current source was an alternating current of 50 cycles per second, which furnished at 93 volts a maximum of 43 amperes. The electrodes consisted of wires of silver, gold and platinum which were screwed into cooled copper rods. The outgoing gases were analyzed and from the results the amount of decomposition occurring in the flame was calculated. The reaction between methane and nitrogen by this method gave just hydrogen cyanide and hydrogen.

RÉSUMÉ OF PHYSICAL-CHEMICAL CONSTANTS OF METHANE

Specific gravity (air = 1)	0.559
Boiling point	—164° C, 760 mm
Melting point	184° C
Freezing point	—185.8° C
Solidifying point	—186° C
Triple point	—183.15° C, 70 mm
Triple point	—185.8° C, 80 mm
Critical temperature	—82.85° C
Critical pressure	45.6 atmospheres
Critical density	0.1623
Critical density	0.1519
Coefficient of expansion	$3681/10^6$ $3679/10^6$
Specific gravity of liquid	0.415
Heat of formation at constant pressure	21,750 cals.
Heat of formation at constant volume	21,170 cals.
Heat of combustion	213,500 cals.

CH_4 forms a hydrate with water at —2° C under 30 atmospheres

C. SYNTHESIS AND DECOMPOSITION OF METHANE

1. Direct Union of Carbon and Hydrogen

In spite of the fact that Dalton, as far back as 1809, investigated the methane equilibrium with its elements, no work of any great consequence was done till recently.

Bone and Coward[74] initiated a long series of experiments when starting with very pure carbon and hydrogen; they succeeded in turning 75 percent of the carbon to methane at 1100°–1200° C. In their experiments no doubt a part of the gases were lost through the walls of the reaction tube. For example, they obtained 422 cc of methane from 0.306 g carbon. They also noted that platinum furthered the reaction.

J. N. Pring[75] discovered that at 1200° C the reaction velocity was very slow, that is, it took 22 hours to form 0.35 percent methane. Under these conditions the rate of decomposition was even slower. At 1500° C 2 hours equilibrium gives 0.17 percent. Greatest values were obtained using platinum between 1050°–1500° C. At 1200° C 0.55 percent and at 1500° C 0.30 percent were obtained from both sides. Above 1550° C more and more methane is obtained because of the decomposition of acetylene, although the amount of the latter at 1850° C is too small for analysis. It can be shown, however, that above 1500° C acetylene is converted into ethylene and methane. Incidentally it was observed that carbon monoxide seemed to have no influence on the equilibrium of methane at the temperatures under consideration, and that it did not change the velocity of reaction.

The relationship used by Pring was as follows:

$$K_T = -18{,}507 + 5.9934T \log T + 0.002936T^2 + RT \log \frac{CH_4}{(H_2)^2}$$

The constant K was found in the above equation to be 21.1 by Mayer and Altmayer. The apparatus used in the experiments was a rod of carbon or graphite tube with a narrow slit along the top, inside of which the carbon to be used was placed. All contact between the heated carbon and everything else but the hydrogen was carefully avoided by the experimenters. The percentage of methane was determined by removing the hydrogen present by means of palladium; acetylene by formation of cuprous acetylide or silver acetylide; and the other gases by suitable means, and finally exploding the methane present with oxygen. The carbon used in the experiments was derived from sugar charcoal carefully purified by alternately treating one hour with chlorine, nitrogen and hydrogen at 1550° C and then for one-half hour *in vacuo* at 1220° C. When using amorphous carbon, upon which platinum was deposited as a catalyser, and heating to 1050° C for one and one-half hours, characteristic results gave 0.052 percent of carbon monoxide and 0.866 percent of methane.

Further work by Pring and Fairlie[76] on the synthesis of hydrocarbons at high temperatures has an important bearing upon the equilibrium of methane. According to their experimental results carbon and hydrogen combine to form methane between 1200° C and 1500° C while ethylene forms at temperatures above 1700° C. In the presence of hydrogen either ethylene or acetylene forms methane at temperatures above 700° C.

The authors attempted to apply Haber's equation to the equilibrium of methane:

$$\log_e \mathrm{K} = \frac{\mathrm{Q}_\circ}{\mathrm{R}_t} - \frac{\sigma \log_e \mathrm{T}}{\mathrm{R}} - \frac{\sigma_{\mathrm{I}}\mathrm{T} + \sigma_{\mathrm{II}}\mathrm{T}^2}{\mathrm{R}} + \frac{\mathrm{K}}{\mathrm{R}} \quad \mathrm{K} = \frac{\mathrm{CH}_4}{p(\mathrm{H}_2)^2},$$

where $\mathrm{Q}_\circ$ is the heat of reaction at absolute zero, and $\sigma, \sigma_{\mathrm{I}}\mathrm{T} + \sigma_{\mathrm{II}}\mathrm{T}^2$ are the sums of the specific heats at constant pressure of the substances disappearing, carbon and hydrogen; and the substance, methane, appearing. The constant K is a quite indeterminate value, known as 21.1 between the temperatures of 250° C and 850° C. At the temperature of 1200° C Haber's equation gives the equilibrium ratio $\mathrm{CH}_4/(\mathrm{H}_2)^2 = 0.07$.

The specific heat value was omitted because it was not known. Furthermore, it was recognized that the variables of the equation were not sufficiently precise for calculations involving high temperatures.

The materials used were of the following purity: The hydrogen analyzed 98 percent with the balance as nitrogen. The carbon gave a two percent impurity composed of the oxides of silicon, iron and other substances. The methane was generated by the action of water upon aluminium carbides which gave a number of other gases such as hydrogen sulfide, acetylene, etc., which were removed by the usual means. The residual gas was liquefied and the methane evaporated off.

The furnace used in the experiments was of special design, having a capacity of 750 cc, and pressures of 100 to 200 atmospheres were applied during operation. At a temperature of 1275° C an analysis of the gas gave 0.002 percent acetylene and 21 percent of methane.

The synthetic formation of methane from the elements proceeded with greatest rapidity at high gaseous pressure. The equilibrium of methane formation was reached after a period of two hours with the use of carbon in a compact form, with or without catalyst, at temperatures of 1200° C to 1300° C and pressures 30 to 50 atmospheres. At temperatures above 1400° C equilibrium was reached in fifteen minutes while at 200 atmospheres the reaction was much more rapid in reaching equilibrium. When carbon was used in a finely divided condition with hydrogen at high temperatures, the reaction reached equilibrium with great rapidity, the reaction being endothermic in character. Under the conditions of temperatures of 1100° C to 1200° C and pressures up to 200 atmospheres no other saturated paraffin hydrocarbons were formed except methane. The ratio of $CH_4/(H_2)^2$ under the above conditions was found to be constant and represents the true equilibrium constant K. The change of free energy in the transformation of carbon into graphite increases rapidly in the range of temperatures from 1200° C to 1600° C; however, the values for amorphous carbon are not quite so definitely known for graphite on account of the gradual transformation which the former undergoes into the latter at the temperatures utilized in this set of experiments.

By application of Kirchhoff's law relating to specific heats one can see that the mean specific heat of amorphous carbon must be much higher than that of graphite between

0° C and 1200° C and that this difference increases with increase of temperature.

The 0.002 percent of ethylene formed at 1275° C does not exert any appreciable effect upon the methane yield, the latter being 21.5 percent. At temperatures between 1800° C and 2100° C by exerting high pressures upon the system no appreciable effect was noted on the yield of ethylene and acetylene when the results are compared with those obtained in earlier work at atmospheric pressure.

The work of Pring and Fairlie may be summarized in the statements

1. Acetylene is not formed below 1200° C.
2. Methane forms about one hundred times as rapidly as ethylene.
3. At 1400° C the ratio of ethylene to methane is 1 : 10.
4. At 1650° C acetylene appears.
5. Methane probably forms directly from the elements.

Similar results are reported elsewhere by Pring and Fairlie[77] for temperatures 1100° C to 2000° C and pressures of 10 to 200 atmospheres. They point out that the velocity of methane formation increases very rapidly with increase of pressure and that the ratio of $CH_4/(H_2)^2$ is constant for any given temperature and pressure. Furthermore, when amorphous carbon was used the percentage yield of methane was greater, a fact which they attributed to a metastable condition. No appreciable effect was noted upon the percentage yields of acetylene or ethylene with increase of pressure and no other hydrocarbon formation was observed. The term "metastable equilibrium" was used to cover the same multitude of sins now more popularly covered by such terms as "free energy," "surface action," and a host of et ceteras.

Of no less interest is the direct synthesis of methane with the aid of catalysts. Ipatiev[78] is responsible for some work with metals and the oxides of the metals. Disagreeing apparently with Mayer and Altmayer, who assume that the synthesis of methane in the presence of nickel is aided through the hydrogen compounds of this metal, he explains the phenomena through the coöperation of the metallic oxide which can produce catalytic oxidation and reduction. The outline of reaction is as follows:

Actor H_2 — NiO catalyser : Actor H_2 — C acceptor

The nickel oxide oxidizes the carbon present to carbon dioxide and the latter is reduced by the hydrogen according to the reversible reaction

$$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O.$$

The water formed during the reaction in turn oxidizes the metal to the oxide which means the regeneration of the metallic oxide. This process being a continuous one, a small amount of oxide can cause a relatively large percentage yield of methane. Support of the correctness of this view was sought in the fact that at least a small amount of water was necessary in this as well as in many other well-known reactions, and that the reaction represented by the above equation is reversible. This is proved by numerous experiments made at different temperatures and pressures with varying concentrations of gases. The carbon used in the experiments was of a 99 percent purity and the hydrogen was further purified from extraneous gases present by potassium hydroxide, potassium permanganate, copper sulphate, sulphuric acid, and cupric chloride. The synthetic production of methane from the elements in the presence of reduced nickel under high pressure takes place at temperatures of 510° C to 520° C. The following examples are illustrative:

A. Three grams of nickel oxide at 510° C and 110 atmospheres pressure gave at the end of twenty-six hours 6.5 percent of methane.

B. Three grams of stannous oxide at 515° C and 102 atmospheres pressure gave at the end of seventeen hours 6.2 percent of methane.

Further experiments showed that the higher the temperature the greater the yield of methane, but that there is a temperature limit beyond which the reaction cannot be carried because of hydrogen diffusing through the walls of the reaction zone. Experiments further indicated that methane in the presence of reduced metals and water can be decomposed with separation of hydrogen, but with zinc dust at a temperature of 502° C no decomposition took place.

The following general conclusions may be drawn from the above work:

1. From a large excess of hydrogen in relationship to the carbon dioxide no complete reduction of the carbon dioxide can take place.

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$$

2. With too great excess of carbon dioxide, free hydrogen was always found to be present, less being present the larger the original concentration of the carbon dioxide.
3. The use of catalysers as nickel oxide and reduced nickel acted similarly in reducing carbon dioxide but the action of cupric oxide was much weaker than the nickel catalysers.
4. With concentrations of hydrogen and carbon dioxide which approach the theoretical values, reduction approaches a certain limiting value.

The work done by others before Bone and Coward is as follows: 1809, Dalton and William Henry[79,80] studied the decomposition of methane and ethane by subjecting them to the action of electric sparks. 1839, Marchand[81] proved that the ultimate resolution of hydrocarbons into elements at high temperatures is not in general the immediate result of a single chemical change. He obtained much methane on decomposing ethylene. 1860, Buff and Hofmann[82] supported the above conclusion. The decompositions were performed by means of platinum wire. V. B. Lewes also remarked that the denser hydrocarbons were formed at incipient red heat. 1863–69, Berthelot[83-86] maintained that hydrocarbons are never directly resolved into elements. The primary change is either polymerization (*e. g.*, acetylene to benzene) or coalition of two or more molecules to form denser hydrocarbons with the elimination of hydrogen and so on to carbon.

$$\begin{array}{ll} 2CH_4 = C_2H_2 + 3H_2 & 2CH_4 = C_2H_6 + H_2 \\ C_2H_6 = C_2H_4 + H_2 & 2C_2H_6 = 2CH_4 + C_2H_2 + H_2 \\ C_2H_4 = C_2H_2 + H_2 & 2C_2H_4 = C_2H_6 + C_2H_2 \end{array}$$

1873, T. E. Thorpe and S. Young showed that primary decomposition gives olefine and lower paraffin.

$$CH_3CH_2CH_2CH_3 = CH_3CH_3 + CH_2CH_2.$$

1886, Armstrong and Miller[87] suggested the formation of benzene directly from hexane, no acetylene being present in oil gas from petroleum. 1894–5, V. B. Lewes[88,89] adduced evidence as to the formation of acetylene from methane. 1896, Haber[90] noted that on the primary decomposition of *n*-hexane between 600°–800° the elimination of methane was involved,

$$CH_3CH_2CH_2CH_2CH_3 = CH_3CH_2CH_2CHCH_2 + CH_4$$

and that, the tendency in the aromatic series was toward the formation of more complex molecules.

$$2C_6H_6 = C_{12}H_{10} + H_2.$$

1897, Bone and Jerdan[91,92] stated that at 1000°–1200° C methane is the only hydrocarbon formed synthetically.

Some of the conclusions reached by Bone and Coward are

1. Methane is the most stable of the hydrocarbons. It is the principal product of the decomposition of the three hydrocarbons considered, acetylene, ethylene, and ethane, especially above 800° C. Methane is decomposed mainly into carbon and hydrogen with evidence of a surface reaction.
2. The decomposition of acetylene, ethylene, and ethane is not a surface one.
3. Acetylene is the principal product of the decomposition of ethylene and not of methane and ethane, Lewes' equation being disproved thereby.
4. Acetylene polymerizes at low temperatures, the maximum value being attained at 600°–700° C, and little being in evidence at 1000° C.

5. Acetylene and ethylene show a tendency to combine with hydrogen at low temperatures to form ethylene and ethane, respectively. This tendency is found to be negligible at 1000° C.
6. One of the principal factors at 800° C and above is the direct hydrogenation of residues as $:CH$, $:CH_2$ and possibly $.CH_3$ to methane when the atmosphere is rich in hydrogen.
7. Berthelot's theory is disproved. (Berthelot's theory is that hydrocarbons are never resolved into their elements directly.)
8. No single equation will do to express these reactions.
9. Equations may, however, be given for intervals, *e. g.*,

$$C_2H_6 \longrightarrow C_2H_4 + H_2 \longrightarrow C + CH_4 + H_2.$$

10. The primary effect of temperature on C_2H_6 and C_2H_4 is to form $:CH_2$ and $:CH$ which may (*a*) form $H_2C:CH_2$ and $HC:CH$, (*b*) break down to C and H, (*c*) be hydrogenized to CH_4, or (*a*), (*b*), and (*c*) simultaneously.

The reactions may be written:

$$\begin{array}{l} \mathrm{H : H} \\ \mathrm{HC : CH} = 2(:\mathrm{CH_2})_2 + \mathrm{H_2} = \\ \mathrm{H : H} \end{array} \left\{ \begin{array}{l} (a)\ C_2H_4 + H_2 \\ (b)\ 2C + 2H_2 + H_2 \\ (c)\ \text{plus } H_2 = 2CH_4 \end{array} \right.$$

$$\begin{array}{l} \mathrm{H : H} \\ \mathrm{HC : CH} = 2(:\mathrm{CH}) + \mathrm{H_2} = \\ \end{array} \left\{ \begin{array}{l} (a)\ C_2H_2 + H_2 \\ (b)\ 2C + H_2 + H_2 \\ (c)\ \text{plus } 2H_2 = 2CH_4 \end{array} \right.$$

11. C_2H_2 polymerizes as follows:

$$\mathrm{HC:CH} = 2(:\mathrm{CH}) = \left\{ \begin{array}{l} (a)\ 2C + H_2 \\ (b)\ \text{plus } 3H_2 = 2CH_4 \end{array} \right.$$

For these compounds the rate of decomposition is much slower than the rate of combustion. This explains why a flame is propagated by them, and why oxidation takes precedence.

Contact Catalysis of Methane

The phenomena of contact catalysis is of highly theoretical and industrial significance. In hydrocarbon reactions, contact surfaces play a more important role than is generally believed; for widely different results are obtained when a clean iron tube is used or when covered with carbon, or filled with some metallic or metallic oxide substance. Slater[93] in a series of experiments on the influence of different surfaces on the decomposition of methane used in a finely ground state, silica, anhydrous alumina, magnesium, calcium and barium oxide, wood charcoal, graphite, carborundum, iron and copper.

According to our present ideas of contact catalysis as enunciated by Bancroft,[94] catalysis in the presence of graphite should be less than in other cases, *i. e.*, in the direction of the formation of methane. This seems to be borne out by the following figures. Carbon as a product of the decomposition of methane favors least its synthesis.

Catalyst	Percent hydrogen	Catalyst	Percent hydrogen
CaO	15.6	Iron	73.1
MgO	11.4	Charcoal	69.4
Tube, empty	11.0	CaO	35.2
SiO_2	8.7	Tube, empty	10.1

Catalyst	Percent hydrogen	Catalyst	Percent hydrogen
Charcoal	33.9	Graphite	66.0
CaO	23.9	SiC	44.0
Tube, empty	16.2	Copper	27.9
SiO_2	12.3	Tube, empty	18.0
MgO	12.0	SiO_2	15.0
Al_2O_3	10.4		
BaO	6.5		

Hamburger[95] studied the influence of adding small amounts of methane and carbon monoxide to a tungsten lamp filled with nitrogen. He found that concentrations of methane as low as 0.14 percent were highly injurious, due to a carbide of tungsten forming and decomposing to carbon at high temperature. At a temperature of 3000° C the formation of cyanogen and hydrogen cyanide occurs in the presence of small amounts of methane and tungsten in a nitrogen-filled lamp.

2. Synthesis of Methane not Directly from the Elements

The work which established some of the physical constants and served perhaps as suggestion of the researches discussed in the previous section was that of Mayer and Altmayer.[96] This work was on the synthesis of methane from calcium hydride.

The calcium hydride used was made by passing hydrogen over metallic calcium at ordinary temperature or at "dark red heat." When hydrogen is passed over specially prepared calcium it is absorbed at a temperature of 240° C and more quickly at rising temperatures, but at 675° C calcium hydride is decomposed and it is best to keep the temperature above 270° C until the reaction ceases. The gray powder with carbon monoxide at a temperature of 500° C gave a methane yield of 65.6 percent but upon further increase of temperature the percentage yield of methane decreased. However, when the velocity of the gas is increased at 500° C the amount of methane increases, but there is obviously a limit to the velocity of carbon monoxide passage for increased yield of methane. The other products of the reaction are carbon and calcium carbide.

When carbon dioxide and calcium hydride react the maximum yield of methane occurred at 500° C of 60.24 percent. The following equation expresses some of the reaction products:

$$2CO_2 + 4CaH_2 \longrightarrow CH_4 + C + 2H_2 +$$

In this case calcium carbide is formed in lesser quantities, but there are traces of calcium formate formed and considerable quantities of calcium carbonate. At a temperature of 270° C soot and calcium hydride give hydrogen as a reaction product but methane is also formed at higher temperatures, the maximum yield being 40.68 percent at a temperature of 500° C. At the same temperature in a current of hydrogen 19 percent of methane was formed. During the reaction some calcium nitride was also produced, due to some nitrogen being present as an impurity.

The above constituted a first step in the direction of investigating the nature of catalytic formation of methane with the belief that it is promoted by the formation of hydrides.

In a series of papers, Mayer, Heuseling, Altmayer and Jacoby[97] investigated these and similar questions further and adduced the following facts:

1. Halogen substitution products of methane are reduced by hydrogen.
2. Berthelot obtained methane by the reduction of acetaldehyde and acetone.
3. Methane may be obtained by passing gaseous carbon disulfide with hydrogen sulfide over dark glowing copper.
4. Methane may be produced by the passage of carbon disulfide and antimony hydride through glowing pipes.
5. Methane may be produced from aluminium and manganese carbides with water.

In general, that reduction reactions will yield methane or in the case of hydrolysis, carbides will also do the same. Therefore the syntheses of methane from carbon monoxide, carbon dioxide and water or hydrogen were to be expected.

They observed that the velocity of methane formation from carbon monoxide and hydrogen, and from carbon dioxide and hydrogen proceeded with the same rapidity with nickel oxide as with nickel. When iron was used only small amounts of methane were formed which indicated that the iron was oxidized by oxides of carbon present. The greatest speed of reaction in methane formation occurred when finely divided carbon from the decomposition of carbon monoxide was used, while from graphite and from carbon obtained electrolytically methane was produced in small amounts only.

With the same catalysts further investigations were carried on, using water vapor in the form of steam in place of hydrogen.

$$
\begin{aligned}
CO + H_2O &\leftrightarrows CO_2 + H_2 \\
C + 2H_2O &\rightleftarrows CO_2 + 2H_2 \\
CO_2 + 4H_2 &\rightleftarrows CH_4 + 2H_2O
\end{aligned}
$$

The discoveries thus obtained were then extended experimentally to illuminating gas and the possible technical applications were discussed also with respect to the water gas process.

By thermodynamical applications these relations were more closely studied in the analysis of methane. Similarly the equations between carbon, carbon dioxide, and carbon monoxide were subjected to a new valuation. Finally they showed theoretically that through the combination of carbon dioxide and methane the quantitative relationship of the reactions may be established. If this last equation is combined with the expression of the water gas reaction, one obtains the equation for methane analysis:

$$
\begin{aligned}
CO + 3H_2 &\rightleftarrows CH_4 + H_2O \\
CO_2 + 4H_2 &\rightleftarrows CH_4 + 2H_2O
\end{aligned}
$$

The thermodynamic equations of Mayer and Altmayer and their co-workers were used in the preceding discussions.

A further review of the values tabulated by Mayer and Altmayer may be worth while. It will be remembered that the thermodynamic equation for the equilibrium shows that with decreasing hydrogen pressure the equilibrium pressure of methane rapidly falls. For instance, at 850° C a decrease of hydrogen pressure from 0.9841 to 0.1 atmosphere lowers the methane content from 1.59 to 0.16 percent and, looking over their table, one sees that as hydrogen and methane are frequently 82 to 90 percent of the coal gas product, some of the data given are applicable. At 604° C the rate of decomposition of methane per degree rise in temperature is at a maximum. Of course the hydrogen liberated by the decomposition of methane prevents by its accumulation of partial pressure the further decomposition of methane. Thus above 607° C the retarding action of $(H_2)^2$ pressure is already greater than the effect of heat in driving the reaction forward. As a result at 800° C there is less increase in the rate of decomposition per degree of temperature than at 400° C.

At the higher temperatures all tests show higher methane content than the equilibrium would lead us to expect. Several explanations could be suggested.

1. While some parts of the coal are at a moderate temperature, the methane produced there is not decomposed with sufficient rapidity during the time the gas is in the retort to correspond with equilibrium proportions. The truth of this contention may be indicated by an experiment showing that less methane is decomposed (about $^1/_3$ as much) in a packed tube than in an unpacked one in say 25 minutes.
2. The presence of hydrogen assists the decomposition of ethylene into methane and this secondary formation of methane would go to swell the methane content provided it were with drawn from the retort with sufficient rapidity to prevent the further decomposing effect of heat.
3. There is also a possibility of the steam reacting with the methane, namely,

$$CH_4 + H_2O \rightleftarrows 3H_2 + CO.$$

Tests, furthermore, show that at higher temperatures the yields of hydrogen and carbon monoxide are increased. There is, moreover, a gain in luminosity of the gas. It has been claimed, especially in carburetted water gas, that carbon monoxide has advantages in developing luminosity. The following reactions may occur in the interaction between the constituent gases in the luminous flame:

$$2CO + 2H_2 \rightleftarrows CH_4 + CO_2$$

A practical investigation on the synthetic production of methane was carried on by E. Erdmann.[98] Water gas freed from carbonic acid was conducted at 250° C over finely divided metallic nickel with the necessary amount of hydrogen to complete the equation

$$CO + 3H_2 = CH_4 + H_2O.$$

A difficulty was encountered in the fact that water gas produced in the usual way does not contain carbon monoxide and hydrogen in the correct proportions. Theoretically $3H_2 : CO$ are required, but practically 5 : 1 is needed. Furthermore, the nickel catalyst used was poisoned by the sulphurous gases, or by the deposition of a coat of carbon. Pure hydrogen was considered as too expensive for use. The hydrogen and carbon monoxide were segregated from blue water gas by physical means in correct proportions. The water gas is deprived by condensation at the temperature of liquid air of an amount of carbon monoxide to produce an escaping gas of only 17 percent carbon monoxide. The condensed carbon monoxide is then gasified and used for driving compressors. The extreme cooling also removed sulphur present. And finally the precipitation of the carbon can be prevented by diluting the carbon monoxide with hydrogen.

The above facts are made use of in the Bedford process. In this process the water gas is first purified in a water tower and then sawdust is used to remove the tar present. The carbon dioxide present is removed by compression to 10 atmospheres, the residue of 0.1 percent being removed by the use of lime, or subsequent liquefaction and absorption in cold alcohol. The gas now free of carbon dioxide contains 41 percent monoxide, 54 percent hydrogen and 5 percent nitrogen. At ten atmospheres pressure it is made to enter a Linde apparatus for the separation of carbon monoxide and hydrogen. The liquid carbon monoxide and nitrogen are collected in a receiver. The gas is split up into 2 parts, one 93 percent carbon monoxide, the other 5–14 percent carbon monoxide. These proportions depend on the adjustment of the expansion valves. In working, the valves are adjusted so as to obtain a final gas of 17 percent carbon monoxide, 79 percent of hydrogen and 4 percent of nitrogen.

The reduction apparatus consists of three silica tubes $1^1/_2$ m 120 cm each containing 20 g. of finely divided nickel pumice. The tubes are arranged vertically in a casing and provided with electrical heating (temp. 280–300°). Since the reaction is exothermic there is a suitable arrangement for allowing the dissipation of all extraneous heat, after the process is started. The water formed in the reaction is condensed. The resulting products are: traces of carbon monoxide and carbon dioxide, 30 percent methane, 62 percent hydrogen, and 6–7 percent nitrogen. The nickel, when coated with carbon, can be restored to its original catalytic properties if a gas weak in carbon monoxide is passed through the tube. The earlier figures on the cost of the synthetic methane were 4,484 cc for 3 s. 1.8 d., or 8.5 d. per liter.

P. Sabatier[99] confirmed a great many of the facts of the Bedford process.

Along similar lines, but more strictly theoretical and still possibly of industrial application, is the work of G. W. Andrews[100] on the water gas equilibrium in hydrocarbon flames.

1. The constant $K_t = \frac{C_{CO} \times C_{H_2O}}{C_{CO_2} \times C_{H_2}} = 3.98$ is found to be independent of the nature of the hydrocarbon mixture or pressure of the gas before ignition, also of the maximum flame temperature.
2. The constant does not correspond to the maximum flame temperature but is characteristic of a hypothetical temperature which is probably between 1500–1600° C.
3. No calculation is attempted of the flame temperature, which is, however, estimated as not above 1600° C.
4. The reaction proceeds with rapidity during the cooling period of hydrocarbon flames, and the adjustment of the equilibrium down to a comparatively low temperature is prompt.
5. The amount of methane in the final gases never exceeded 1.05 percent (being usually only 0.3–0.6 percent). No conclusions could be drawn.

6. The most general conclusion is that the explosion combustion of many hydrocarbon oxygen mixtures gives rise to products which approximately at least conform to water gas equilibrium with a value of 4 for K_t and that this value is not greatly altered even when large quantities of carbon are separated or a considerable percent of methane formed in the ultimate products.

The author quoted Bone on secondary reactions: "At higher temperatures of flame secondary thermal decompositions come into operation at an earlier stage and play a more important rôle than in slow combustion, but they do not precede the onslaught of the oxygen on the hydrocarbon, but arise in consequence of it."

3. Catalytic Production of Methane not by Direct Synthesis

There is a series of patents, notably by M. L. Vignon,[101-107] on the production of methane by the reaction of carbon monoxide with steam in the presence of lime, which serves as a catalyst. The reaction is carried on at 1000° C with steam. The yields are about 88 percent hydrogen and 12 percent methane from a gas consisting of 99.1 percent of carbon monoxide and 0.9 percent hydrogen. The results for various catalyzers are as follows:

Catalyzer	Temp. ° C	Percent by volume CH_4	Percent by volume H_2	Percent by volume CO
Al_2O_3	950	3.8	5.9	90.3
MgO	900	6.7	4.7	88.6
SiO_2	750	8.4	10.9	80.7
Fe	950	11.2	20.3	68.5
Ni	400	12.5	1.5	86.0
Cu	700	6.3	2.2	91.5

Probably in the case of iron, aluminum oxide, and silicon dioxide an intermediate carbide is formed.

4. Electrosyntheses from Methane

Thenard and Berthelot[108] passed a silent electric discharge through methane and carbon dioxide and claimed that they obtained an insoluble carbohydrate. Berthelot[109] observed a trace of butyric acid in the reaction products. The residual gases consisted of a little acetylene and of considerable carbon monoxide.

Similarly from a mixture of methane and nitrogen (100 CH_4 and 100 N_2) Berthelot[110] obtained 117.7 hydrogen, 3.4 methane, 74 nitrogen and a solid body approximately of the composition $C_8H_{12}N_4$.

Striking is the work of W. Loeb,[111] who subjected moist methane under ordinary pressure to the influence of the silent discharge and obtained an insoluble, white substance which separated out on the sides of the vessel. Its composition seemed to be $C_9H_{15}O$. Previously Losanitsch had produced from methane and acetylene an insoluble compound which absorbed oxygen and passed into carburetted hydrogen gas. This compound showed no traces of being caused through the formation of the spark, but contained traces of ash, due to the glass being attacked by the discharge. These traces were considered as making the carbon content rise to 2 percent and water to 0.3 percent. The formation of the esters of aliphatic acids such as butyric, caproic, and others, can be understood by the changes methane undergoes.

1. $CH_4 + H_2O = CO + 3H_2$.
2. $CO + H_2O = HCOOH = CO_2 + H_2$.
3. $HCOOH + (CH_2 : CH_2)x = CH_3(CH_2)_{2x-1}\ COOH$.

In these experiments the sides of the vessel were 2 mm apart. The electrisator was filled with distilled water, so that the methane was compressed from a definite volume and the lower part of the discharge tube remained full of water. The gaseous products were removed every 2–4 hours, the other substances at the end of a week. The substance is readily removed by shaking with water and alcohol. At the end of 20 hours, 0.2 to 0.3 g was obtained. This substance ($C_9H_{15}O$) is not changed by boiling with alkalies or dilute acids, but concentrated H_2SO_4 darkens and dissolves it. The gaseous products consist of CO_2, $C_n\ H_{2n}$, CO, C_nH_{2n+2}, and about 35–45 percent hydrogen.

Duration	Cc CH_4	Gas after expt.	Cc CO_2	C_nH_{2n}	CO	H_2	$CH_4 + C_2H_6$
4 hrs. 30 min.	52.0	60.4	0.5	0.1	0.8	36.90	9.00
2 hrs. 40 min.	50.5	57.4	0.6	0.7	1.1	39.48	12.20
2 hrs. 30 min.	49.2	57.3	0.1	0.4	1.4	43.92	12.96

Maquenne[112] passes mixtures of methane and oxygen through the silent discharge and obtains HCHO and HCOOH.

Losanitsch and Jovitschitsch[113] on subjecting mixtures of methane and carbon monoxide to the silent discharge obtained acetaldehyde and its condensation and polymerization products.

Similarly, Hemptinne[114] reports the formation of an aldehydic substance from methane in the silent discharge.

5. Formation of Methane Electrically

Loeb and Lorenz[115] report that on electrolysis of an aqueous solution of methyl alcohol containing $KC_2H_3O_2$, besides carbon monoxide and carbon dioxide there were obtained methane and KCH_3CO_2.

Lassar-Cohn[116] on electrolyzing fused $KC_2H_3O_2$ found carbon dioxide at the anode and carbon, hydrogen and methane at the cathode.

Clark and Smith[117] on electrically oxidizing succinic acid in alkaline solution obtained oxygen, carbon monoxide, carbon dioxide, ethylene, methane, tartaric and oxalic acids.

Truchot[118] on decomposing ethyl ether found ethylene, hydrogen and methane.

Loeb[119] on sending a voltaic discharge in air between carbon points obtained formic acid, 39 percent methane and 45 percent hydrogen, and small quantities of carbon dioxide, carbon monoxide and acetylene.

Maquenne[120] reports the following products from methyl alcohol on silent electric discharge being passed through:

Pressure	3 mm	100 mm
CO	24.3	19.6
CO_2	0.0	0.0
$C_2H_2 + C_2H_4$	4.3	0.9
CH_4	51.0	36.7
H_2	20.4	42.8

Similarly,[121-122] methane has been obtained from: formic methyl ester, formic ethyl ester, acetic methyl ester, glyceric acid, ethyl alcohol, propyl alcohol, isopropyl alcohol, allyl alcohol, glycol, acetaldehyde, paraldehyde, propylaldehyde.

S. M. Losanitsch[123] reports that isopentane on being exposed to silent electric discharge condenses to higher products (when going through at the rate of 3 or 4 bubbles per minute). The separated gas consists of hydrogen, methane and about 5 percent by volume of unsaturated hydrocarbons. The condensed product, after distillation of the unchanged isopentane, remains as an oily, perfumed liquid, which is soluble in ether and less so in alcohol. This is separated by distillation into a volatile and non-volatile substance, the latter being a thick, yellow, clear mass; the former, colorless, mobile and fragrant liquid, from which is obtained C_8H_{18}, C_nH_{2n}, $C_{20}H_{38}$, $(C_8H_{14})_n$. These analyses show that the electric condensation products of isopentane have the same properties as other electrocondensation products.

Similarly there have been described in detail decompositions of hexane, ethyl ether, acetaldehyde, ethyl acetate, ethylene, benzol, methylal, acetal, mixtures of the above with hydrogen and ammonia, giving rise along with other interesting products, also *methane*.

Aside from the scientific interest in the methane equilibrium, there is the industrial interest in the products of decomposition. The investigation, as to the products formed on electrical discharge of various types through the gas, is still in a very incomplete state (see Sections on electrosyntheses for the white substance obtained by Loeb, etc.). The thermal equilibrium, however, has been analyzed above.

The industrial application of the above data has not been worked out at all satisfactorily, though much experimentation, principally unpublished, has been done. The chief aim of methane decomposition is to obtain a special grade of carbon, for printers' ink and the like. As an example, E. Szarvasy claims in U. S. Pat. 1,199,220 that *pure retort carbon* is produced from methane by heating, to a glowing temperature, particles of carbon previously produced by the same process and then passing methane over the carbon to dissociate the methane and build up the particles; particles of smaller size are submitted intermittently. The necessary temperature is maintained by supplying hydrogen and air or oxygen before introducing the methane. The reaction is preferably carried out in an inclined rotating retort. One would be inclined to doubt the commercial success of this process. Similarly G. Fernekes in U. S. Pat. 1,066,894 claims to get lampblack from methane by decomposing it at atmospheric pressure, at temperatures 1300° C to 1700° C. This is very doubtful in view of the facts given previously. A great deal is still to be expected on the *industrial side* in producing carbon in any form but coke.

U. S. Pat. 1,023,783 I. N. Knapp, passes natural gas through incandescent carbon to convert methane into acetylene, benzene and other hydrocarbons.

A. Heinemann (U. S. Pat. 1,134,677), produces propylene from acetylene and methane by passing a mixture of equal parts of acetylene and methane through catalytic contact mixtures of platinum, copper, aluminum or magnesium on pumice at temperatures 100–200° C, claiming a 70 percent yield.

D. MISCELLANEOUS ON METHANE

1. Biological

The occurrence of methane in the breath of sheep, in the intestinal gases, indicates the existence of methane-forming bacteria. Methane fermentations have been investigated to some extent, in particular by Omelianski.[124] His experiments cover the methane fermentation of cellulose and the methane fermentation of ethyl alcohol by anaerobic bacteria. As an example of his results the following will serve: the fermentation of the fecal matter of rabbits on one percent ethyl alcohol gave after two weeks a gas which was 87.4 percent methane, 11.5 percent carbon dioxide and 1.1 percent hydrogen. The material obtained at the bottom of this culture was transferred to fresh media and a gas of 12 per cent carbon dioxide and 88 percent methane was obtained. Similar results were reported with garden soil.

Giglioli and Masoni[125] have published a series of papers on the biologic absorption of methane. They describe the conditions of burning of methane by bacteria, not enzymatic in character, however.

N. L. Söhngen[126] has published observations on the rôle of methane in organic life, showing that all fatty acids of an even number of carbon atoms give methane on fermentation.

$$CaC_4H_6O_4 + H_2O = 2CH_4 + CO_2 + CaCO_3$$

and

$$2CaC_2H_2O_4 = CH_4 + CO_2 + 2CaCO_3, \text{ etc.}$$

Whenever hydrogen was added more methane was formed. The reaction of $4H_2 + CO_2 = CH_4 + 2H_2O$ was thereby verified independently. Furthermore, the ravages of *bacillus methanicus* were described, namely $CH_4 + 2O_2 = CO_2 + 2H_2O$.

The distribution of the various methane organisms is described by Giglioli and Masoni.[127]

2. Sources and Supply of Methane

Methane gas issues out of the earth in practically every part of the globe. Wherever organic matter is found in a state of decomposition methane is one of the by-products. It is found in volcanoes, extinct craters, coal mines, stagnant pools, and oil fields throughout the world. Billions of cubic feet of natural gas from wells and coal mines are lost daily. Up to the present no commercial method has been developed to utilize the methane gas which is found in coal beds and mines.

Our most prolific source of methane gas is from natural gas wells and from casinghead gas. In the year 1916 there was produced and sold 753,000,000,000 cubic feet of gas and for the year 1917 approximately 900,000,000,000 cubic feet valued at $145,000,000. It has been estimated that 1,000,000,000,000 cubic feet of natural gas would be produced and sold in the year 1918. Analyses[128] of thirty-two samples of natural gas from twenty-five cities in the United States, the percentage of methane ranged from 50.6 to 97.3 percent with an average of 78.2 percent. The main use of natural gas or methane gas at the present time is for power, heating and lighting, with smaller quantities being used for making lampblack or carbon black.

The use of natural gas for fuel is a simple, direct and, at present, economical one, but one may question its use for the production of carbon black, the burning of brick, use in the cement and glass industry or for the smelting of metals. May we not yet see practically all of our power and heating done by the use of coke from by-products coke ovens recovering thereby also the liquid products from thermal decomposition of coal? May we not find higher forms of utilization of our natural gas than its present use? May we not divert at least a part to the various uses outlined above? Would not this be true conservation?

E. RESEARCH POSSIBILITIES ON METHANE

The following demand further or new research:

1. The checking of the density determinations of methane.
2. The establishing of a table of densities and volume of methane in natural gas of different compositions.
3. The establishing of the electro negative-positive valency of carbon. Some work indicates valency of six for carbon in methane.
4. Determination of the conditions for liquefying methane.
5. Design of methane refrigeration system.
6. The study of the relation between the ionization of methane and its reactivity.
7. The study of the effect of various wave-lengths on the reactivity of the gas, especially the ultra-red.

8. The study of the effects of pressure on absorption of rays, and hence on reactivity.

9. The effect of the substitution of various groups for the individual hydrogens. (A reaction series of methane substitution products.)

10. Effect of X-rays on methane. (See 7.)

11. The determination of the relation between heat conductivity and velocity of flame propagation.

12. Determination of the effect of moisture and other factors on the explosibility of mine gas.

13. The solubility of methane in solvents and solvent mixtures.

14. Methane in internal combustion engines.

15. Solutions of methane for use in internal combustion engines.

16. The effect of oxidizing agents on methane.

17. Methane combination with other hydrocarbons.

18. The combination of methane with unsaturated compounds.

19. The nitration and sulphonation of methane.

20. The occlusion of methane by metals.

21. The occlusion of methane by coal and other materials.

22. The effect of radium on explosibility and reactivity of methane.

23. The catalytic production of methyl alcohol from methane.

24. The production of intermediate oxidation products of methane on incomplete combustion.

25. Incomplete halogenation of methane precisely controlled.

26. Indirect formation of lampblack from methane.

27. Direct formation of lampblack from methane.

28. The formation of nitrifiable carbides from methane.

29. The most direct process of turning methane to benzol.

30. The transformation of methane to fatty substances.

31. Further research on the methane equilibrium with special attention to catalysis.

32. The effect of a large series of surfaces on methane stability.

33. The formation of carbohydrates from methane electrically.

34. The formation of complex nitrogen compounds from methane electrically.

35. Thorough investigation of the effect of the silent discharge on methane.

36. Reactions of methane in the silent discharge with nitrogen.

37. Reactions of methane in the silent electric discharge with carbon monoxide.

38. Reactions of methane in the silent discharge with carbon dioxide.

39. Reactions of methane in the silent discharge with ammonia.

40. Reactions of methane in the silent discharge with other hydrocarbons.

41–46. as 35–40 with different types of discharge.

47. Oxidation of methane in the silent discharge and others.

48. Producing higher hydrocarbons from the lower ones by the action of heat, by catalysts and in solution.

49. Bacterial oxidation of methane.

50. Bacterial nitrifying of methane.

51. Mixed methane fuels.

52. Cyanates from methane.

53. Efficient methane preparation and purification.

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British	United States	German	Swiss
264	500,651	190,555	20,911
1,032	598,195	197,394	44,225
1,089	615,266	199,973	52,110
2,598	654,466	220,354	55,749
3,735	801,728	228,539	60,534
4,409	889,096	229,057	64,929
5,037	889,097	254,068	65,918
8,767	1,042,723	255,073	68,325
11,010	1,050,978	260,599	
11,107	1,144,457	262,325	
12,541	1,169,817	263,692	Norway
12,604	1,206,155	268,277	2,911
12,946	1,226,811	281,723	11,692
13,069	1,235,342	285,931	13,026
14,855			18,956
15,040			19,985
15,513	Austria	French	23,792
16,049	71,147	199,977	25,585
16,275		202,700	25,704
18,945		210,365	
19,804		262,949	
22,039	Sweden	294,979	
23,835	39,866	417,794	
26,326		458,546	
26,371			

MISCELLANEOUS PATENTS ON METHANE

United States	French	German	British
220,397	353,291	217,157	13,861 (1906)
427,744	355,325	222,919	14,971 (1908)
880,900	356,471	237,499	17,017 (1909)
891,753	400,654	260,477	27,045
956,734	416,699		
983,199	420,933		
989,755	427,774		
1,009,428			Canadian
1,023,783			131,896 (1911)
1,066,894		Norway	
1,134,677	Sweden	26,837 (1916)	
1,199,220	40,495 (1916)	27,040 (1916)	