EQUILIBRIA INVOLVING CARBON AND HYDROGEN.

A Thesis

by

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EQUILIBRIA INVOLVING CARBON AND HYDROGEN.

PART I.

INTRODUCTION.

1. Introductory.

One phase of this subject, viz. the thermal decomposition of hydrocarbons, has received the attention of a great many investigators. As long ago as 1809, Dalton and Henry[1] studied the decomposition of methane and of ethylene when subjected to the ~~combined~~ continued action of electric sparks. Yet one hundred years later, W. A. Bone is forced to say[2] "we are still far from understanding the precise modes of decomposition of even the simplest hydrocarbons, whilst the final elucidation of the question as it affects the higher members of the various series will probably tax our experimental resources to the utmost for many years to come."

It is characteristic of the majority of the earlier investigators, that they attempt to explain the mechanism of decomposition; and it is quite natural that the earliest belief was that the hydrocarbon was ultimately resolved into its elements. But in 1839, Marchand[3] obtained large quantities of methane by the decomposition of ethylene at red heat; and Buff and Hoffmann[4] observed that when a platinum wire was electrically heated to dull redness in ethylene, the gas was decomposed yielding carbon and much methane without an appreciable change in volume. The suggested mechanism was

$$C_2H_4 \longrightarrow C + CH_4.$$

From that date to the present we find suggested many varied mechanisms, some of which are reviewed in the present paper.

Berthelot[*] after a comprehensive study of the behavior of hydrocarbons at high temperatures summarised his views in the following passage[*]:

"... la décomposition immédiate d'un carbure d'hydrogène ne répond pas à sa résolution en eléments, mais à sa transformation en polymères ou en carbures plus condensés avec perte d'hydrogène. Cette transformation ne s'effecte point d'ailleurs à une température absolument fixe et comparable à celle d'ébullition d'un liquide; mais elle s'opère pendant un vaste intervalle de température compris entre le rouge sombre et le rouge blanc: durant cette intervalle le carbure est décomposé en proportion d'autant plus forte et avec vitesse d'autant plus grande que la température est plus élevée .... Entre chaque genre de réaction et la réaction réciproque il s'établit fréquemment une sorte d'équilibre mobile, variable avec la température et les corps qui se trouvent en présence, équilibre analogue à celui qui se produit lors la dissociation des composés binaires."

With regards to the four hydrocarbons, methane, ethane, ethylene and acetylene he suggests the following mechanisms:

Methane is decomposed either into acetylene and hydrogen or into ethane and hydrogen,-

$$2\ CH_4 \longrightarrow C_2H_2 + 3\ H_2$$

$$2\ CH_4 \longrightarrow C_2H_6 + H_2.$$

Ethane yields either ethylene and hydrogen or acetylene, methane and hydrogen,-

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

$$2\ C_2H_6 \longrightarrow 2\ CH_4 + C_2H_2 + H_2.$$

Ethylene yields either acetylene and hydrogen, or acetylene and ethane,-

$$C_2H_4 \longrightarrow C_2H_2 + H_2$$

$$2\ C_2H_4 \longrightarrow C_2H_6 + C_2H_2.$$

It is to be noted that he regarded acetylene as the ultimate product of thermal decomposition.

Thorpe and Young,* however, as a result of their investigations concluded that the primary decomposition of a paraffin did not necessarily involve loss of hydrogen; and Armstrong and Miller* drew attention to the almost complete absence of acetylene in the products of the manufacture of oil gas from petroleum.

V. B. Lewes* from his work upon ethylene, concluded that ethylene is primarily transformed into equal volumes of acetylene and methane thus:

$$3\ C_2H_4 = 2\ C_2H_2 + 2\ CH_4$$

and that the acetylene is subsequently either polymerised or decomposed further into carbon and hydrogen.

Haber[10] in a paper on the decomposition of the higher hydrocarbons vigorously attacked Berthelot's and Lewes' views. He investigated the decomposition of n-hexane and proved conclusively that it decomposed primarily into methane and an olefine, a change which he regarded as typical of the higher hydrocarbons.

The most thorough work upon the decomposition of hydrocarbons has been done by Sir Wm. Bone[11] and his students, and on account of its importance, it will now be reviewed in some detail.

Bone and Jordan[12] proved that methane is the only hydrocarbon formed synthetically from its elements at temperatures between 1000° and 1200°, and this result was confirmed by Bone and Coward.[13] The validity of this direct synthesis was questioned by Berthelot,[14] Pring and Hutton,[15] and Mayer and Altmayer,[16] but further work by Bone and Coward[17] and particularly by Coward and Wilson[18] proved conclusively that methane was actually synthesized from its elements at these temperatures.

Bone and Coward[19] devoted their attention in particular to the decomposition of methane, ethane, ethylene and acetylene at temperatures ranging from 500° to 1200°; and paid special attention to the influence of the time factor on the various decompositions. Bone remarks with reference to work of previous investigators: "Whereas the influence of temperature on the nature and sequence of the changes involved has received considerable attention, the equally important factor of time has been largely disregarded."

The main conclusions reached by Bone and Coward may be summarised as follows:

(1) Methane which is the most stable of the four hydrocarbons examined is the principal product of the decomposition of the other three, especially above 800°. It decomposes directly into carbon and hydrogen and the process, which is probably reversible for all temperatures, is chiefly a surface phenomenon.

(2) The decomposition of the other three hydrocarbons is not a surface effect but takes place throughout the body of the gas.

(3) Acetylene is a principal product of the decomposition of ethylene but not of either ethane or methane.

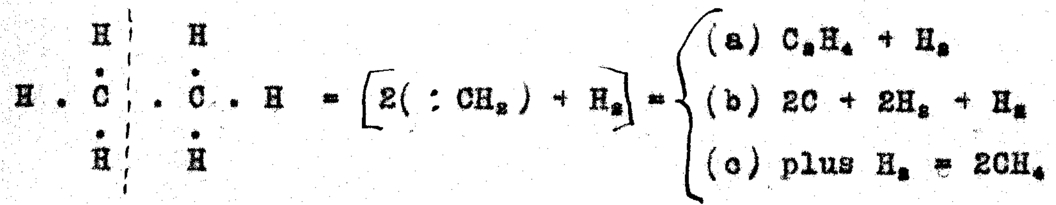
(4) At comparatively low temperatures acetylene exhibits a strong tendency to polymerise, so that where it is formed by a primary decomposition, there is always a marked secondary formation of aromatic hydrocarbons at low temperatures. Above 600°, this tendency diminishes rapidly.

(5) Both acetylene and ethylene tend to combine with hydrogen at low temperatures to form ethane but this factor also diminishes as the temperature rises.

(6) One of the principal factors operative at 800° and higher is the direct hydrogenation of such residues as $\vdots\mathrm{CH}$, $:\mathrm{CH}_2$, and possibly $\cdot\mathrm{CH}_2$ to methane. In this way only, can the very great production of methane during the decomposition of the other three hydrocarbons be accounted for. The assumption of this factor explains also the superior stability of methane over the other hydrocarbons at all temperatures examined..

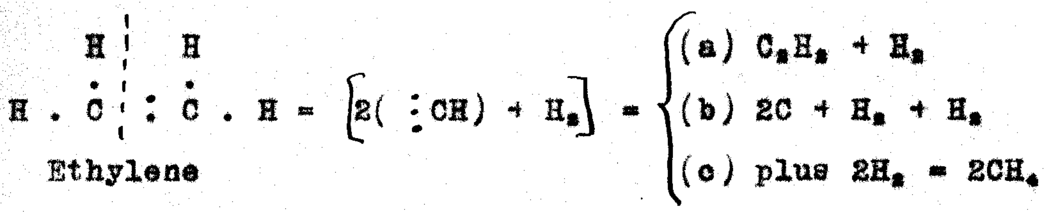
(7) The mode of decomposition of any particular hydrocarbon cannot be expressed by means of a single chemical equation.

(8) The decompositions of ethane, ethylene and acetylene may be represented by the following schemes, the dotted line representing the tendency to dissolve the bond between carbon atoms, which becomes effective at the higher temperatures.

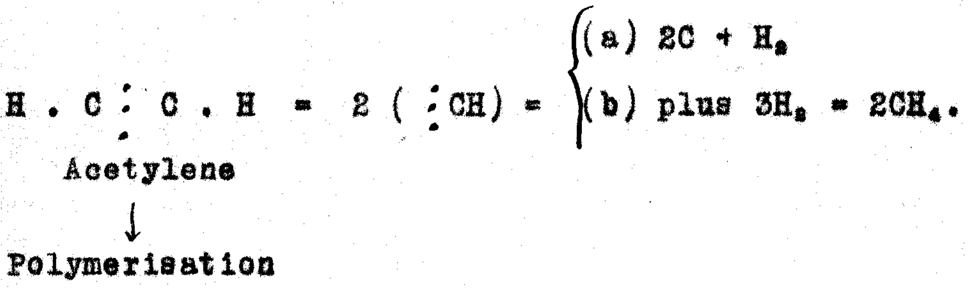


$$\mathrm{H}\cdot\overset{\mathrm{H}}{\underset{\mathrm{H}}{\dot{\underset{\cdot}{\mathrm{C}}}}}\,\vdots\,\cdot\overset{\mathrm{H}}{\underset{\mathrm{H}}{\dot{\underset{\cdot}{\mathrm{C}}}}}\cdot\mathrm{H} = \left[2(:\mathrm{CH}_2) + \mathrm{H}_2\right] = \begin{cases}(a)\ \mathrm{C}_2\mathrm{H}_4 + \mathrm{H}_2\\ (b)\ 2\mathrm{C} + 2\mathrm{H}_2 + \mathrm{H}_2\\ (c)\ \text{plus } \mathrm{H}_2 = 2\mathrm{CH}_4\end{cases}$$

Ethane



$$\underset{\text{Ethylene}}{H \cdot \overset{H}{\dot{C}} \, \vdots \, \overset{H}{\dot{C}} \cdot H} = \left[2(\vdots CH) + H_2\right] = \begin{cases}(a)\ C_2H_2 + H_2 \\ (b)\ 2C + H_2 + H_2 \\ (c)\ \text{plus } 2H_2 = 2CH_4\end{cases}$$



$$H \cdot C \vdots C \cdot H = 2(\vdots CH) = \begin{cases}(a)\ 2C + H_2 \\ (b)\ \text{plus } 3H_2 = 2CH_4.\end{cases}$$

Acetylene

↓

Polymerisation

In the preceding pages the writer has reviewed briefly the mechanisms suggested by various investigators. Of them, and of the experiments which suggested them it can be said only that they give a fair indication of what actually takes place.

It is apparent that in no cases were the experiments continued until a state of neutral equilibrium was reached.

2. Theoretical Considerations.

In the following treatment the writer has considered the subject from the stand-point of qualitative and quantitative equilibria.

If we consider the three hydrocarbons, methane, ethylene and ethane, it is quite conceivable that we might have any or all of the following reactions, proceeding either simultaneously or successively .

(1) $CH_4 \rightleftharpoons C + 2H_2$

(2) $2CH_4 \rightleftharpoons C_2H_4 + 2H_2$

(3) $2CH_4 \rightleftharpoons C_2H_2 + 3H_2$

(4) $C_2H_4 \rightleftharpoons 2C + 2H_2$

(5) $C_2H_4 \rightleftharpoons C_2H_2 + H_2$

(6) $3C_2H_4 \rightleftharpoons C_6H_6 + 3H_2$

(7) $C_2H_6 \rightleftharpoons 2C + 3H_2$

(8) $C_2H_6 \rightleftharpoons C_2H_4 + H_2$

(9) $C_2H_6 \rightleftharpoons C_2H_2 + 2H_2$

(10) $3C_2H_2 \rightleftharpoons C_6H_6$

etc.

In the above equations the writer has indicated a series of equilibria involving the three hydrocarbons, methane, ethylene and ethane and in addition, acetylene and benzene. Now it is quite possible to apply the Phase Rule to such equilibria. The maximum number of phases is 2, the gas and the solid, the variants are fixed as temperature and pressure; and the number of components is evidently 2. Hence the equation N - R + 2 = V, is satisfied. (N = no. of components, R = no. of phases and V = the variants). The conclusion is reached therefore, that whether the initial system be methane, ethylene or ethane, the final system must be one in equilibrium. This system may consist of any or all of the substances indicated, but each of these compounds must be present in such a proportion as to present a symphony of equilibria amongst them all.

The question now arises, whether it is possible to predict the quantitative composition of the equilibrium system for a definite temperature and pressure. To answer this question it is necessary to turn to Thermodynamics for criteria of equilibrium and the simplest is evidently the free energy function. Gibbs in his paper on Heterogeneous Equilibria states that for any isothermal and isopiestic change in a system in equilibrium so

$$* \quad \partial \zeta \geqq 0$$

i.e. the free energy is continually tending towards a minimum; and finally for a system in neutral equilibrium the free energy change is zero.

Now if it were possible to calculate the free energy decrease attending the synthesis of each of the hydrocarbons considered above, it could be said that where that decrease

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* This is really Gibbs' Thermodynamic potential.

is positive, the final system is the stable one; and where on the other hand, the free energy had increased, it would be necessary to state that the final system was an unstable one. This free energy decrease involved in the synthesis of a compound is a measure of its stability;- it is a measure of the affinity of the elements to form the particular compound. Indeed, in place of the term free energy, many European writers use the equivalent term - affinity.

G.N.Lewis and his collaborators have done much during recent years to provide tables of Free Energies of Formation of Compounds, analogous to tables of Heats of Formation.[*1] For the writer's purpose, however, the only useful information obtainable from these tables is that the free energy decrease ($-\Delta F$) for the synthesis of methane from graphitic carbon and hydrogen, is +12,800 calories. This Lewis had calculated from the work of Pring and Fairlie[*3] on the methane equilibrium at temperatures above 1200° C. This means simply that methane is a stable compound, a fact borne out by numerous experimental investigations.

But it is not necessary to stop at this point. The free energy of such a reaction as

$$aA + bB + \text{-----} \rightleftharpoons eE + fF + \text{-------}$$

is given by the expression[*4]

$$-\Delta F = RT\left(\ln K_p - \ln \frac{p_E'^{\,e} \cdot p_F'^{\,f}}{p_A'^{\,a} \cdot p_B'^{\,b}}\right)$$

which as shown involves the equilibrium constant. If now, the pressure quantities in the second term within the bracket be each arbitrarily made equal to 1 atmosphere, the expression simplifies to

$$-\Delta F = RT \ln K.$$

So that we have in the equilibrium constant, a criterion for the stability of each of the various systems under consideration.

Again the Van't Hoff Equation

$$d \ln K_p = \frac{\Delta H}{RT^2} \cdot dT$$

should enable K_p for a given reaction to be calculated when ΔH, the increase in heat content attending the reaction is known. But the above relation is really a differential equation and its integration will involve some unknown constant of integration. At the present time the best solution lies in the use of approximate expressions, of which the Nernst Approximation** has been most successful.

$$\log K = \frac{-\Delta H}{4.571\ T} + \Sigma v\ 1.75 \log T + \Sigma vC.$$

ΔH = increase in heat content of the system as written in the thermochemical equation.

Σv = change in the number of molecules formed by the reaction.

ΣvC = the summation of the "chemical constants" of the reacting substances existing only in the gaseous state.

Table I gives the values for K_p at different temperatures for each of the equilibria considered above. The values for ΔH were calculated from the heat contents of the various compounds involved.

Table I.

Reaction	ΔH	Approximate K_{200}	K_{400}	K_{600}	K_{800}
(1) $CH_4 \rightleftharpoons C+2H_2$	18,900	6.4×10^{-4}	3.2×10^{-1}	13	142
(2) $2CH_4 \rightleftharpoons C_2H_4+2H_2$	52,400	3.1×10^{-19}	8.9×10^{-12}	1.2×10^{-7}	2.4×10^{-4}
(3) $2CH_4 \rightleftharpoons C_2H_2+3H_2$	95,900	1.6×10^{-32}	6.4×10^{-19}	2×10^{-11}	1.2×10^{-4}
(4) $C_2H_4 \rightleftharpoons 2C+2H_2$	-14,600	6.9×10^{11}	1.2×10^{10}	1.2×10^{9}	4.8×10^{8}
(5) $C_2H_4 \rightleftharpoons C_2H_2+H_2$	43,500	3.3×10^{-14}	6.3×10^{-8}	1.8×10^{-4}	2.7×10^{-2}
(6) $3C_2H_4 \rightleftharpoons C_6H_6+3H_2$	-32,500	1.3×10^{19}	8×10^{14}	5.1×10^{12}	2×10^{11}
(7) $C_2H_6 \rightleftharpoons 2C+3H_2$	23,300	6.7	3.2×10^{4}	4×10^{6}	1.2×10^{8}
(8) $C_2H_6 \rightleftharpoons C_2H_4+H_2$	37,900	8.7×10^{-12}	2.8×10^{-6}	2.1×10^{-3}	1.9×10^{-2}
(9) $C_2H_6 \rightleftharpoons C_2H_2+2H_2$	81,400	3×10^{-23}	1.7×10^{-12}	6.6×10^{-7}	7×10^{-3}
(10) $3C_2H_2 \rightleftharpoons C_6H_6$	-163,000	2.6×10^{56}	3.1×10^{34}	7.6×10^{22}	10^{15}

It must be emphasized that no single reaction may be considered exclusively by itself. All the above reactions must be considered as being vitally interrelated, and the calculated values for K_p must be reviewed with respect to all possible systems.

A consideration of reactions (1), (2) and (3) shows that the sole tendency in the temperature interval 200 - 800° C. is for the initial system methane to pass to the final system (at equilibrium) methane, carbon and hydrogen.

Reactions (2), (4), (5), (6), (8) show that the initial system ethylene tends to pass to an equilibrium system involving methane, benzene, carbon, hydrogen and ethane.

Reactions (1), (7), (8) and (9) show that the initial system ethane tends to pass to an equilibrium system, methane, carbon and hydrogen; but ethane is evidently fairly stable up to 400°.

There is little tendency in these three systems to give acetylene so that the equation (10) need not be considered.

The question now arises whether benzene will be stable over this temperature interval.

$$C_6H_6 \rightleftharpoons 6C + 3H_2$$

$$K_{300} = 2.5 \times 10^{14}$$

$$K_{800} = 5 \times 10^{14}$$

These values indicate that benzene should not exist over this temperature interval. In this connection it is interesting to note that Sabatier[**] states with respect to the direct hydrogenation of benzene in the presence of metallic nickel that above 200° and especially "au delà de 300°, une partie du benzène est hydrogénée en methane, et il y a dépôt d'un peu de charbon sur le nickel."

It must be emphasized again that the above deductions are based on the assumption that sufficient time elapses to give an equilibrium state. This time may be one second or a million years.

The final conclusion from the above consideration of equilibrium constants is that whether the initial system be methane, ethylene or ethane, the final equilibrium system will be methane, carbon and hydrogen in the proportions required to satisfy this equilibrium. But "man kann nicht mathematisch beweisen, dass die Natur so sein müsse, wie sie ist." Can the above be shown experimentally?

Firstly, is it possible to find evidence of the truth of these deductions in the work of other investigators?

3. The Decomposition of Methane and its Synthesis from the Elements - Review.

That methane could be formed synthetically by direct union of carbon and hydrogen was first demonstrated by Bone andJordan,[27] in 1897. They heated pure sugar carbon in a current of dry hydrogen in a porcelain tube at 1200° C. and obtained about 1% of methane in the products. Berthelot[28] attempted the same synthesis, but could obtain no methane. He attributed the methane obtained by Bone and Jordan to impurities contained in the carbon used by the English investigators.

However, Bone and Coward[29] in a series of experiments starting with very pure carbon and hydrogen, succeeded in changing 75% of the carbon into methane, confirming thereby the direct synthesis of methane from the elements.

Pring[30] found that at 1200° C. the reaction velocity was very slow:- 22 hours were required to form 0.35% methane. Under these conditions, the rate of decomposition was even slower. At 1500° C., after 2 hours the percentage of methane was 0.17%.

Pring and Fairlie[31] found that below 1000° C. and at atmospheric pressure the reaction was extremely slow, even in the presence of a catalyst like platinum.

Further work by Pring and Fairlie[32] showed that 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 form methane at temperatures above 700° C. They attempted to apply Haber's equation to the methane equilibrium:

$$\log_e K = \frac{Q_0}{R_t} - \frac{\log_e T}{R} - \frac{{}_1T + {}_2T^2}{R} + \frac{K}{R}.$$

$$K = \frac{(CH_4)}{}$$

and at the temperature of 1200° C., this gave the equilibrium ratio

$$\frac{(CH_4)}{(H_2)^2} = 0.07.$$

Their work may be summarized as follows,

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.

They found further that high pressure hastened the attainment of equilibrium. Under a pressure of 30 - 50 atmospheres equilibrium was reached at the end of 2 hours with a temperature of 1200 - 1300° C. and at the end of 15 minutes at 1400° C., with or without a catalyst. The reaction was still more rapid at other pressures.

Sabatier and Senderens[33] by the action of hydrogen upon an intimate mixture of carbon and nickel obtained by reduction of its oxide at 250 - 300° C. ascertained that methane was formed at 250° C. but at the same time there was formation of water vapor. After some time, however, the hydrogen ceased to react. The same chemists found no methane when the temperature was raised to 400° C.

Mayer, Henseling, Altmayer and Jacoby[34] experimenting with the effects of catalysts on the synthesis of methane, found nickel, cobalt and iron efficient in the order given.

It is necessary now to consider investigations carried out from the other side, i.e. reactions involving the decomposition of methane.

Bone and Coward,[35] working at temperatures between 500° C. and 1200° C., declared that the rate of decomposition was inappreciable at temperatures below 700° C. unless a very large surface was exposed by packing with porous material. They believed decomposition to be largely a surface effect and as such affected by the deposit of carbon. Packing with quicklime resulted in a more rapid attainment of equilibrium. An analysis of the products from an hour's heating at 1030° C. revealed the decomposition of all but 0.7% of methane.

Slater[36] initiated an investigation to determine whether the rate of dissociation of methane depended upon the physical and chemical nature, as well as on the amount, of heating surface exposed to the gas. On the basis of dissociation in an empty tube it was found that silica, magnesia, alumina and baryta slowed up the reaction, while quicklime, copper, carborundum, graphite, charcoal and iron accelerated the decomposition. Heated with powdered iron at 910° C. for ten minutes, a gas analyzing 99.4% methane gave a product that was 73.1% hydrogen. Slater concluded that each substance exerts a specific influence on the rate of decomposition which therefore depends upon the nature of the substance as well as on the amount of the heating surface.

Mayer and Altmayer[37] studied the methane equilibrium in the presence of cobalt and nickel catalysts, using a dynamic method. These investigators derived the following thermodynamic equation:

$$21.1 + \frac{18,507}{T} - 5.9934 \ln T - 0.002936T = R \ln \frac{p_{CH_4}}{p^2_{H_2}}$$

They then state: "Durch beliebiges Einsetzen der Temperaturwerte T können wir die Gleichgewichtskonstante p berechnen. Hieraus sind mit Hilfe einer quadratischen Gleichung die Gleichgewichtswerte fur CH_4 und H_2 zu ermitteln."

Their calculated equilibrium values for temperatures from 600° C. to 800° C. are here reproduced.

Table II.

Temperature °C.	% CH_4	% H_2
600	31.68	68.32
700	11.07	88.93
800	4.41	95.59
850	1.59	98.41

They attack the observations of Bone and Jordan[27] that in their experiments upon the synthesis of methane at 1200°C. they obtained 1 - 2 % of methane. The above results seem to indicate that methane cannot be formed from carbon and hydrogen at 1200°C. However, the later evidence produced by Bone and Coward[28] is incontrovertible. The explanation of this apparent discrepancy will be given at a later point in this paper.

Coward and Wilson[18] also using a dynamic method studied the methane equilibrium at the following temperatures: 850°C., 1000°C., 1100°C. and obtained the equilibrium concentrations given below. These experiments were carried out, with and without the presence of a nickel catalyst.

Table III.

Temperature °C.	% CH_4	% H_2
850	2.5	97.5
1000	1.1	98.9
1100	0.6	99.4

4. The Decomposition of Ethylene - Review.

Dalton[1] was the first to notice that carbon and hydrogen were formed from ethylene by heat decomposition.

March and Magnus[39] observed that ethylene decomposed on heating, not only into carbon and hydrogen but also into methane. Berthelot[40] reported also ethane and acetylene.

Magnus found that the products of the decomposition of ethylene at a red heat contained 90% methane and that almost pure hydrogen was obtained at a white heat. Berthelot[41] in a series of papers reported similar results.

Day[42] sums up the work of the previous investigators by saying: "It seems clear that at the highest temperatures ethylene separates directly into its elements. Below this point marsh gas and carbon are obtained ($C_2H_4 \rightarrow CH_4 + C$), then marsh gas and several liquid products among them benzene, styrene, etc. under certain conditions." Day circulated ethylene through a glass tube heated to various temperatures for different lengths of time, and found little reaction up to 400°C. At this temperature 132 cc. of ethylene contracted to 63 cc. in 171 hours. No hydrogen was present in the final gas which was a mixture of 22.4 cc. methane, 24.8 cc. ethane, and 15.6 cc. ethylene or other olefines.

Norton and Noyes[43] passed ethylene slowly through a glass tube heated to red heat, and passed the products of combustion through bromine, whence they isolated solid bromides of the composition C_4H_6Br. The gas collected consisted of methane and ethane. Norton and Noyes believed t that the formation of the bromides was due to the reaction

$$2\ C_2H_4 \rightarrow C_4H_6 + H_2.$$

Bone and Coward[**] carried out what was probably the most valuable investigation on the thermal reactions of ethylene. They circulated ethylene for a period of 2 1/2 hours through a tube heated to 570 - 580° C. Acetylene, ethane, methane and hydrogen were produced but the quantity of carbon separated was negligible. Methane accumulated during the first 60 minutes and then decreased slightly, acetylene varied irregularly from 12% of the gas after 2 minutes heating to 6% of the gases at the end of the experiment. The mechanism that they suggest has already been considered.

The importance of the time factor is shown especially well by the following table taken from their work on the decomposition of ethylene at 800° C.

Table IV.

Temperature - 800° C.

Time in minutes	1	5	15	60
% C_2H_2	3.00	23.9	3.85	nil
% C_2H_4	57.25	1.4	9.65	0.9
% C_2H_6	3.25	5.0	1.3	nil
% CH_4	29.4	53.4	64.45	67.7
% H_2	7.1	17.0	20.75	31.4

When ethylene was heated to 950° C., 90 per cent decomposed within one minute, and all was decomposed after 15 minutes. Small amounts of aromatic hydrocarbons were produced, but large quantities of carbon separated. The gases were methane and hydrogen. At 1100° C., ethylene was rapidly and completely decomposed into carbon, methane and hydrogen.

Leslie,[**] in summing up the work on the thermal decomposition of ethylene makes the statement: "While it must be admitted that the work of the above mentioned investigators has not entirely clarified the course of the reactions involved ---- it can at least be said that we are possessed of fair indications as to the nature of these reactions."

Sabatier and Senderens[**] have studied the thermal decomposition of ethylene in the presence of catalysts.

When ethylene was passed with moderate rapidity, over nickel obtained from its oxide by hydrogen, and heated to a temperature not exceeding 325° C., the issuing gas was a mixture of 10 volumes of hydrogen with about 60 volumes of ethane and 30 volumes of methane. At higher temperatures the proportion of ethane dimished and only traces remained when the temperature was that of red heat. It appeared that the first change in the decomposition was the formation of carbon and ethane, the latter at higher temperature decompoing into carbon and hydrogen. Direct experiments showed that ethane was partially decomposed by nickel at 325° and that methane was decomposed especially above 390° C.

Sabatier also makes the statement,- "Avec une colonne assez longue de nickel réduit, ou un courant suffisamment lent d'éthylène, on peut arriver dès 325° à une transformation à peu près complète en formène, mêlé d'un peu d'hydrogène. Il serait beaucoup moins aisé d'attendre la décarburation totale du formène, celle-ci n'étant pas encore très rapide au rouge sombre." The following statement should also be quoted as it has a confirmatory bearing upon the theoretical conclusions:

"Le gaz recueillis ne contiennent pas en proportion appreciable de gaz absorbables par le brom, et ne donnent pas de réaction avec la solution ammoniacal de chlorure cuivreux: ils ne renferment donc aucunes dose mesurables de carbures éthyléniques ou acétyléniques. Ils sont constitués par un mélange d'hydrogène et de carbures formèniques."

Again "dans aucun cas, ---- nous n'avons pu condenser dose perceptible de produit liquide."

Finely divided platinum and copper have no action on ethylene below 400° C., but cobalt above 300° C. partially decomposes it into ethane, methane and hydrogen together with carbon, but without any acetylene. Iron above 350° C. has less action but decomposes a small part of the gas into ethane, hydrogen and carbon.

When a mixture of hydrogen with an excess of ethylene is passed over reduced nickel heated to a temperature not exceeding 150°, ethane is the sole product of the reaction.

This reduction of ethylene to ethane at 150° C. furnishes an interesting example of the utility of the calculated equilibrium constants in prophesying the course of a reaction.

$$C_2H_6 \rightleftarrows C_2H_4 + H_2 - 37,900.$$

$$K_{150} = \frac{p_{C_2H_4} \cdot p_{H_2}}{p_{C_2H_6}} = 6 \times 10^{-14}$$

That is, the numerator is exceedingly small, indicating complete transformation to ethane.

The writer has tested out this reaction to determine whether it is possible to obtain such a complete conversion. Measured volumes of ethylene and hydrogen were passed back and forth between two burettes over metallic nickel at 150° C. until there was no further change in volume. The final gas was then analyzed and the hydrogen gone to form ethane determined. The results are given in Table V.

Table V.

Temperature - 150° C.

Vol. of C_2H_4 cc.	Vol. of H_2 cc.	$V_1 = \Sigma V$ cc.	V_2 cc.	$V_1 - V_2$ cc.	Analysis of Final Gas			Hydrogen gone to C_2H_6 Calc. ΔV.
					C_2H_4 cc.	C_2H_6 cc.	H_2 cc.	
200	135	335	200	135	36.3	63.7	0.0	127
195	110	305	195	110	45.7	54.3	0.0	106
105	195	300	195	105	0.0	52.4	47.6	105

5. The Decomposition of Ethane.

The thermal decomposition of ethane has been the subject of few investigations. The work of Bone and Coward[47] is the only experimentation of importance. Hollings and Cobb[48] have confirmed the above work. In one experiment ethane was circulated through a tube heated to 675° C. The results of this experiment are given in Table VI.

Table VI.

Temperature - 675° C.

Time in hours	Analysis of gas				
	C_2H_2	C_2H_4	C_2H_6	CH_4	H_2
0.5	4.1	24.7	34.7	8.4	28.1
1.5	5.1	24.1	9.8	19.9	41.1
3.0	2.8	16.4	7.3	32.9	40.6
6.0	1.9	0.7	2.0	54.5	40.9

At 800° C. ethane decomposes rapidly. In one minute's heating the gas had the composition acetylene 1.9%, ethylene 11.2%, ethane 17.9%, methane 31.3% and hydrogen 37.7%. After one hour's heating only methane and hydrogen remained. Similar results were obtained at the higher temperatures.

6. Conclusions Drawn from Review (3, 4, 5).

A careful perusal of the above review of the work upon methane, ethylene and ethane shows that the conclusions drawn in Section 2 are supported by experimental investigation. As Bone has pointed out, in the majority of investigations, the time factor has been neglected. His own investigations, however, show that with increasing time the initial system approaches nearer and nearer to what W. L. Miller[48] calls "neutral equilibrium."

The statement by Sabatier quoted on p. seems to contradict some of the conclusions in Section 2 with respect to ethane. This required experimental investigation the results of which are to be found in Section

7. The Methane Equilibrium. (Amorphous Carbon)

Only two investigations seem to have been carried out on the methane equilibrium at temperatures below 1000° C. Mayer and Altmayer[18] studied it from 300° to 600° C. They derived an equation based on the integration of the Van't Hoff Isochore and used their determined equilibrium constants to calculate the constant of integration. Then, making use of this equation viz.

$$21.1 + \frac{18,507}{T} - 5.9934 \ln T - 0.002936\, T = R \ln K_p,$$

they derived values for K_p for temperatures from 250° to 850° C., and from these constants calculated the equilibrium concentrations of methane and hydrogen for the given temperatures. These concentration values are reproduced in part in Table VII.

Table VII.

Temperature °C.	% CH_4	% H_2
250	98.79	1.21
300	96.90	3.10
350	93.12	6.88
400	86.16	13.84
450	76.80	23.20
500	62.53	37.47
550	46.69	53.31
600	29.40	70.60
650	19.03	80.97
700	11.07	88.93
750	6.08	93.92
800	4.41	95.59
850	1.59	98.41

They attack the observation of Bone and Jordan[27] that in their experiments upon the synthesis of methane at 1200° C., they obtained 1 - 2% methane.

On the other hand Coward and Wilson[16] studied the equilibrium from 850° to 1100° C. with and without a nickel catalyst; and were able to obtain constants for these temperatures. They claim that below the lower tmmperature 850° C., equilibrium cannot be attained within any reasonable period of time." They say, "It is not concluded that it is impossible to prepare carbon in a sufficiently active state to attain equilibrium at this temperature (650° C.) but the claim of Mayer and Altmayer to have succeeded at still lower temperatures is much weakened by the fact that they record no attempt to discover whether their gaseous products contained carbon monoxide.

" If as it seems fair to assume, therefore, they overlooked carbon monoxide much of their so-called methane may have had no actual existence. That there must have been carbon monoxide present in their products can scarcely be doubted in view of, first, the presence of large amounts of nitrogen and second, their use of somewhat large amounts of nickel, which as is known, is difficult to obtain free from nickel oxide by the reduction of the latter at a low temperature."

Their apparent total disagreement admits of a simple explanation. Mayer and Altmayer in the equation derived by them used the value 18,507, which is the heat of formation of methane from graphitic carbon, whereas both they and Coward and Wilson were using amorphous carbon. The heat of formation of methane from amorphous carbon and hydrogen is 21,730 calories, calculated from the mean of Thomsen's and Berthelot's values.

On account, however, of the contradictory claims of the two sets of investigators, it is necessary to have some criterion of what the equilibrium concentrations really are.

Saunders[20] by the application of the Nernst Heat Theorem developed the following equation for the methane equilibrium and showed that it gave results in agreement with Mayer and Altmayer's determined values,-

$$\log K_p = \frac{4,583}{T} - 1.75 \log T + 0.000630\, T - 0.7.$$

The extent of the agreement of this equation with Mayer and Altmayer's values is shown in Table VIII.

Table VIII.

T° K.	log K_p calcd.	log K_p exptl.
600	2.45	2.5
800	0.45	0.40
900	-0.21	-0.37
1000	-0.74	-1.0

The writer has used Saunder's Equation to calculate values of K_p between 500 and 1100° C. for

$$C + 2H_2 \rightleftharpoons CH_4 + 21,730.$$

These are given in Table IX.

Table IX.

T ° C.	T ° K.	K_p calcd.
500	773	4.6
600	873	0.95
700	973	0.23
750	1023	0.17
800	1073	0.086
850	1123	0.053
900	1173	0.036
1000	1273	0.018
1100	1373	0.010

Table X contains the equilibrium concentrations of CH_4 and H_2 calculated by the writer using the values for K_p given in Table IX. The method of calculation will be evident from the following.

$$C + 2H_2 \rightleftarrows CH_4.$$

Let $2x$ = mols of hydrogen in the equilibrium mixture.

$1 - x$ = mols of methane.

Whence

$$K_p = \frac{p_{CH_4}}{p^2_{H_2}} = \frac{\left(\frac{1-x}{1+x}\right) \cdot 1}{\left(\frac{2x}{1+x}\right)^2 \cdot 1^2}.$$

So that percentage of hydrogen = $\frac{2x}{1+x} \cdot 100.$

Table X.

Temperature °C.	% CH_4	% H_2
500	63.9	36.1
600	37.9	62.1
700	16.3	83.7
750	13.0	87.0
800	7.5	92.5
850	4.5	95.5
900	3.6	96.4
1000	2.0	98.0
1100	0.8	99.2

The above table reconciles the results of Mayer and Altmayer, Bone and Coward, Bone and Jordan and of Coward and Wilson. It is evident however from Coward and Wilson's work, that Mayer and Altmayer were particularly fortunate in obtaining very active catalysts. That it is quite possible to obtain such an active catalyst will be shown later in the description of the writer's experimental work.

8. Scope of the Present Investigation.

The investigation initiated by the writer had the following objects:

1. To show, if possible, that whether the initial system were methane, ethylene or ethane, the final system (above 400° C.) would be methane, carbon and hydrogen in equilibrium concentrations.

2. To determine the equilibrium constants for a series of temperatures with methane as the initial system.

3. To determine equilibrium constants in the same way with ethylene as the initial system.

4. To determine the free energy of formation of methane from amorphous carbon and hydrogen.

9. The Rate of Decomposition of Methane.

The equation $CH_4 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C + 2H_2$ accurately expresses the methane equilibrium.[14,17,18.] It is evident that the rate of decomposition of methane is proportional to the concentration of the methane at any instant; while the reverse reaction proceeds at a rate proportional to the square of the concentration of hydrogen.

In the following treatment

x = decrease in partial pressure of methane at time t.

x_∞ = decrease in partial pressure of methane when $t = \infty$, i.e. when equilibrium has been reached.

The following table is then self-explanatory.

Time	Partial Pressures $CH_4 \rightleftharpoons C + 2H_2$	
0	a	b
t	$a-x$	$b+2x$
t_∞	$a-x_\infty$	$b+2x_\infty$

Then $\dfrac{d(b+2x)}{dt} = k_1(a-x) - k_2(b+2x)^2$.

$$2\frac{dx}{dt} = k_1(a-x) - k_2(b+2x)^2.$$

At equilibrium $0 = k_1(a-x_\infty) - k_2(b+2x_\infty)^2$.

$$2\frac{dx}{dt} = k_1(x_\infty-x) + 4k_2\Big[b(x_\infty-x) + (x_\infty^2-x^2)\Big]$$

$$=(x_\infty-x)\Big[k_1 + 4k_2(b+x_\infty+x)\Big]$$

$$= 4k_2(x_\infty-x)\left[\frac{k_1}{4k_2} + b + x_\infty + x\right].$$

But $\dfrac{k_1}{k_2} = \overline{\underline{K}} = \dfrac{p^2_{H_2}}{p_{CH_4}}$.

$$\therefore \frac{dx}{dt} = 2k_2(x_\infty-x)\left[\frac{\overline{\underline{K}}}{4} + b + x_\infty + x\right].$$

Put $\left(\dfrac{\overline{\underline{K}}}{4} + b + x_\infty\right) = \beta$,

and $\dfrac{dx}{dt} = 2k_2(x_\infty-x)(x+\beta)$.

$$\frac{dx}{(x_\infty-x)(x+\beta)} = 2k_2dt,$$

which when integrated and the constant of integration added gives

$$\ln \frac{(x+\beta)}{(x_\infty-x)} - \ln \frac{\beta}{x} = 2k_2(x_\infty+\beta)t \quad \text{or}$$

$$\log \frac{(x+\beta)}{(x_\infty-x)} - \log \frac{\beta}{x_\infty} = 2k_2(x_\infty+\beta)t \times 0.4343$$

$$\log \frac{(x+\beta)}{(x_\infty-x)} - \log \frac{\beta}{x_\infty} = 0.8686\ k_2(x_\infty+\beta)t \qquad (1)$$

whence k_2 can be determined for any value of t, when x and x_∞ are known.

The meaning of x and of x_∞ requires careful consideration. These are changes in the partial pressure of methane, respectively at time t and when equilibrium has been reached.

From the equation $CH_4 \rightleftarrows C + 2H_2$, it is evident that when the partial pressure of methane has decreased by x the total pressure has become 1+x. Thus x and x_∞ are not values measured under atmospheric pressure but under a pressure of 1+x atmospheres. It is usual, however, in experimental work to allow the volume to change while the pressure is kept constant at one atmosphere. The partial pressures obtained under these conditions are obviously such that the total pressure is one atmosphere. Yet the values of x and x_∞ can be calculated from analytical data for atmospheric pressure. The "physical" correction for the partial pressure of hydrogen determined under a total pressure of one atmosphere is given by the equation $\frac{2x_\infty}{1+x_\infty} = p_{H_2}$, but in addition it is necessary strictly to apply a "chemical" correction as well. This will be apparent from the following concrete example.

For 1000°C., the equilibrium concentration of hydrogen, calculated by the method given below, is 0.98 atmospheres.

$$\frac{2x_\infty}{1+x_\infty} = 0.98, \text{ whence } x = 0.96,$$

i.e. the partial pressures of hydrogen and methane respectively are 1.92 and 0.04 atmospheres under a total pressure of 1.96 atmospheres.

But $\frac{p^2_{H_2}}{p_{CH_4}} = K_p$; and it is evident that the value of the expression on the left hand side of the equation tends to increase, assuming no reaction to take place. Therefore, to restore the equilibrium ratio K_p, combination of hydrogen with carbon must occur to form methane. In the present example, let y = this decrease in partial pressure of hydrogen.

Then $\frac{(1.92 - y)^2}{(0.04 + y)} = K_p = 55.5$ (for 1000°C.).

y by trial is found to be between 0.02 and 0.03. Since, however, the value 0.98 calculated for the equilibrium concentration of hydrogen is itself in error 3% at least, the refinement obtained by applying this second correction (in itself strictly accurate) would be solely imaginary. The writer has therefore used the expression

$$\frac{2x_{\infty}}{1-x_{\infty}} = p_{H_2}$$

as a first approximation to determine x_{∞}. In the case of the determination of x, the "physical" correction is the only one that can be applied.

It is possible now to test Equation 1 by data for 985°C., given by Bone and Coward.* Table XI gives the results of a series of experiments in which methane was shut up in heated tubes (unpacked) at atmospheric pressure for different periods of time.

Table XI.

Temperature	985	985	1000	985	985
Time in minutes	1	5	15	30	60
C_2H_2	0.5	0.5	nil	nil	nil
C_2H_4	0.3	0.5	1.3	0.3	nil
CH_4	90.4	75.4	65.25	61.85	48.2
H_2	8.8	23.6	33.3	38.8	51.2

For purposes of calculation we can call the temperature 1000°C. Table IX gives for $\frac{p_{CH_4}}{p^2_{H_2}}$ the value 0.018, and Table X gives 0.02 atmospheres as the partial pressure of methane at equilibrium. The value of $\underline{K}$ required for Equation 1 is the reciprocal of the above, i.e. is equal to 55.5.

x_∞ may be calculated from

$$\frac{2x_\infty}{1+x_\infty} = 0.98, \quad x = 0.96.$$

Again in this series of experiments $b = 0$ so that

$$\beta = \frac{55.5}{4} + 0.96 = 14.86.$$

It is necessary now to calculate the values of x corresponding to the analytical data of Table XI. These values are given as follows.

Time (mins.)	1	5	15	30	60
x	0.046	0.134	0.200	0.241	0.345

The fact that x at the end of 60 minutes is 0.345 while $x_\infty = 0.96$ is in itself sufficient evidence of the slowness of the decomposition of methane.

Equation 1 may be rearranged as follows:

$$k_s = \frac{1}{0.8686(x_\infty+B)t}\left[\log\frac{x+B}{x_\infty-x} - \log\frac{B}{x_\infty}\right]$$

The values of k_s obtained by means of this equation using the data of Table XI are given in Table XII.

Table XII.

Time (mins.)	1	5	15	30	60
$k_s \times 10^8$	1.7	0.96	0.52	0.32	0.32

k_s is evidently approaching a constant value within the neighborhood of 0.32×10^8.

Bone and Coward[3] emphasize the fact that an abnormal period occurs at the start of the reaction; this in their opinion being due to the reaction taking place at the walls of the reaction tube. After these have been covered with carbon, the reaction proceeds, to a greater degree normally. Table XIII gives the values for $k_3 \times 10^3$ calculated with the fifth minute considered as the zero point.

Table XIII.

Time in minutes	1	5	15	30	60
$k_3 \times 10^3$	---	---	0.24	0.16	0.15

The agreement is much better.

For the present investigation of equilibrium conditions, it is desirable to determine the time required for the partial pressure of methane to fall to one-half its original value, i.e. to fall from a total pressure of one atmosphere to one-half an atmosphere, the total pressure remaining constant.

$$\frac{2x}{1+x} = 0.5, \qquad x = 0.333.$$

$$t = \frac{1}{0.8686\ k_3(x_\infty+\beta)}\left[\log \frac{x+\beta}{x_\infty - x} - \log \frac{\beta}{x_\infty}\right]$$

and for $x = 0.333$, $k_3 = 0.15 \times 10^{-3}$, t for 985° C. becomes equal to 93 minutes.

Obviously, the time required for lower temperatures would be so great as to preclude the possibilities of reaching equilibrium with methane as the initial system in the absence of a catalyst.

PART II.

EXPERIMENTAL.

10. The Catalytic Decomposition of Methane.

From the considerations dealt with in Chapter 9, it is obvious that any attempt to determine the equilibrium constant of the system represented by $C + 2H_2 \rightleftharpoons CH_4$, with methane as the initial system, will require the use of a very efficient catalyst. The present section deals with experiments carried out by the writer in the search for such a catalyst.

(1) The Materials Used.

Methane - The methane used was prepared by the well-known reaction

$$CH_3COONa + NaOH \rightarrow Na_2CO_3 + \overline{CH_4}.$$

Methane obtained by this reaction is not pure and contains considerable hydrogen. This however, is of little consequence for these experiments, as we are concerned in fact with a system which itself consists of methane and hydrogen. Methane obtained by the above reaction analyzed as an average value 90 - 92% CH_4, 6 - 10% H_2, after corrections had been made for any fortuitous nitrogen.

The Contact Materials.

(a) Quick-lime. This was ordinary calcium oxide, packed into the reaction tube in 1/4 inch lumps.

(b) Ordinary bone black. This was given no especial treatment.

(c) Cu-CuO. This was prepared by reducing granular CuO by means of purified hydrogen. The hydrogen was passed over the CuO for 1 hour at 300° C.

(d) Fe-Fe_2O_3. This was prepared from precipitated $Fe(OH)_3$ by igniting and then reducing the oxide in the same way as used in the preparation of catalyst (c).

(e) Silica gel. This was prepared according to the method described by Patrick.[21]

(f) Wood charcoal. This was ordinary wood charcoal and was given no especial treatment.

(g) MnO_2. This was prepared by precipitating $Mn(OH)_2$ from $MnSO_4$ solution. The precipitate was collected on a filter and allowed to oxidize in the air for several days. It was then dried and ignited at a dull red heat.

(2) Apparatus.

The heating unit was a cylindrical electric furnace with a lamp bank in circuit for regulating the current to give any desired temperature. The furnace was calibrated by means of an iron-constantin thermocouple with millivoltmeter, so that the temperature corresponding to a given current was always known.

The gasometer containing the methane was connected by means of two large calcium chloride tubes with the reac-tube which itself was of fused silica.

The gas, accordingly, passed from the gasometer through the U-tubes and then through the reaction tube, after which it passed through another pair of calcium chloride tubes into a second gasometer. These gasometers were large glass bottles fitted with large separatory funnels and drains whereby the pressure was regulated. The admission of water through the funnel of the first bottle increased the pressure on the contained gas, and the opening of the drain of the second bottle removed water and lowered the pressure. By proper regulation gas could be transferred from one to the other at any desired rate. The calcium chloride tubes were provided to keep the gases in the reaction chamber free from water.

(3) Experimental Method.

The furnace was heated to the desired temperature by the use of the full current. The time required for this was determined by a previous series of experiments. The required resistance for the given temperature was then inserted and the furnace was allowed to remain untouched for 2 hours to be certain that it was in temperature equilibrium. Nitrogen was then passed at a rapid rate through the whole system excepting the two gasometers. Following this the two gasometers were connected in their proper positions and the methane passed through the reaction tube at a rate of 1-2 liters per hour. After about 3 liters of methane had passed through the tube the experiment was stopped, the gasometers disconnected from the furnace, and the resulting gas mixture was analyzed.

(4) Method of Analysis.

The gas was analyzed for CO_2, unsaturated hydrocarbons, O_2, and CO by the usual absorption methods. The percentages of CH_4 and H_2 were determined by combustion at a bright red-heat, by means of granular CuO contained in a quartz tube of about 3 cc. capacity. From the reactions

$$4\ CuO + CH_4\ (g) \rightarrow CO_2\ (g) + 2\ H_2O\ (l) + 4\ Cu$$

$$CuO + H_2\ (g) \rightarrow H_2O\ (l) + Cu,$$

it is evident that the contraction after combustion is equal to the cc. hydrogen, and that the contraction after treatment with KOH is equal to the cc. of methane.

(5) Experimental Results. See Table XIV.

The analyses given have been calculated to a nitrogen-free basis for purposes of comparison.

Table XIV.

Temp. °C.	Catalyst	Analyses Original Gas CO_2	C_2H_4	O_2	CO	CH_4	H_2
600	None	0.0	0.6	0.0	1.3	91.2	6.9
	CaO	0.0	2.1	0.3	0.6	85.0	12.0
	Bone black	0.0	1.4	0.0	2.0	85.5	13.1
	Cu-CuO	No increase in volume obtained.					
	Wood charcoal	No increase in volume obtained.					
700	None	0.0	1.4	0.0	1.1	95.6	1.9
760	None	0.6	0.0	0.0	0.0	92.9	6.5
	Fe-Fe_2O_3	0.0	1.4	0.0	0.0	89.5	9.1
	Silica gel	0.0	3.5	0.0	0.0	89.5	7.0
	MnO_2	No increase in volume obtained.					

It is evident from the above table that none of the contact agents used are efficient catalysts. It remains necessary, now to consider the catalytic action of the catalyst Ni-NiO. A nickel catalyst was used both by Mayer and Altmayer[27] and by Coward and Wilson[28] in their respective investigations of the methane equilibrium.

Coward and Wilson prepared their nickel catalyst thus: "One gram of pure carbon was intimately mixed with 1 gram of

Analyses Final Gas					
CO_2	C_2H_4	O_2	CO	CH_4	H_2
0.3	1.2	0.0	0.9	88.9	8.7
0.0	1.1	0.0	1.1	83.5	14.4
0.0	0.2	0.0	0.0	80.0	17.8
Gas not analyzed.					
Gas not analyzed.					
0.3	0.7	0.0	1.0	87.6	10.4
0.8	0.6	0.4	0.3	85.7	12.2
2.5	0.0	0.0	2.2	81.4	13.8
0.7	1.6	0.0	0.0	83.5	14.2
Gas not analyzed.					

nickel oxide obtained by igniting the nitrate and the mixture heated to 300° C. in hydrogen until no more water vapor formed." On the other hand Mayer and Altmayer used a catalyst which contained considerable nickel oxide.

The following experiment threw some light on this nickel catalyst.

The writer prepared a catalyst consisting of about 3 grams of nickel oxide on asbestos and reduced it at 275° C. over 9 days. On the ninth day the reduction gave 0.0305 g. of water. It is exceedingly difficult to free nickel oxide completely of oxygen at a low temperature. In passing, it may be mentioned that much polemical discussion exists as to whether the so-called nickel catalyst is nickel or nickel oxide. The writer is inclined to the view expressed by Langmuir[**] that it is necessary to have both the metal and the oxide phase present.

The following epxeriment taken from a previous paper by the writer[**] tests this view. A catalyst was prepared by distributing nickel oxide on asbestos. A mixture of C_2H_4 and H_2 was then passed back and forth at 150° C. over this catalyst. For 45 minutes nothing happened; then suddenly a reduction in volume occurred and at the same time water vapor was evolved. Evidently as soon as the metallic phase made its appearance, the catalyst became active.

Accordingly, the writer's technique in making up a nickel catalyst was to take say 10 grams of nickel nitrate, convert it to the oxide, dissolve this in nitric acid, evaporate to dryness, take up in water and evaporate to dryness, take up again with water, add asbestos fibres and ignite the dried material to the oxide. The catalyst then consisted of asbestos impregnated with nickel oxide. This was then reduced for 1/2 to 3/4 hours with hydrogen, and was then used as a catalyst.

Table XV gives the results obtained by the use of this material as a catalyst for the decomposition of methane. It is emphasized that the same sample of catalyst was used for all the experiments tabulated in this table.

Table XV.

Ni-NiO as catalyst.

Temp. °C.	Catalyst	Original Gas					
		CO_2	C_2H_4	O_2	CO	CH_4	H_2
600	None	0.0	0.6	0.0	1.3	91.2	6.9
	Ni-NiO	0.0	1.7	0.0	0.0	88.0	10.3
	Ni-NiO	0.0	1.7	0.0	0.0	88.0	10.3
700	None	0.0	1.4	0.0	1.1	95.6	1.9
	Ni-NiO	0.0	0.4	0.0	0.2	91.0	8.4
	Ni-NiO	0.0	0.4	0.0	0.2	91.0	8.4
780	Ni-NiO	0.9	4.0	1.3	2.4	83.5	7.9

When the values for CH_4 and H_2 in Table XV are compared with the equilibrium values given in Table X, it is evident that

Final Gas.

CO_2	C_2H_4	O_2	CO	CH_4	H_2
0.3	1.2	0.0	0.9	88.9	8.7
1.6	0.0	0.0	0.0	81.2	17.2
0.5	0.0	0.0	0.5	81.3	17.7
0.3	0.7	0.0	1.0	87.6	10.4
0.0	0.0	0.0	0.8	56.0	43.2
0.0	0.0	0.0	0.0	62.0	37.9
2.5	0.0	0.0	1.9	23.6	71.9

the probability is great that equilibrium may be obtained, when methane is used as the initial system. Chapter 11 describes the experiments carried out by the writer in the endeavor to reach this equilibrium.

11. The Methane Equilibrium with Methane as the Initial System.

(1) The Materials Used.

Methane - The methane used in these experiments was prepared from ethylene. The ethylene itself was prepared by the dehydration of ethyl alcohol by phosphoric acid. The gas so prepared after being washed by cold water and concentrated sulphuric acid analyzed 96 - 98% C_2H_4. The methane was prepared from this by passing the ethylene back and forth several times over the Ni-NiO catalyst in a fused silica tube kept at about 550°C.

(2) Apparatus.

The apparatus used was with one exception that already described in 10. The exception consisted in that the furnace used was now one in which the reaction tube fitted fairly tightly. The ends of the furnace were packed with asbestos fibre about the reaction tube. By this means, it was possible to obtain a uniform temperature for about six inches of the reaction tube. The furnace was calibrated as before and was recalibrated frequently during the course of the investigation. The temperatures are accurate to 10 degrees or better.

(3) Experimental Method.

This differed from that described in 10 in the following:

The gaseous reaction products were passed backwards and forwards over the catalyst (itself always placed between

2 asbestos plugs, in the space of uniform temperature) until there was no further increase in volume, indicating the approach to equilibrium. The products were then passed in the same way at least another half-dozen times. The final gaseous product was then analyzed.

To avoid the presence of much nitrogen, pure dry hydrogen was used for the preliminary washing out of the apparatus.

The gaseous products were in all cases collected over a 1:1 mixture of glycerol and water.

(4) Method of Analysis.

This was identical with that described in 10.

(5) Experimental Results. See Table XVI.

Table XVI.

Temp. °C.	Catalyst	Original Gas						
		CO_2	C_2H_4	O_2	CO	CH_4	H_2	N_2
565	None	0.0	6.3	0.0	1.2	25.8	58.4	8.3
565	Ni-NiO	0.0	0.0	0.0	2.6	50.4	38.5	8.5
670	Ni-NiO	0.9	0.0	0.0	1.8	36.1	57.7	3.5
670	Ni-NiO	1.0	0.0	0.0	2.1	55.8	34.6	6.5
770	Ni-NiO	0.0	0.0	0.0	1.5	22.6	72.2	3.7

The difficulty of reproducing a given state is well known. Lewis and Randall[54] make the following statement,-

Final Gas							K_p
CO_2	C_2H_4	O_2	CO	CH_4	H_2	N_2	
0.4	0.0	0.0	1.6	24.4	64.4	9.2	---
0.5	0.0	0.0	1.4	32.7	58.9	6.5	0.95
0.5	0.0	0.0	1.9	24.0	68.8	5.3	0.51
0.0	0.0	0.0	2.7	20.4	69.0	7.9	0.43
0.0	0.0	0.0	1.2	9.2	85.9	3.7	0.12

"Many solid substances obtained by sudden precipitation from solution or from a vapor, or in a reaction chamber, belong to this type. One of the most important of the numerous substances ----- is the so-called gas carbon. Charcoal is another substance of this type, in which the arrangement of the particles is due largely to the previous configuration of the substance from which the charcoal was produced. Now it is doubtful whether it would be possible to find two samples of gas carbon precisely alike, and great caution must therefore be used in discussing such substances thermodynamically."

In view therefore of the above, the constants obtained in this series are fairly satisfactory. They are also in very fair agreement with the calculated values. In a later part of this paper these values will be compared with those obtained using ethylene as the initial system, with the calculated values, and with those obtained experimentally by Mayer and Altmayer.

12. The Catalytic Decomposition of Ethylene.

(1) The Materials Used.

Ethylene - The ethylene was prepared by the action of phosphoric acid upon absolute alcohol. The gas so prepared, after being washed with concentrated sulphuric acid and cold water, analyzed 96 - 98% C_2H_4.

(2) Contact Materials.

(a) Ni-NiO - This was prepared according to the method described in the preceding chapter.

(b) Thallium sulphate - Prepared by impregnating asbestos with a solution of thallium sulphate in the manner already described.

(c) Cerium Oxide - Prepared by impregnating asbestos with cerium nitrate and then igniting the impregnated material.

(3) The Apparatus.

This consisted of a "train" similar to that described in the previous chapter. For temperatures up to 360° C., a pyrex glass tube heated in a gas oven was used as the reaction chamber. The temperature of the tube was taken by thermometers and the temperature of the gas oven could be controlled easily to 5 degrees. For temperatures above 360° C. the electric resistance furnace was used.

(4) Experimental Method.

In the early series of experiments the gas was passed but once over the catalyst; but in those experiments designed to test the stability of ethane at various temperatures, the gaseous products were passed backwards and forwards over the catalyst a varying number of times, at the rate of 1 - 2 liters per hour. Hydrogen was used for the preliminary washing out of the apparatus.

(5) Method of analysis.

Carbon dioxide, unsaturated hydrocarbons, oxygen and carbon monoxide were determined by the usual absorption methods.

Hydrogen was determined by combustion at 270 - 300° C. with CuO in a small quartz tube, heated in a small gas oven the temperature of which could be controlled easily. To assist the rate of combustion of hydrogen, some metallic copper was always present at the start of the combustion.[**] The reduction in volume after combustion was equivalent to the cc. of hydrogen in the gas.

It was found, however, that when the percentage of hydrogen in the gas was small, there was some loss due to the combustion of some ethane. This was overcome by increasing the partial pressure of hydrogen by adding 15 to 20 cc. of pure electrolytic hydrogen. Tests then showed this method to be satisfactory. The temperature for rapid and complete combustion of the hydrogen alone varied slightly with the quartz tubes used. For the tube finally used in this series, the average temperature was 280° C.

The following actual analyses show the reliability of this method.

Test 1. The gas was a mixture of CH_4, C_2H_6 and H_2.

Volume of gas taken = 27.0 cc.
Volume of pure hydrogen added = 33.4 cc.
Total volume = 60.4 cc.

The burette containing the gas was connected through capillary tubing with the quartz tube containing the copper oxide which in turn was connected with a gas pipette containing phosphorus. The gas was passed into the phosphorus pipette and allowed to remain there for 5 minutes to absorb oxygen. This was done 3 times. Then the gas was passed backward and forward ten times through the quartz tube heated to 300° C. There was no change in volume after about the sixth passage. The quartz tube was then cooled to room temperature by pouring water upon it, and when temperature equilibrium had been obtained the new volume was determined. In this case it was 24.0 cc.

Reduction in volume = 60.4 - 24.0 = 36.4 cc. and 36.4 - 33.4 = 3.0 cc. H_2 in the original gas, assuming no methane or ethane have burned.

To determine whether any CO_2 was in the gas it was passed into KOH solution.

Volume before KOH = 24.0
Volume after KOH = 24.0
CO_2 = 0.0

Test 2.

Volume taken = 23.0 cc. (methane and ethane only, no hydrogen.)

Volume H_2 added = 15.4 cc.

Total = 38.4 cc.

Volume after combustion at 300° C. = 23.0 cc.

(1) Reduction in volume = 15.4 cc.

Volume after KOH = 22.8 cc.

(2) Reduction in volume = 0.2 cc.

Many more tests were made of the method, all of which proved that it was quite satisfactory. No greater volume of CO_2 than 0.3 cc. was ever found. In tests where CH_4 was the only hydrocarbon present, no CO_2 was ever found after the fractional combustion.

Methane and ethane were determined in the residue from the combustion of the hydrogen. The quartz tube was heated directly by a free flame some three inches wide; and the temperature was that of a bright red heat.

From the equations

$$4\ CuO\ (s) + \underset{x\ cc.}{CH_4\ (g)} \rightarrow \underset{x\ cc.}{CO_2\ (g)} + 2H_2O\ (l) + 4Cu\ (s)$$

$$7\ CuO\ (s) + \underset{y cc.}{C_2H_6\ (g)} \rightarrow \underset{2y\ cc.}{2CO_2\ (g)} + 3H_2O\ (l) + 7Cu\ (s)$$

it is evident that the increase in volume after combustion equals y cc. = cc. of C_2H_6.

And again

$x + 2y$ = cc. CO_2, from which x is easily determined.

(6) Experimental Results. See Table XVII.

These analyses have been calculated to nitrogen free. Where no analysis of the original gas is given it is to be assumed that "pure" C_2H_4 was used.

Table XVII.

Temp. °C.	Catalyst	Analyses of Products						
		CO_2	C_2H_4	O_2	CO	CH_4	C_2H_6	H_2
150	None	0.4	85.4	0.0	0.0	0.0	0.0	14.2
200	None	0.4	88.2	0.0	0.0	0.0	0.0	11.9
250	None	0.0	88.4	0.0	0.0	0.0	0.0	11.7
300	None	No change in volume. Gas not analyzed.						
150	Ni-NiO	0.0	83.0	0.0	0.0	0.0	6.0	11.0
150	Ni-NiO	0.0	87.4	0.0	0.2	0.0	3.1	9.3
150	Ni-NiO	0.0	85.6	0.4	0.0	0.0	4.9	9.1
200	Ni-NiO	0.0	81.5	0.0	0.0	0.0	10.2	8.3
200	Ni-NiO	0.0	80.0	0.0	0.2	0.0	10.4	9.4
250	Ni-NiO	0.0	46.4	0.0	0.6	?	?	?
250	Ni-NiO	0.0	40.4	0.0	1.0	?	?	?
250	Ni-NiO	0.0	67.5	0.0	1.4	2.5	22.3	6.3
300	Ni-NiO	0.0	4.4	0.0	0.9	51.9	31.8	11.0
300	Ni-NiO	0.6	1.6	0.0	1.3	32.9	47.0	16.6
300	Ni-NiO	0.5	0.5	0.0	1.3	44.4	38.5	14.8
325	Ni-NiO	2.8	0.0	0.0	0.6	56.0	32.2	8.4
325	Ni-NiO	0.8	18.4	0.0	0.8	33.1	29.9	17.0
325	Ni-NiO	0.4	5.9	0.4	0.8	30.5	40.4	11.6

325	Ni-NiO	0.4	6.0	0.4	0.9	30.5	40.4	21.4
350	Ni-NiO	0.0	0.9	0.0	1.3	42.3	34.1	21.4
350	Ni-NiO	0.9	0.0	1.7	0.0	40.2	36.7	20.5
160	Thorium Sulfate	Leak developed. Gas analyzed but showed no satumated hydrocarbons						
200	Thorium Sulfate	0.0	72.4	0.8	0.0	0.0	3.7	23.1
285	Thorium Sulfate	0.4	74.1	1.3	0.0	0.0	6.2	18.4
150	Cerium Oxide	Product contained no saturated hydrocarbons						
285	Cerium Oxide	Product contained no saturated hydrocarbons						

It is evident from Table XVII, that above 250° C., methane is formed in addition to ethane by the catalytic decomposition of ethylene. Ethane, however, appears to be stable even up to 350° C.; and this is in direct contradiction to Sabatier's statement that with a sufficiently long tube or a sufficiently slow rate ethylene might be completely decomposed into methane, hydrogen and carbon.** It was necessary to test the validity of this view as it conflicts directly with the theoretical conclusions drawn in Chapter 2.

The following experiments establish incontrovertibly the stability of ethane up to 360° C. in the presence of nickel catalyst.

Ethylene analyzing 95% C_2H_4 was passed back and forth from one gasometer to another over Ni-NiO catalyst II (see Table XVII) heated to 360° C.

The data obtained were as follows:-

Volume of C_2H_4 used - 2300 cc.
Rate - about one litre per hour
Total time gas being circulated - 5 hrs. 15 min.
Volume of resulting gas - 1800 cc.
Decrease in volume - 500 cc.
The experiment was continued the following day.
Final volume of resulting gas - 1800 cc.
Total additional time gas being circulated - 3 hrs. 15 min.
Total time - 8.5 hrs.

Analysis of Final Product

(calculated to nitrogen free)

CO_2	0.0
C_2H_4	0.0
O_2	0.0
CO	0.7
CH_4	68.2
C_2H_6	25.2
H_2	5.9

It would be useless, therefore, th attempt to determine the equilibrium constant for the methane, carbon, hydrogen system at or below 360° C., when ethylene was used as the initial system.

To test the stability of ethane at higher temperature, circulation experiments were performed at 510° C. and 565° C. The results obtained were as follows.

Temperature 510° C. No catalyst.

Volume of C_2H_4 - 2600 cc. Volume of product - 3900 cc.

Time gas circulated - 5 hours.

Analysis of Product.

CO_2	0.0	CO	1.3
C_2H_4	6.9	CH_4	28.2
O_2	0.0	C_2H_6	0.0
		H_2	63.6

Temperature 565° C. No catalyst.

Gas used - product obtained at 510° C.

Volume of gas used - 3200 cc. Volume of product - 3250 cc.

Time gas circulated - 4 hours.

Analysis.

CO_2	0.4
C_2H_4	0.0
O_2	0.0
CO	1.8
CH_4	26.9
C_2H_6	0.0
H_2	70.9

Temperature 565° C. No catalyst.

Volume of ethylene used - 22000. Volume of product - 4450.

Time gas circulated - 5 hours.

Analysis.

CO_2	0.0
C_2H_4	0.0
O_2	0.0
CO	1.3
CH_4	14.6
C_2H_6	0.0
H_2	84.1

These experiments show that above 500° C. methane and hydrogen are the chief products of the decomposition;

but the concentrations of methane and hydrogen in the final gas are so far from the equilibrium values (see Table X), that it would be hopeless to attempt to reach the equilibrium state in the absence of a catalyst.

13. The Action of Carbon Monoxide on the Catalyst.

An examination of Table XV shows that the final gas contained up to 3% carbon monoxide. Coward and Wilson[18] also noted the presence of carbon monoxide in their final gas and raised the question as to whether carbon monoxide might not play some important part in the synthesis of methane. They say,- "It is just conceivable, although contrary to the results of other investigations[26], that carbon monoxide would be reduced by the large excess of hydrogen present to methane and water; the latter would regenerate carbon monoxide by reation with carbon. If carbon monoxide acts as a catalyst in the synthesis, then the two reactions - whatever they might be precisely - indicated as A and B in the scheme

$$\begin{tikzcd}
C \arrow[rr] \arrow[dr, "A"'] & & CH_4 \\
& CO \arrow[ur, "B"'] &
\end{tikzcd}$$

would each be fast in comparison with the rate of the direct synthesis. Hence the accumulation of carbon monoxide exhibited in the experiments would only be possible provided that the reversion of methane to carbon and hydrogen were a very rapid reaction indeed when the methane was increased above 0.7 per cent. That this is not the case is shown by experiments ---- on the decomposition of methane at 1100°C. The carbon monoxide is therefore produced as a side reaction between carbon and water vapour, and plays no part in the formation of at least the great proportion of the methane formed."

But there is another side to this question viz.: what is the action of carbon monoxide upon the Ni-NiO catalyst? Carbon monoxide is well known as a catalytic poison, and where a catalyst is used continuously as in the experiments tabulated in Table XV, this continued action of the carbon monoxide formed may result in a considerable lessening in the efficiency of the catalyst.[60]

This poisoning action of carbon monoxide on a nickel-nickel oxide catalyst was clearly shown by the results obtained from an experiment in which a leak developed. The data of this experiment are tabulated below:

Temperature 770° C. Ni-NiO Catalyst.

Volume of original gas-850 cc. Volume of product - 1050 cc.

Time gas circulated - 5 hours 15 minutes.

Analyses

Original gas		Final gas	
CO	1.5%	CO	11.6%
CH_4	32.9	CH_4	10.2
H_2	58.1	H_2	50.5
N_2	7.5	N_2	27.7

The catalyst from this experiment was used for a circulation experiment with ethylene as the initial system. The temperature of the furnace was 615° C., for which temperature the equilibrium concentrations should be approximately 38% H_2, 62% CH_4.

It was soon evident, during the course of this experiment that the reaction was not proceeding normally. The volume increases following each succeeding passage of the gaseous products were about one-fourth of those ordinarily obtained, and as the experiment proceeded the increases became more and more abnormal. The data of the whole experiment are given below.

Temperature 615° C.

Catalyst - Ni-NiO from preceding experiment.

Volume of ethylene used - 600 cc. Volume of product - 1350 cc

Time gas circulated - 5 hours.

Analysis of product.

CO	3.4%
CH_4	50.4
H_2	41.7
N_2	4.5

As these values are still far from the equilibrium concentrations the circulation of gas was continued for another 3 hours. There was a further small increase in volume after each passage of gas, but it was quite evident to the observer that the catalyst was functioning with very little efficiency. The further data for the experiment were as follows:

Temperature 615° C. Ni-NiO catalyst.

Volume of gas used - 1100 cc. Volume of product - 1250 cc.

Time gas circulated - 3 hours.

Analyses.

Original gas		Final gas	
CO	3.4%	CO	3.6%
CH_4	41.7	CH_4	40.7
H_2	50.4	H_2	52.0
N_2	4.5	N_2	3.7

These values give $\frac{p_{CH_4}}{p^2_{H_2}} = 1.50$ as against the calculated value $K_{900} = 0.95$.

It is perhaps significant that the CO content rose in this experiment to the highest recorded for any experiment other than that in which the leak developed.

The results of these experiments demonstrate the necessity of using a freshly prepared nickel-nickel oxide catalyst for each equilibrium experiment. This procedure or a slightly modified form of it was followed in the experiments to be described in the next section.

14. Methane Equilibrium with Ethylene as the Initial System.

The apparatus used was the same as that already described in 12. The ethylene was prepared in the usual way from absolute alcohol by the dehydrating action of phosphoric acid. The experimental method, however, was varied slightly.

Preliminary experiments showed that the successive analyses of the product differed after each passage over the catalyst until a point was reached where the analyses remained constant, i.e. until the equilibrium point was reached. This was found to correspond fairly well with the point where further passages produced no further increase in volume. Accordingly the gas was passed until the change in volume became zero, and was then circulated for 2 to 3 hours in addition. It was felt that in this way equilibrium was undoubtedly obtained. As a matter of fact, as will be shown, a single passage of ethylene over the special nickel-nickel oxide catalyst produces a system very close to equilibrium whereas in the actual experiments recorded the products circulated from 9 to 15 times depending upon the temperature.

The catalyst consisted of the specially prepared nickel-nickel oxide on asbestos. At the end of an experiment, before the next one was started one-half of the catalyst was removed and replaced by freshly prepared material. It was hoped that in this way, not only would the life of the catalyst be lengthened, but also that the percentage of carbon monoxide in the gas would be reduced.

The method of analysis was varied slightly. After a preliminary analysis to determine the absence of ethane, the analysis was repeated using the direct combustion method for the determination of methane and hydrogen.

Experimental Results.

The following results show how closely equilibrium is approximated following only one passage of ethylene over the catalyst:

Table XVIII.

Temp. °C.	Analyses CO	H_2	C_2H_4	CH_4	$\frac{p_{CH_4}}{p^2_{H_2}}$*	K_p (calc.)
510	1.0	48.0	8.1	37.6	1.6	3.9
565	0.0	60.0	0.0	33.8	0.94	1.3
615	0.0	64.5	0.0	29.6	0.72	0.67
670	0.0	76.4	0.0	19.9	0.34	0.35

* C_2H_4 not considered.

It seemed probable that continued circulation of the gaseous products would lead to lower values for K_p than those calculated upon the basis of amorphous carbon alone. It is inevitable that some graphitization of the carbon will occur when it is subjected to a high temperature over a long period of time.[63]

In the actual equilibrium experiments, every attempt was made to reproduce as nearly as possible the same system in the duplicate experiments.

The experimental results follow:

Table XIX.

Temp. °C.	Analyses CO_2	O_2	CO	CH_4	H_2	$\frac{p_{CH_4}}{p^2_{H_2}}$	K_p(calc.)
510	0.0	0.0	2.6	50.4	38.5	3.4	3.9
510	1.0	0.0	2.1	55.8	34.6	4.6	3.9
565	0.9	0.0	1.8	36.1	57.7	1.1	1.3
615	0.0	0.0	1.5	22.6	72.2	0.43	0.67
*615	0.0	0.0	0.0	20.3	77.1	0.34	0.67
670	0.0	0.0	1.2	12.6	81.5	0.19	0.35
670	0.0	0.8	0.9	12.3	82.7	0.18	0.35

* Fresh catalyst replaced all of the old contact material.

It is interesting to note that the variation between the determined value, and that calculated on the basis of amorphous carbon alone increases with increasing temperature. This is exactly what one would expect.[62]

Table XX is a summary, in which the writer's values (C) are compared with the average values of Mayer and Altmayer (M & A). The initial system is specified in each case. To complete the table, calculated values are given (amorphous carbon), as are also the determined values of Coward and Wilson (C & W) for temperatures above 800° C.

Table XX.

Temp. °C.	Calc. K_p	M & A	C	C & W	Initial System
508	3	3.6	---	---	CH_4
506	---	1.8	---	---	C + H
510	3.9	---	3.4	---	C_2H_4
510	3.9	---	4.6	---	C_2H_4
536	---	2.8	---	---	CH_4
536	---	1.7	---	---	C + H
565	1.3	---	1.1	---	C_2H_4
565	1.3	---	0.95	---	CH_4
567	---	1.9	---	---	CH_4
567	---	1.3	---	---	C + H
577	---	0.78	---	---	C + H
607	---	0.57	---	---	C + H
615	0.67	---	0.43	---	C_2H_4
615	0.67	---	0.34	---	C_2H_4
625	---	0.34	---	---	C + H
670	0.35	---	0.43(?)	---	CH_4
670	0.35	---	0.51(?)	---	CH_4
670	0.35	---	0.19	---	C_2H_4
670	0.35	---	0.18	---	C_2H_4
770	0.12	---	0.12	---	CH_4
850	0.05	---	---	0.025	CH_4
1000	0.02	---	---	0.011	C + H

1000	0.02	---	---	0.015	C + H
1000	0.02	---	---	0.011	CH_4
1100	0.01	---	---	0.006	CH_4
1100	0.01	---	---	0.006	C + H

Table XX shows that Mayer and Altmayer's results are of the same order as those determined by the writer. In addition, it shows that the determined results are as a rule somewhat lower than the calculated.

The results obtained with ethylene as the initial system probably represent the equilibrium between amorphous carbon, methane and hydrogen more closely than any of the other values. These results are strictly comparative. In each of these experiments fresh catalyst was used so that the solid phase was actually amorphous carbon rather than partially graphitized material; although it must be admitted that some graphitization may have taken place over the long period during which the gases were circulated. In figure 1, the values for log K_p for these experiments are plotted against $\frac{1}{T}$. The linear relationship obtained is very satisfactory. Table XXI gives the values of log K_p and $\frac{1}{T}$ used in the construction of the graph.

Table XXI.

Temperature	K_p	log K_p	$\frac{1}{T}$
510	3.4	0.5315	0.00128
510	4.6	0.6628	0.00128
565	1.1	0.0414	0.00120
565	0.95	-0.0223	0.00120
615	0.43	-0.3665	0.00113
615	0.34	-0.4685	0.00113
670	0.19	-0.7212	0.00106
670	0.18	-0.7446	0.00106

14. The Free Energy of Formation of Methane from Amorphous Carbon and Hydrogen.

The Van't Hoff Equation states that

$$d \ln K_p = \frac{\Delta H}{RT^2} . dT.$$

and ΔH, the increase in heat content may be expressed in terms of the heat capacities of the substances involved, viz.:

$$d\ (\Delta H) = \Delta C.dT$$

where ΔC represents the difference in the heat capacities of the products and the reactants.

ΔC can always be expressed in the form

$$\Delta C = \Delta C_o + \alpha T + \beta T^2 + ----$$

If we substitute this value for ΔC in Equation (2) and integrate we have

$$\Delta H = \Delta H_o + \Delta C_o T + \frac{\alpha}{2} T^2 + \frac{\beta}{3} T^2 + ---- \qquad (3)$$

Again the Free Energy expression for the Second Law of Thermodynamics is given by

$$d \frac{(-\Delta F)}{T} = \frac{\Delta H}{T^2} . dT$$

$$\text{or } d \frac{(-\Delta F)}{T} = (\Delta H_o + \Delta C_o T + \frac{\alpha}{2} T^2 + \frac{\beta}{3} T^2 + ---) \frac{dT}{T^2}$$

$$= \Delta H_o . \frac{dT}{T^2} + \frac{\Delta C_o dT}{T} + \frac{\alpha}{2} dT + \frac{\beta}{3} T.dT + --$$

$$\text{from which } - \frac{\Delta F}{T} = - \frac{\Delta H_o}{T} + \Delta C_o \cdot \ln T + \frac{\alpha}{2} T + \frac{\beta}{6} T^2 + I$$

so that the Free Energy Decrease

$$-\Delta F = -\Delta H_0 + \Delta C_0 \ln T + \frac{\alpha}{2}T^2 + \frac{\beta}{6}T^3 + IT. \qquad (4)$$

Dixon, Campbell and Parker** determined the C_p/T curve for methane and gave the linear equation

$$C_p^T = 3.47 + 0.019T$$

to represent their results. This equation is used in the calculations given below.

For hydrogen $C_p^{0.T} = 6.52 + 0.00044T$ (**)

For carbon $C_p^{0.T} = 1.1 + 0.0024T - 4.0\times10^{-7}T^2$ (**)

This latter equation gives the value 2.4 for the atomic heat of carbon at ordinary temperatures. The atomic heat of amorphous carbon at ordinary temperatures is 2.6.

These values give

$$\Delta C_0 = -10.67$$

$$\alpha = +0.01572$$

$$\beta = +4\times10^{-7}$$

Again Equation (3) may be written

$$-\Delta H_0 = -\Delta H + \Delta C_0 T + \frac{\alpha}{2}T^2 + \frac{\beta}{3}T^3.$$

$$= -\Delta H - 10.67T + 0.00786T^2 + 10^{-7}T^3.$$

For T = 293°K, $-\Delta H = 21{,}730$ calories.

$$\therefore -\Delta H_0 = 21{,}730 - 10.67\times293 + 0.00786\times\overline{293}^2 + 10^{-7}\times293^3$$

$$= 19{,}280 \text{ calories.}$$

Equation (4) then becomes

$$-\Delta F = 19,280 - 10.67T\ln T + 0.00786T^2 + 0.6\times10^{-7}T^3 + IT \quad (5)$$

The value of I, the constant of integration may now be determined from the values of $-\Delta F$ calculated from the determined equilibrium constants.

Table XXII gives these values of I.

Table XXII.

Temperature °C.	I
510	-16.9
510	-16.8
565	-16.1
565	-16.1
615	-15.3
615	-15.5
670	-14.7
670	-14.7
770	-13.6
850	-13.2
1000	-12.5
Average	-15.0

There is evidently a trend of I with the temperature. This same trend in the value of I is encountered when it is calculated from Pring and Fairlie's equilibrium constants.[41] for the equilibrium between methane, hydrogen and graphite. In the present case, the trend is no doubt due to the gradual transition from amorphous carbon to graphite, for the deviation from the average value increases with increasing temperature. The average value, -15, has been used however to calculate the value of $-\Delta F$ for 298°K.

$$-\Delta F = 19{,}280 - 10.67T \ln T + 0.00786T^2 + 0.0000006T^3$$
$$+ 15T$$

which gives for $T = 298$ that $-\Delta F_{298} = 12100$ calories. Lewis and Randall[**] have calculated $-\Delta F_{298}$ for the reaction

$C\ (\text{graph}) + 2H_2 = CH_4;\quad -\Delta F_{298} = 12800$ calories

$C(\text{amorph}) + 2H_2 = CH_4;\quad -\Delta F_{298} = 12100$ calories.

From which for the reaction

$C\ (\text{amorph}) \longrightarrow C\ (\text{graph}).\quad -\Delta F_{298} = -700$ calories.

PART III.

SUMMARY.

1. Calculations of equilibrium constants for the possible reactions involved in the decomposition of methane, ethylene and ethane indicated that above 400° the final system should be one of methane, carbon and hydrogen, irrespective of which hydrocarbon was used as the initial system.

2. A review of the literature on the decomposition of these hydrocarbons, both by heat alone and in the presence of catalysts, showed that the experimental results of previous investigators were in harmony with the conclusions drawn from the calculated equilibrium constants.

3. An equation was developed for calculating the reaction-rate constants k_1 and k_2 for the forward and reverse reactions of the equilibrium $CH_4 \rightleftharpoons C + 2H_2$. The validity of this equation was confirmed by means of Bone and Coward's experimental results.

4. Use of the above equation indicated that it would be hopeless to attempt to study the methane equilibrium in the range 400° - 800°, in the absence of a catalyst.

5. The apparent disagreement of other investigators with regard to the stability of methane above 850° was reconciled by calculation of the equilibrium concentrations of methane and hydrogen in equilibrium with amorphous carbon.

6. Various catalysts were used experimentally in the attempt to accelerate the decomposition of methane. The failure of the contact agents tried led to an examination of the nickel catalyst used by Mayer and Altmayer; and by Coward and Wilson. The results of these two sets of investigators are in direct contradiction one with the other.

7. Experimental evidence was obtained that the most efficient nickel catalyst would be one containing both the metal and oxide phases.

8. A specially prepared nickel-nickel oxide catalyst proved most efficient in promoting the decomposition of methane.

9. Equilibrium constants for the reaction C (amorph) + $2H_2 \rightleftarrows CH_4$ were determined with methane as the initial system by circulating the gaseous products repeatedly over the catalyst. These were in very fair agreement with those calculated for the above system, but were on the whole rather high.

10. The catalytic decomposition of ethylene was studied and it was found again that the special nickel-nickel oxide catalyst was most effective in bringing about this decomposition.

11. Up to 250° C., ethane was the only saturated hydrocarbon formed in the catalytic decomposition of ethylene.

12. Above this temperature methane also made its appearance, the percentage of methane following one passage of the gas over the catalyst, increasing with the temperatures.

13. Experiments in which the gaseous products were passed repeatedly over the catalyst proved conclusively that ethane was stable in the presence of a nickel catalyst up to 360°.

14. Experiments in which ethylene was passed through a heated tube at 500° and the gaseous products were repeatedly passed through the tube showed that the final gaseous products were almost entirely methane and hydrogen; but in proportions very far from the equilibrium values.

15. Experiments in which the gaseous products of the catalytic decomposition of ethylene were circulated repeatedly over a nickel-nickel oxide catalyst showed that the

methane equilibrium should be attained in this manner.

16. The action of carbon monoxide on the catalyst was studied and it was shown that its continued action rendered the catalyst inefficient for the methane equilibrium.

17. Equilibrium constants for the methane equilibrium were obtained by repeatedly circulating the products of the catalytic decomposition of ethylene over the nickel catalyst. These constants are on the whole somewhat lower than the calculated constants, and are lower than those obtained with methane as the initial system.

18. The logarithms of the equilibrium constants obtained with ethylene as the initial system plotted against the reciprocal of the absolute temperature gave a straight line.

19. The free energy decrease attending the formation of methane at 25° from amorphous carbon and hydrogen was calculated to be 12,100 calories.

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