HYDROCARBONS FROM CARBIDE*
THERMODYNAMICS

By

R. NEGISHI, OSAMU KIMURA, and OSAMU KAMIIKE.

The purpose of this and of other papers, some of which will appear later in this journal, by the senior author is to show that many useful hydrocarbons can be synthesized directly from calcium carbide, without first converting it into acetylene which is then polymerized, as is commonly done at present. Quite a voluminous number of investigations on the subject of acetylene polymerization appear in the literature; they are listed extensively by Egloff, Ellis, Fischer, and others,[1] and there is no need of mentioning all of them here. Recently, however, there appeared several interesting papers[2] on the catalytic polymerization of acetylene which merit special reference. In these reports, the yield of liquid products is excellent, being over 300 gram per cubic meter of acetylene, and the reaction temperatures are low, 208 and 290°C, as compared with the usual temperature range of 500 to 700°C employed in most of the acetylene polymerization reactions.

Studies on the direct synthesis of hydrocarbons from calcium carbide[3,4] (hydrocarbons from other carbides, see Putman and Kobe[3]) are, on the other hand, quite meager, and for this reason, the authors have endeavored to make some theoretical as well as experimental investigations** on the subject.

Moreover, from the concepts that the activation of molecules is necessary to effect a chemical reaction and that nascent molecules, atoms, and radicals possess more reactivity, the polymerization of nascent acetylene, or, in other words, the synthesis of hydrocarbons directly from the carbide appears to us most appealing.

* The main portion of this paper was completed in 1939, but its publication was with-held.

1) G. Egloff, " *Reactions of Pure Hydrocarbons*," Reinhold Publishing Corp., N. Y. (1937); C. Ellis, " *The Chemistry of Petroleum Derivatives*," Vol. I and II, Reinhold Publish. Corp., N. Y. (1934 and 1937); F. Fischer, " *Gesammelte Abhandlungen zur Kenntnis der Kohle*," Vol. I—12 (—1936).

2) Shiomi and Iwamoto, *J. Soc. Chem. Ind., Japan*, 41, 831 (1938); Amemiya, *ibid.*, 42, 692 (1939).

3) G. L. Putman and K. F. Kobe, *Chem. Rev.*, 20, 131 (1937).

4) H. Plauson and G. Tischenko, G. P. 346065 (1921); S. P. Gambarjan and L. S. Kasarjan, R. P. 41516; N. V. de Bataafsche Petroleum Maatschappij, Holl. P. 22573; F. Hansgirg, J. P. 127812, 134273, 134712; A. T. Babayan, *J. gen. chem. (URSS)* 8, 602 (1938); *ibid.*, 8, 578 (1938); L. S. Kasajan, *Chem. J. Ser. A J. allg. Chem.*, 4, (66), 1347 (1934).

** Experimental details will be published later by Negishi, Kamiike, and Nibayashi in the J. Soc. Chem. Ind., Japan.

By introducing the water vapor over the carbide, the following overall reactions,

$$CaC_2 + H_2O = CaO + C_2H_2*$$
$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2*,$$
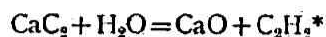
take place, where C_2H_2* is the nascent acetylene molecules possessing a high content of energy and reactivity. When the reactions are more closely considered, it becomes conceivable, that since calcium is a highly electro-positive metal, it must possess a large affinity for the oxygen atom, and at the moment of their combination, highly unsaturated carbon (or even completely unsaturated[5]) and hydrogen atoms may momentarily exist. They would possess an enormous tendency to saturate among themselves and each other, and not only the nascent acetylene molecules formed alone, but the free hydrogen atoms and radicals[6] produced therefrom may also initiate polymerization and hydrogenation reactions.

Since there is no free energy data for the reactions involving the carbide, the authors have made some thermodynamic calculations to fill in the lack, and the results are given in the Tables and Figures below. In the calculations of the standard free energy of formation and the free energy of reaction, calcium (a), graphite carbon, calcium carbonate (calcite), and calcium oxide all in their solid states have been used; the other substances involved have been assumed to be in their gaseous states. The notations and the relations employed are listed below :

F° is the standard free energy of formation.

F is the free energy of reaction.

H is the heat of reaction.

K is the equilibrium constant.

C_p, T, R, and S have their usual meaning.

$$\Delta C_p = \Delta \Gamma_0 + \Delta \Gamma_1 T + \Delta \Gamma_2 T^2 + \ldots\ldots$$

$$d(\Delta H)/dT = \Delta C_p$$

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

$$\Delta F = -RT \ln K = \Delta H - T\Delta S.$$

The signs of F and H will be the same as those use by Lewis and Randall[7]

5) R. Fussteig, *Chimie and Industrie*, **37**, 853 (1937).

6) It is well known that radicals and hydrogen atoms are involved in hydrocarbon reactions. References on the subject are numerous; to mention a few, H. S. Taylor, *J. Phys. Chem.*, **42**, 763 (1938); E. W. R. Steacie and E. A. Brown, *J. Chem. Phys.*, **8**, 734 (1940).

7) G. N. Lewis and M. Randall, " *Thermodynamics and the Free Energy of Chemical Substances*," McGraw-Hill Co. Inc., N. Y. (1923).

(heat absorbed is plus, and that evolved is negative).

Equations for the standard free energy of formation are given in Table I in which those of the hydrocarbons have been calculated from the data given by Thomas, Egloff, and Morrell,[8] making use of the relation,

$$\Delta F^\circ = A + BT,$$

where A and B are constants; all others, unless otherwise stated, have been taken directly from or been calculated from the data found in the International Critical Tables and Landolt-Boernsteins Tabellen.

In Table II the standard free energies calculated by use of the relations given in Table I at 100, 200, 300, 400, and 500°C are given. In Table III the total free energy changes involved at 100, 300, and 500°C in the formation, according to the reactions as written, of the chain compounds, and in Fig. 1 the molal free energies, that is, the free energy change per mole of the substance produced according to the reaction, are given, respectively. Similarly, in Table IV the total and in Fig. 2 the molal free energy changes of simple and condensed ring hydrocarbons are, respectively, shown. Usually, two sets of reactions for the formation of a hydrocarbon are given ; one is for the carbide and water to produce the hydrocarbon and calcium oxide, and the other between the carbide and $CO + H_2$* to form the hydrocarbon and calcium carbonate*. It is of some interest to note that the temperature coefficient of the reactions in which the carbonate is formed is much greater than that of the reactions in which calcium oxide is produced, and the two curves intersect in the temperature range, 100 to 200°C.

As it can be readily seen from the Tables and the Figures, in all reactions involving the solid carbide the accompanying free energy changes are very large. The results of Table V in which three reactions that are experimentally realized are compared with those differing from them only in that the latter contain the carbide illustrate the point effectively. By the addition of the carbide, $-\Delta F$ for the formation of benzene at 300°C is increased by over 80 Kcal., and over 90 Kcal. for that of 1, 3, butadiene ; and in the formation of n-octane, when the carbonate is produced the effect of the carbide is greater than that in which calcium oxide is formed, the increase is over 100 Kcals. If instead of ΔF per mole of hydrocarbon produced, ΔF per mole of carbide reacted is calculated, the increase in the magnitude of $-\Delta F$ will be roughly from 50 to 70 Kcals. at

8) C. L. Thomas, G. Egloff, and J. C. Morrell, *Ind. Eng. Chem.*, 29, 1260 (1937).
* In actual experiments where $CO+H_2$ is used, the effect of the carbide is more pronounced, if a catalyst is used first to initiate a reaction between CO and H_2 and the by-products, usually, either water or carbon dioxide or both, are allowed to react with the carbide. Some carbonate is invariably formed.

Table I.

Standard Free Energy of Formation.

Substance	Equation
Methane	$\Delta F^\circ = -18570 + 21.04\,T$
Acetylene	$\Delta F^\circ = 54882 - 13.56\,T$
Ethylene	$\Delta F^\circ = 11837 + 13.37\,T$
Ethane	$\Delta F^\circ = -23337 + 50.59\,T$
1, 3, Butadiene	$\Delta F^\circ = 25050 + 29.90\,T$
Isobutene	$\Delta F^\circ = -4540 + 63.02\,T$
Isobutane	$\Delta F^\circ = -33771 + 96.88\,T$
n-Butane	$\Delta F^\circ = -32292 + 91.58\,T$
Benzene	$\Delta F^\circ = 18750 + 39.90\,T$
Cyclohexane	$\Delta F^\circ = -31157 + 131.54\,T$
n-Hexane	$\Delta F^\circ = -45020 + 146.04\,T$
Toluene	$\Delta F^\circ = 9616 + 63.17\,T$
n-Octane	$\Delta F^\circ = -55248 + 190.50\,T$
Naphthalene	$\Delta F^\circ = 33287 + 57.43\,T$
Anthracene	$\Delta F^\circ = 47616 + 83.17\,T$
H_2	$\Delta F^\circ = -1778 - 6.5\,T \ln T - 0.000225\,T^2 + 43\,T$
H_2O	$\Delta F^\circ = -57120 + 2.75\,T \ln T - 0.00075\,T^2 - 6.65\,T$ [9]
CO	$\Delta F^\circ = -27070 - 2.05\,T \ln T + 0.00225\,T^2 - 0.20 \times 10^{-6}\,T^3 - 7.92\,T$ [9]
CO_2	$\Delta F^\circ = -94210 + 0.30\,T \ln T - 0.0003\,T^2 + 0.05 \times 10^{-6}\,T^3 - 0.94\,T$ [9]
CaO	$\Delta F^\circ = -152640 - 2.25\,T \ln T - 0.0015\,T^2 + 37.53\,T$
CaC_2	$\Delta F^\circ = -13210 + 6.9\,T \ln T - 31.47\,T$ [10]
$CaCO_3$	$\Delta F^\circ = -290334 + 0.723\,T \ln T - 2.778 \times 10^{-3}\,T^2 - 3.13 \times 10^{-6}\,T^3 + 95350/T + 61.30\,T$ [*]

[*] Since there is no equation for the standard free energy of formation of $CaCO_3$, it has been calculated from the following data taken from Landolt-Boernsteins, pp. 2235, 2273, 2852 (1936):

	C_p	S_{298}/Mole
Ca (a)	$5.31 + 3.33 \times 10^{-3}\,T$	9.55
C (graph.)	$2.673 + 2.617 \times 10^{-3}\,T - 11600/T^2$	1.4
O_2	$8.27 + 0.258 \times 10^{-3}\,T - 1.877 \times 10^{-6}\,T^2$	24.52 (1/2 O_2)
$CaCO_3$ (calcite)	$19.68 + 1.189 \times 10^{-2}\,T - 307600/T^2$	21.85

Furthermore, in the absence of any directly measured value of ΔF_{298}, it has been calculated from
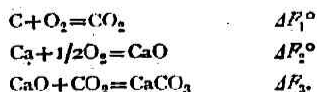
$$\Delta F_{298} = \Delta H_{298} - T \Delta S_{298}$$

in which ΔH_{298} has been assumed equal to ΔH_{291}, or

$$\Delta H_{291} = -289500 \text{ [11]} \cong \Delta H_{298}.$$

Then, by use of the usual relations, ΔF° has been calculated, and the result is

$$\Delta F^\circ = -290334 + 0.723\,T \ln T - 2.778 \times 10^{-3}\,T^2 - 3.13 \times 10^{-6}\,T^3 + \frac{95350}{T} + 61.30\,T.$$

ΔF° for calcium carbonate can also be calculated from the following relations,

$$C + O_2 = CO_2 \qquad\qquad \Delta F_1^\circ$$
$$Ca + 1/2\,O_2 = CaO \qquad \Delta F_2^\circ$$
$$CaO + CO_2 = CaCO_3 \qquad \Delta F_3.$$

9) J. Chipman, *Ind. Eng. Chem.*, 24, 1013 (1932).

10) K. K. Kelley, *Bur. Mines, Bull.* No. 407, 8 (1937).

11) F. R. Bichowsky and F. D. Rossini, "*Thermochemistry of Chemical Substances*," Reinhold Publ. Corp., 120 (1936).

Adding, $Ca+C+1\frac{1}{2}O_2=CaCO_3$, $\Delta F^\circ=\Delta F_1^\circ+\Delta F_2^\circ+\Delta F_3$. The values of ΔF_1°, ΔF_2° are given in Table I. ΔF_3 has been calculated from the data given by Tamaru, Siomi, and Adati[12], employing the usual relations and the fact that

$$\Delta F=0=-RT \ln K \text{ at } 881.7^\circ C^{[12]},$$

where $P_{CO_2}=1$ atmosphere. ΔF_3 thus obtained is

$$\Delta F_3=-42162+3.385\,T \ln T-0.00681\,T^2+0.66\times 10^{-6}\,T^3+19.55\,T.$$

Combining ΔF_1°, ΔF_2°, and ΔF_3, ΔF° finally becomes

$$\Delta F^\circ=-289012+1.455\,T \ln T-0.0086\,T^2+0.71\times 10^{-6}\,T^3+56.14\,T.$$

The agreement between the value of ΔF° calculated from this equation and that of the above is quite satisfactory.

300°C, or in terms of the equilibrium constant, the order of K, which is related to the free energy by $\Delta F=-RT \ln K$, is increased by about 19 to 26. In other words, by the addition of the carbide even those reactions which otherwise would be thermodynamically doubtful become exceedingly possible, and the scope of organic syntheses is expanded enormously.

Table II.

Standard Free Energy of Formation, ΔF°

Temperature Substance	100°C	200°C	300°C	400°C	500°C
Methane	−10719	−8615	−6511	−4407	−2303
Acetylene	49822	48466	47110	45754	44398
Ethylene	16825	18162	19499	20836	22173
Ethane	−4461	597	5656	10715	15774
1, 3 Butadiene	36205	39195	42185	45175	48165
Isobutene	18972	25274	31576	37878	44180
Isobutane	2374	12062	21750	31438	41126
n-Butane	1876	11034	20192	29350	38508
Benzene	33636	37626	41616	45606	49596
Cyclohexane	17920	31074	44227	57382	70536
n-Hexane	9467	24071	38675	53279	67883
Toluene	33184	39501	45818	52135	58452
n-Octane	15827	34877	53927	72977	91927
Naphthalene	54714	60457	66200	71943	77686
Anthracene	78646	86963	95280	103597	111914
H_2	−111	−404	−840	−1395	−2051
H_2O	−53636	−52428	−51178	−49896	−48585
CO	−34246	−36302	−38361	−40417	−42469
CO_2	−93937	−93843	−93747	−93649	−93552
CaO	−143811	−141768	−139803	−137908	−136076
CaC_2	−18330	−19366	−20337	−21257	−22132
$CaCO_3$	−266160	−259979	−253909	−247979	−242212

12) S. Tamaru, K. Siomi, and M. Adati, Z. physik. Chem., 157, 447 (1931).
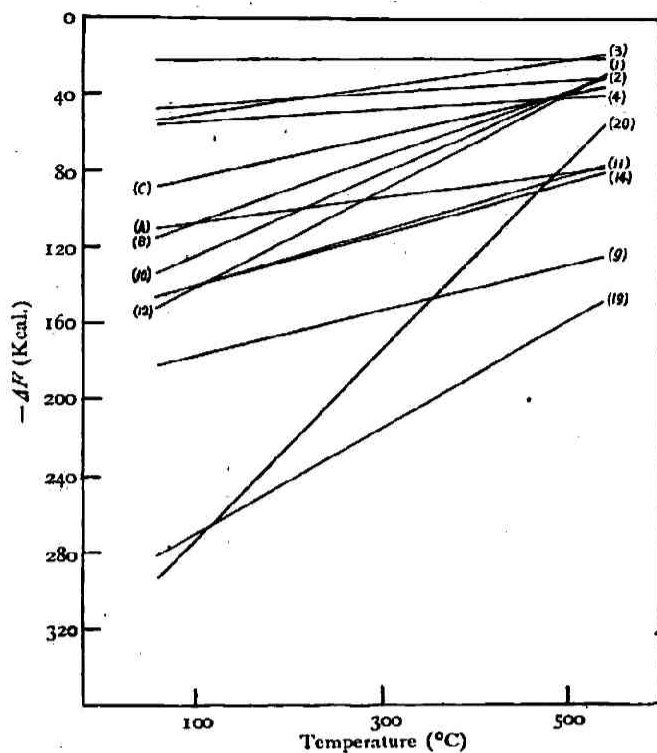
Fig. 1

ΔF of Chain-Hydrocarbons.
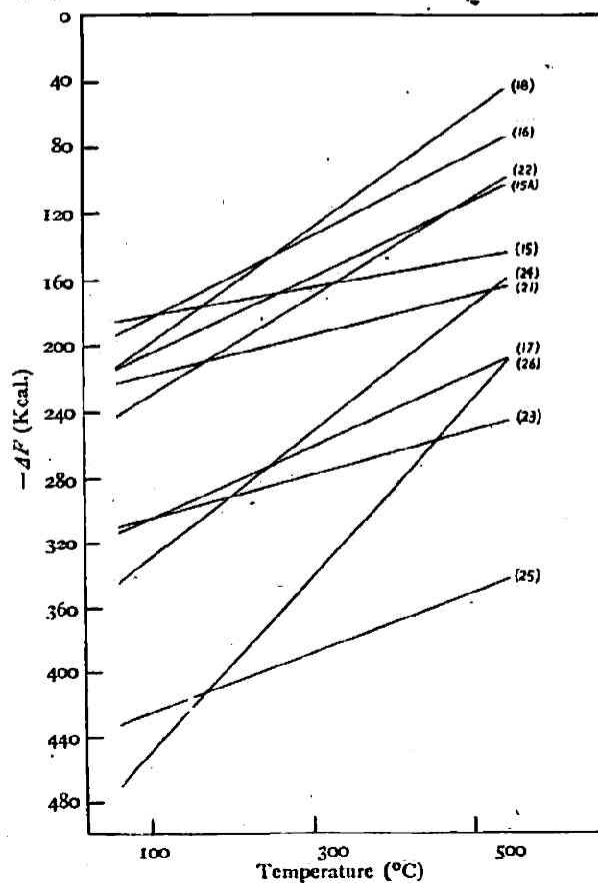

Fig. 2

ΔF of Ring- and Condensed-
Hydrocarbons.

Table III.
Free Energy of Formation of Chain-Hydrocarbons

No.	Sbustance	Reaction	$-\Delta F$		
			100°C	300°C	500°C
1	Acetylene	$CaC_2 + H_2O = CaO + C_2H_2$	22023	21178	20961
2	Methane	$CaC_2 + H_2O + 3H_2 = CaO + 2CH_4$	46475	38995	31906
3	Methane	$CaC_2 + 8H_2 + 3CO = CaCO_3 + 4CH_4$	51575	36953	21369
4	Ethylene	$CaC_2 + H_2O + H_2 = CaO + C_2H_4$	54909	47949	41135
A	1, 3 Butadiene	$2CaC_2 + 2H_2O + H_2 = C_4H_6 + 2CaO$	107374	93551	80502
B	1, 3 Butadiene	$CaC_2 + 3CO + 3H_2 = C_4H_6 + CaCO_3$	108554	73984	38355
C	1, 3 Butadiene	$4CaC_2 + 4CO + 9H_2 = 3C_4H_6 + 4CaO$	85109	63435	40982
9	Isobutene	$2CaC_2 + H_2O + 3H_2 = C_4H_8 + 2CaO$	178021	152858	128970
10	Isobutene	$CaC_2 + 3CO + 4H_2 = C_4H_8 + CaCO_3$	125675	83653	38289
11	Isobutane	$2CaC_2 + 2H_2O + 3H_2 = C_4H_{10} + 2CaO$	140983	111506	83439
12	Isobutane	$CaC_2 + 3CO + 5H_2 = C_4H_{10} + CaCO_3$	142163	92539	39292
14	n-Butane	$2CaC_2 + 2H_2O + 3H_2 = C_4H_{10} + 2CaO$	141481	113064	86057
19	n-Octane	$4CaC_2 + 4H_2O + 5H_2 = C_8H_{18} + 4CaO$	270998	215025	159254
20	n-Octane	$2CaC_2 + 6CO + 9H_2 = C_8H_{18} + 2CaCO_3$	273358	176491	74960

Table IV.
Free Energy of Formation of Cyclic Hydrocarbons

No.	Substances	Reaction	$-\Delta F$		
			100°C	300°C	500°C
15A	Benzene	$2CaC_2 + 2CO + 3H_2 + 2CO_2 = 2CaCO_3 + C_6H_6$	205225	157992	112369
15	Benzene	$3CaC_2 + 3H_2O = C_6H_6 + 3CaO$	181899	163248	146481
16	Benzene	$3CaC_2 + 9CO + 6H_2 = 2C_6H_6 + 3CaCO_3$	183669	133597	83260
17	Cyclohexane	$3CaC_2 + H_2O + 3H_2 = C_6H_{12} + 3CaO$	304554	259673	216528
18	Cyclohexane	$3CaC_2 + 9CO + 12H_2 = 2C_6H_{12} + 3CaCO_3$	199052	128466	56168
21	Toluene	$7CaC_2 + 7H_2O + H_2 = 7CaO + 2C_7H_8$	218218	192770	169279
22	Toluene	$2CaC_2 + 4CO + CO_2 + 4H_2 = 2CaCO_3 + C_7H_8$	231111	170785	110080
23	Naphthalene	$5CaC_2 + 5H_2O = C_{10}H_8 + 5CaO + H_2$	304622	276080	251160
24	Naphthalene	$3CaC_2 + 2CO_2 + 5CO + 4H_2 = 3CaCO_3 + C_{10}H_8$	329248	251857	174901
25	Anthracene	$7CaC_2 + 7H_2O = C_{14}H_{10} + 7CaO + 2H_2$	424491	384416	349701
26	Anthracene	$4CaC_2 + 8CO + 2CO_2 + 5H_2 = C_{14}H_{10} + 4CCO_3$	448277	340434	231295

Table V.
Comparison of ΔF at 300°C.

Substance	Reaction	ΔF/1 Mole Hydrocarbon	Diff. (cals.)
Benzene	$3C_2H_2 = C_6H_6$	-79714	
	$3CaC_2 + 3H_2O = C_6H_6 + 3CaO$	-163248	-83534
1, 3 Butadiene	$C_2H_2 + 2H_2 = C_4H_6$ [13]	-3245	
	$2CaC_2 + 2H_2O + H_2 = C_4H_6 + 2CaO$	-93551	-90306
n-Octane	$8CO + 17H_2 = C_8H_{18} + 8H_2O$	-33329	
	$2CaC_2 + 6CO + 9H_2 = C_8H_{18} + 2CaCO_3$	-176491	-143162
	$8CaC_2 + 8CO + 27H_2 = 3C_8H_{18} + 8CaO$	-138460	-105130

13) A. A. Balandin, Ya. T. Eidus, and E. M. Terent'eva, *Compt. rend. acad. sci.*, (URSS), **27**, 343 (1940). The reaction effected by electric discharges of high frequency was investigated both in circulatory and static systems.

Coupling of the facts that the presence of the carbide increasest he magnitude of $-\Delta F$ and that the nascent acetylene molecules possess a greater reactivity, may lead to a conclusion that there would be an improvement in the yield of hydrocarbons. The answer to this question is not complete, but experimental data are available which have a definite bearing on the subject. Shiomi and Iwamoto[2] and Amemiya[2] have recently obtained some interesting results on the catalytic polymerization of ordinary acetylene. In the former case a catalyst consisting of $Co : Ni : Cr_2O_3 :$ acid clay in a ratio, $1 : 0.2 : 1 : 2$, was used at 208°C, and under the most favorable conditions, 405 cc./cbm. of liquid products was obtained. In the latter investigation, employing a catalyst consisting of Fe : Ni : Kieselguhr = 95 : 5 : 1000, 455.6 cc./cbm. was obtained at 290°C. In our case at 340°C we have obtained, without using any catalyst*, approximately 486 cc./cbm. of dark reddish liquid products of density, 0.9 to 1.0. In our calculation a density of 0.95 and the gas volume at 25°C have been used. The results are shown in Table VI.

Table VI.

Experimenter	Catalyst	Temp. °C	cc/cbm.	Yield Gr.	Density
Shiomi and Iwamoto	$Co : Ni : Cr_2O_3 :$ Acid Clay	208	405	320	0.778*
Amemiya	Fe : Ni : Kieselguhr	290	455.6	389	0.855
Negishi and Kamiike	None	340	486	460	0.95

* For the fraction boiling between 170 and 200°C.

As it can be seen from Table VI that, under the optimum conditions, the polymerization of nascent acetylene gives, even in the absence of a catalyst, the highest yield both in volume and weight.

According to Figures 1 and 2, the absolute magnitude of ΔF is greater for the hydrocarbons with greater number of carbon atoms for both the chain and the simple condensed ring hydrocarbons, and it is more so for the latter. This point has been verified experimentally. In our experiments at one atmosphere with the carbide and various gases saturated with the water vapor at about 80°C, only the " Yellow powder " or cuprene-like substance of quite high molecular weight was formed at 250°C, where thermal cracking** was not likely; at 340°C rather

* Any catalytic effect induced by the formation of calcium oxide and carbonate, or any other products of reaction has been neglected.

** By means of a thermocouple which could measure the temperature at various points along the reacting carbide zone, a temperature difference as much as 100°C from the average temperature of the furnace was indicated.

heavy hydrocarbon liquids; and at higher temperatures less dense liquids, but in all cases aromatic and condensed in nature.　If, however, the results of Table VI are compared, the lower the temperature, where thermal cracking is less probable, the lighter the products formed.　This apparent paradox can be explained by the simple assumption that in these systems two opposing factors are in play; ΔF, on the one hand, favoring the formation of denser products, and, on the other hand, the cracking[14] and decomposition[14][15] effects of the catalyst, and, apparently, the latter factor predominates in these systems.　Moreover, since the decreasing order of the activity[15] of the metals is Co, Ni, and Fe, the first catalyst might be more active than the second; consequently, the products would be lighter, and the reaction temperature could be lower in the first system, as, indeed, is the case.

Since the carbide has a great affinity for the water molecules, not only the free energy, but also the rate of any reaction in which the water is formed as a by-product would increase* by virtue of the shift in the equilibrium when it is present. This is one of the most significant point in connection with the use of the carbide. Since the rate can be increased by the elimination of the by-yroducts formed, the temperature of the reaction need not be raised.　In the usual cases, where the carbide is not added, the rate is often increased at the expense of the equilibrium.** Similarly, any reaction in which carbon dioxide is formed, its rate may also be increased due to the circumstance that the reaction,

$$CaO^* + CO_2 = CaCO_3,$$

where CaO^* is the oxide formed by the reaction between the carbide and water and not that which is present as an impurity in the original carbide, is rapid and complete, as shown in Table VII.　Since in organic syntheses, not infrequently, water or CO_2 or both are formed, the presence of the carbide is particularly beneficial.

---

14)　H. S. Taylor and J. Turkevich, *Trans. Farad. Soc.*, 35, 921 (1939).

15)　G. Egloff, J. C. Morrell, C. L. Thomas, and H. Bloch, *J. Am. Chem. Soc.*, 61, 3571 (1939); C. L. Thomas, G. Egloff, and J. Morrell, *Ind. Eng. Chem.*, 31, 1090 (1939).　Taylor and Turkevich claim that Ni and Co induce strong catalytic cracking or C-C scission, while Thomas, Egloff, and Morrell claim that Ni, Co, and Fe induce but slight catalytic cracking.　However, all agree that these metals induce strong decomposition effects.

* The increase in the rate seems to be experimentally confirmed.　This subject will be treated in a later paper which will be published elsewhere.

** This is particularly true in industrial practice, as for example, in the formation of methyl alcohol from CO and H_2 where the lower the temperature the greater is the equilibrium.　However, higher temperatures are used to increase the rate at the sacrifice of the equilibrium, and in this case, the change of equilibrium with temperature is quite appreciable.

Table VII.

Exp. No.	Total Carbide C Reacted (Gr.)	Total carbonate C Found (Gr.)	Ratio* $\dfrac{\text{Carbide C}}{\text{Carbonate C}}$
Auto. IIIA Ser. 100	79.05	38.91	2.03
Auto. IIIA Ser. 113	79.05	36.41	2.17
Auto. IIIA Ser. 124	68.00	33.4	2.04

* Theoretical ratio is 2.00

Finally, the subject of the mechanism of the nascent acetylene polymerization which seems uninfluenced by the presence of foreign substances, especially, the solid; or that of the carbide as a means of promoting and accelerating many, organic syntheses aside from thermodynamic considerations; and the use of the carbide to elucidate the mechanism of a main reaction will be reserved for later studies. The discussion of this paper, however, will not be complete unless a word is mentioned of the importance of a catalyst in the reactions involving the carbide. The increase of $-\Delta F$ by the addition of the carbide also may mean that of $-\Delta F$ for undesirable and side reactions, and only the proper choice of a catalyst can control the rate and direction of the reaction as well as the character of the products.

Summary

The synthesis of hydrocarbons directly from calcium carbide is thermodynamically very powerful, and by the introduction of the carbide, the scope of organic syntheses may be expanded enormously.

It has been shown that the calcium oxide formed during the reaction will react rapidly and completely with carbon dioxide to produce calcium carbonate.

The increase in the yield and in the rate of reaction effected by the addition of the carbide and by the higher reactivity of the nascent acetylene molecules has been shown experimentally.

The standard free energies of formation of a number of hydrocarbons have been calculated. Equations for the free energy changes of the reactions involving the carbide have been derived.

The great affinities of the carbide for the water molecules and of the calcium oxide formed during the reaction for carbon dioxide play a dominant and important role in the organic syntheses in which water or carbon dioxide or both are formed. By eliminating the products of reaction rapidly and completely, often the rate of reaction can be increased without increasing the temperature; in other

words, the rate of reaction can be increased without sacrificing its equilibrium.

The Central Laboratory,
South Manchuria Railway Company,
Dairen.