[CONTRIBUTION FROM THE MELLON INSTITUTE AND THE UNIVERSITY OF PITTSBURGH, PITTSBURGH, PENNSYLVANIA]

Equilibria in the Systems Fe_2C–Fe–CH_4–H_2 and Fe_3C–Fe–CH_4–H_2[1]

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Introduction

Carbiding iron with carbon monoxide or hydrocarbons in the temperature range 200–300° results in the formation of a product having the approximate composition Fe_2C.[2,3] This carbide is formed and can be reduced in the same temperature range in which the Fischer–Tropsch synthesis is carried out; as a matter of fact, examination of used Fischer–Tropsch catalysts shows some of this carbide to be present.[4] It was proposed years ago[5,6,7] that the carbide is an intermediate in the formation of hydrocarbons. It seemed worthwhile, therefore, to attempt to obtain values for the free energy of formation of Fe_2C in the temperature range of interest in the Fischer–Tropsch synthesis. Such information would help considerably in determining the role, if any, of Fe_2C in hydrocarbon formation in the Fischer–Tropsch synthesis.

The present paper reports equilibrium measurements of methane and hydrogen over Fe_2C and iron according to the reaction

$$CH_4 + 2Fe = Fe_2C + 2H_2 \quad K_1 = (H_2)^2/(CH_4) \quad (1)$$

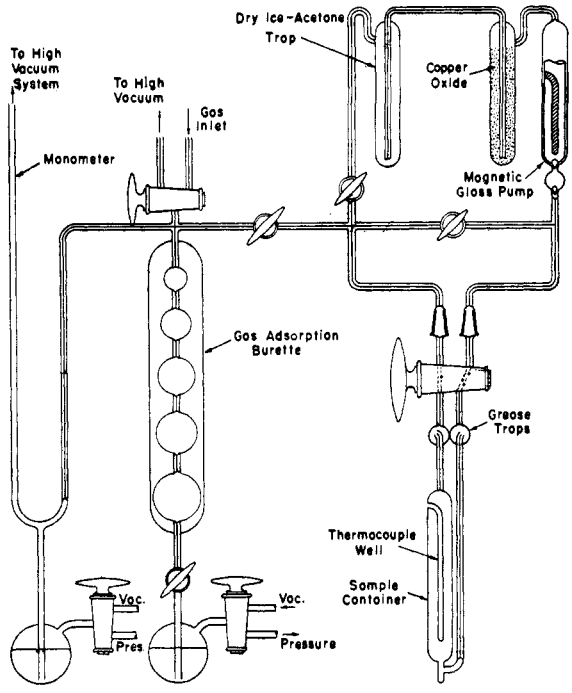
in the temperature range 295–350°. In view of the fact that no consistent data for the equilibrium of methane and hydrogen with the system of Fe_3C–Fe have been reported below 450°, measurements were also made of the equilibrium in the temperature range 320–468° according to the reaction

$$CH_4 + 3Fe(\alpha) = Fe_3C(\beta) + 2H_2 \qquad K_2 = (H_2)^2/(CH_4) \quad (2)$$

Fe_3C (β) being designated by Kelley[8] as the form existing above 190°.

Experimental

Apparatus and Procedure.—A diagram of the apparatus used is shown in Fig. 1. The general procedure was to circulate gas of the desired initial composition over a previously prepared sample of Fe–Fe_2C or Fe–Fe_3C, until the pressure became constant. The gas was then analyzed for hydrogen; methane was obtained by difference. The circulating system consisted of the sample container, a trap used for removing water during an analysis, a trap containing copper oxide used to oxidize hydrogen to water during an analysis, a magnetic glass pump[9] for circulating the gas, and a by-pass which allowed gas to be circulated through the catalyst during equilibration or around it during analysis. Pressures were read to 0.1 mm. on a single-leg absolute mercury manometer. An adsorption buret was used to determine the adsorption of nitrogen at −195°, and hence, by the B. E. T.[10] method the surface area of the original iron sample. Additional apparatus, not shown, consisted of a furnace to heat the sample, a mercury diffusion pump, a mechanical backing pump, a gas purification train, and storage bulbs for the purified gases.



ADSORPTION AND CIRCULATING SYSTEM USED IN EQUILIBRIUM STUDIES IN THE SYSTEM C-H-Fe

Fig. 1.—Apparatus for the determination of equilibria in the systems Fe_2C–CH_4–H_2–Fe and Fe_3C–CH_4–H_2–Fe.

The glass sample container was 12 mm. in diameter and 100 mm. long. It contained a centrally located thermocouple well. Both inlet and outlet connections to the container were made of 2 mm. capillary tubing. The linear velocity of the gas was sufficiently high (5 cm./sec.) to avoid errors due to thermal diffusion.

The sample was heated by means of a nichrome wound furnace having an aluminum core of one inch inside diameter and two inches outside diameter. The temperature of the furnace was controlled by the change in resistance with temperature of an auxiliary winding. The controller circuit was somewhat similar to that described by M. Benedict.[11] The temperature of the furnace was constant to within ±0.25° during an experiment. Measurement of the temperature distribution over the sample container showed a lengthwise variation of about 0.5° at 400°.

Temperatures were measured by means of a chromel–alumel thermocouple inserted in the well of the sample tube. The cold junction of the thermocouple was contained in an ice-bath. Temperatures were read in millivolts on a

(1) Joint contribution from the Gulf Research & Development Company's Multiple Fellowship, Mellon Institute, and the University of Pittsburgh, Pittsburgh, Pa.

(2) (a) Bahr and Jesson, *Ber.*, **66**, 1238 (1933), (b) Hägg, *Z. Krist.*, **89**, 92 (1934).

(3) Jack, *Nature*, **158**, 60 (1946).

(4) Hofer, *Bur. Mines Rep. Invest.*, 3770, 35 (1944).

(5) Fischer and Tropsch, *Gesam. Abhandl. Kenntnis der Kohle*, **8**, 190 (1929).

(6) Fischer and Bahr, *ibid.*, **8**, 267 (1929).

(7) Fischer and Tropsch, *ibid.*, **10**, 313 (1932).

(8) Kelley, *Bur. Mines Bull.*, #407 (1937).

(9) Porter, Bardwell and Lind, *Ind. Eng. Chem.*, **18**, 1086 (1926).

(10) Brunauer, Emmett and Teller, THIS JOURNAL, **60**, 310 (1938).

(11) Benedict, *Rev. Sci. Inst.*, **8**, 252 (1937).

Leeds and Northrup precision portable potentiometer to ±0.25°. The thermocouple used, 30 gage chromel-alumel, was calibrated against a previously standardized chromel-alumel couple. Total temperature uncertainty was estimated to be ±1°.

The procedure for a typical experiment was as follows: Gas of the desired initial composition was circulated over the sample for an additional eight to ten hours after the pressure became constant. At the end of this time, the pressure was read, and the sample closed off. The gas mixture was then analyzed for hydrogen by circulating it through the by-pass, over copper oxide at 300° and through a Dry Ice-acetone trap. The equilibrium constant K_1 or K_2 for reaction (1) or (2) was then calculated.

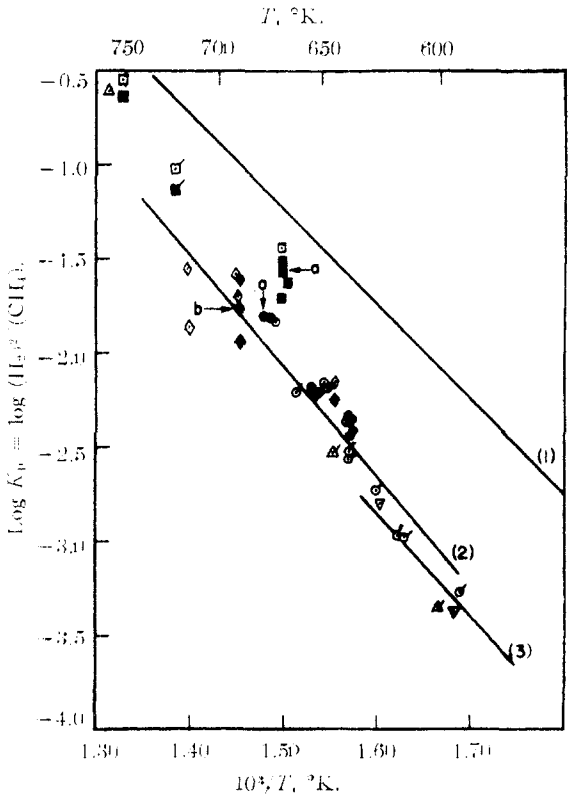


Fig. 2.—Preliminary equilibrium data for reactions 1 and 2. Points labeled "a" represent two points, one from the hydrogen and one from the methane side; the one labeled "b" represents six points, four from the methane and two from the hydrogen side. Curves 1, 2 and 3 are plots of the best values for the equilibrium data for the systems C–H_2–CH_4 (as given by Rossini[14]), Fe_3C–Fe–H_2–CH_4 (our data as per Fig. 4), and Fe_2C–Fe–H_2–CH_4 (our data as per Fig. 3), respectively. Open symbols, equilibrium approached from hydrogen side; solid symbols, equilibrium approached from methane side.

Symbol	Expt.	Sample	Temp. of carbiding or heat treatment, °C.	Carbiding gas	Carbidic carbon, %
⊙	1–16	A	370	CH_4	0.5
⊡	17–24	A	500 (12 hr.)	...	0.5
⊡′	25–26	A	450	CH_4	1.7
◇	27–40	B	450	CH_4	0 to 1
▽	41–42	C	275	C_4H_{10}	7.4
			450 (12 hr.)	...	7.4
○	48–54	D	275	C_4H_{10}	7.0
△	55	D	495 (12 hr.)	...	7.0
△	83–84	E	235	CO	4.7

Preparation of the Iron Carbides.—Fe_2C can be prepared either by carbiding iron with carbon monoxide at 200–300° or by using butane or some other hydrocarbon as the carbiding agent.[12] The use of a hydrocarbon has the advantage of being easier to control than the use of carbon monoxide. There is no tendency for the catalyst to heat up and deposit free carbon when butane is used for carbiding at 250–300°, whereas sudden exposure of a reduced iron catalyst to carbon monoxide at such temperatures would result in the formation of much free carbon and a sudden rise in temperature. Furthermore, some iron oxide tends to form when carbon monoxide is used as the carbiding agent. Accordingly, most of the samples were prepared using butane as the carbiding gas. X-Ray diffraction patterns of samples so prepared are identical with those prepared by carbiding with carbon monoxide[12] and are the same as those prepared by Hägg.[2] Samples A to C mentioned in the legend for Fig. 2 were prepared from an iron synthetic ammonia catalyst (#423) containing 2.26% Al_2O_3, 0.62% SiO_2, and 0.2% ZrO_2 as promoters. All other samples were prepared from a synthetic ammonia catalyst (#339) containing 2.2% Al_2O_3 and 0.76% ZrO_2 as promoters. The surface area of each of these two catalysts was about 17 sq. m./g. as determined by the B.E.T. method.[10] Prior to carbiding the iron oxide catalysts were reduced in a stream of pure dry hydrogen at 500°.

Fe_2C was prepared by heating the Fe_2C to 475–500° for two to three hours. This treatment causes a complete disappearance of the Fe_2C lines in the X-ray diffraction pattern, and the appearance of Fe_3C lines. Unfortunately, the conversion of Fe_2C to Fe_3C was accompanied by a slight decomposition of the carbide, as evidenced by the presence of some carbon that would not reduce in hydrogen at 275°. In the temperature range employed, however, this small amount of free carbon did not affect the final equilibrium values for reaction 2 because apparently the formation or reduction of free carbon during a run was slow compared to the formation or reduction of the carbide.

Results

The experimental data in the present work may be divided into the following three categories: preliminary experiments (Fig. 2); final experiments on the system Fe–Fe_2C–CH_4–H_2 (Table I and Fig. 3); and final experiments on the system Fe–Fe_3C–CH_4–H_2 (Table II and Fig. 4).

A total of about fifty preliminary experiments was carried out. These are plotted in Fig. 2. There were several reasons for designating certain experiments as preliminary. Experiments 1 to 40 are so classed because the solid phase either contained no carbide or contained only about 1.0% carbidic carbon, all of it formed by the reaction of CH_4 with the iron. In experiments 1–16 the equilibrium constants correspond closely to those later found for the Fe–Fe_3C–CH_4–H_2 system, but are slightly high. Since the methane carbiding was carried out at 370° for these runs, the carbon was present principally as Fe_3C. However, since the carbiding and measurements were all made in the temperature range 360 to 400°, some slight influence of free carbon on the equilibrium might have been involved. Before run 17 the sample used in runs 1 to 16 was heated for twelve hours at 500°. Accordingly, experiments 17 to 24 were made in the temperature range 400 to 490° on a sample that had been subjected to this heat treat-

(12) Podgurski, private communication.

TABLE I

EQUILIBRIUM CONSTANTS[a] FOR THE REACTION $CH_4 + 2Fe(\alpha) = Fe_2C + 2H_2$

Expt.	T, °C.	Composition of the initial gas, % H_2	% CH_4	Composition of the equilibrated gas H_2, %	% CH_4, %	Pressure of H_2, atm.	Pressure of CH_4, atm.	Total pressure, atm.	K_p/atm.
43	321.0	14.87	85.13	3.92	97.08	0.0121	0.2963	0.3084	0.00049
44	351.0	16.83	83.17	5.26	94.74	.0232	.3189	.4421	.00128
45	341.0	6.41	93.59	5.01	94.98	.0248	.4687	.4935	.00130
46	343.9	100.00	0.00	5.28	94.92	.0170	.3050	.3220	.00095
47	331.0	100.00	0.00	4.54	95.46	.0140	.2945	.3806	.00067
56	316.1	100.00	0.00	3.44	96.56	.0166	.3257	.3373	.00041
57	306.2	100.00	0.00	3.07	96.93	.0095	.3007	.3103	.00030
58	296.3	100.00	0.00	2.50	97.50	.0075	.2930	.3005	.00019
59	305.2	0.00	100.00	2.36	97.64	.0104	.4283	.4387	.00025
60	308.0	100.00	0.00	3.35	96.65	.0143	.4133	.4276	.00050
61	310.3	100.00	0.00	2.64	97.36	.0113	.4161	.4274	.00031
62	310.3	0.00	100.00	2.61	97.39	.0118	.4384	.4501	.00032
63	312.0	0.00	100.00	2.95	97.05	.0102	.3356	.3485	.00031
64	316.1	0.00	100.00	3.08	96.92	.0135	.4263	.4398	.00043
65	329.5	100.00	0.00	4.08	95.92	.0181	.4264	.4425	.00094
66	323.3	0.00	100.00	3.19	96.81	.0173	.5249	.5422	.00057
67	326.5	100.00	0.00	4.18	95.82	.0149	.3405	.3554	.00065
74	333.4	100.00	0.00	3.84	96.16	.0168	.4201	.4369	.00067
75	336.6	100.00	0.00	4.71	95.29	.0216	.4371	.4587	.00107
76	337.8	100.00	0.00	4.56	95.42	.0200	.4160	.4360	.00086
79	336.1	100.00	0.00	4.52	94.98	.0185	.3917	.4103	.00083
81	344.2	15.11	84.89	4.62	95.38	.0185	.3814	.3999	.00090
82	359.1	13.24	86.76	5.01	94.99	.0229	.4341	.4570	.00120

[a] Details of preparation and pretreatment of the samples for these runs may be tabulated as

Runs	Sample	Temp. of carbiding or heat treatment, °C.	Carbiding gas	Carbidic carbon, %
43–47	D	275	C_4H_{10}	7.0
56–67	F	275	C_4H_{10}	6.9
74–76	H	275	C_4H_{10}	6.2
79	J	275	C_4H_{10}	4.6
81–82	K	275	C_4H_{10}	4.3

ment. Runs 25 and 26 were made after a further carbiding with CH_4 at 450° to a 1.68% carbidic carbon content following run 24. The results of experiments 17 to 26 are clearly intermediate between values for the Fe–Fe_3C–CH_4–H_2 and the C–CH_4–H_2 systems, respectively. Apparently sufficient quantities of Fe_3C and free carbon were present to make the rate of reaction of the CH_4–H_2 mixture with Fe_3C–Fe comparable with the rate of reaction with the free carbon supported on the iron. Experiments 27–40 were made either with no prior carbiding or with as much as 1% carbidic carbon formed by the reaction of iron with CH_4 at 450°. In general, these experiments are in fair agreement with the data later selected (shown as Curve 2, Fig. 2) as characteristic of the system Fe_3C–Fe–CH_4–H_2. Only experiment 40 appears for some unknown reason to have been considerably in error.

The sample used in experiments 41 and 42 was prepared in the preferred manner by carbiding with butane at 275°. However, the sample was heated to 450° for twelve hours to convert the Fe_2C to Fe_3C. An anomalous pressure change (initial hydrogen evolution followed by hydrogen consumption) suggested that stopcock grease may have contaminated the surface of the sample with Fe_2C during the experiments. At any rate the final equilibrium values obtained in these experi-

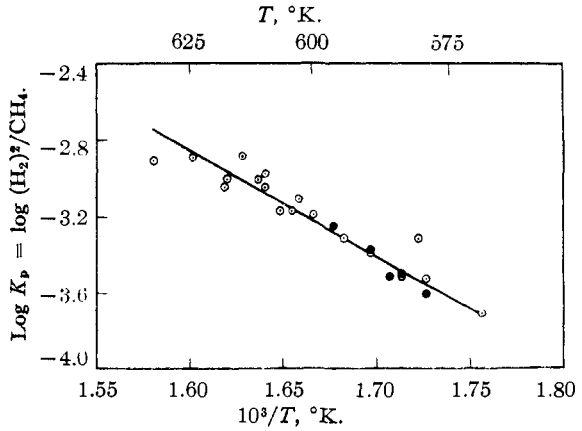


Fig. 3.—Values of the log of the equilibrium constants log $(H_2)^2/CH_4$ for reaction 1: open circles, equilibrium approached from the excess hydrogen side; solid circles equilibrium approached from the excess methane side.

TABLE II

EQUILIBRIUM CONSTANTS[a] FOR THE REACTION $CH_4 + 3Fe(\alpha) = Fe_3C(\beta) + 2H_2$

Expt.	T, °C.	Composition of the initial gas, % H_2	% CH_4	Composition of the equilibrated gas—— H_2, %	% CH_4, %	Pressure of H_2, atm.	Pressure of CH_4, atm.	Total pressure, atm.	K_p/atm
68	348.3	100.00	0.00	7.50	92.50	0.0245	0.3017	0.3262	0.00198
69	349.0	5.40	94.60	6.01	93.99	.0301	.4805	.5112	.00196
70	337.2	100.00	0.00	5.41	94.59	.0245	.4266	.4511	.00141
71	337.2	4.31	95.69	5.34	94.66	.0252	.4458	.4706	.00142
72	329.3	100.00	0.00	4.72	95.28	.0218	.4402	.4620	.00108
73	320.5	2.56	97.44	3.68	97.32	.0170	.4625	.4455	.00065
77	372.1	100.00	0.00	9.91	90.09	.0366	.3325	.3691	.00402
78	386.3	14.63	85.96	10.96	89.04	.0519	.4217	.4736	.00639
80	391.8	100.00	0.00	13.09	86.91	.0483	.3209	.3692	.00728
85	355.1	100.00	0.00	7.98	92.02	.0265	.3055	.3320	.00230
86	397.1	100.00	0.00	13.19	86.81	.0590	.3881	.4471	.00897
87	415.9	27.92	72.08	15.33	84.67	.0966	.5344	.6311	.01750
88	358.9	5.93	94.07	6.11	93.56	.0402	.5836	.6238	.00277
89	452.6	100.00	0.00	25.95	74.05	.1214	.3466	.4880	.0425
90	468.0	100.00	0.00	30.67	69.33	.1604	.3625	.5229	.0710

[a] Details of preparation and pretreatment of the samples for these runs may be tabulated as follows:

Runs	Sample	Temp. of carbiding or heat treatment, °C.	Carbiding gas	Carbidic carbon, %
68–73	G	Sample F reduced at 300° and heated 3 hr. 500°	...	4.2
77–78	I	Sample H (Table I) heated 3 hr. 500°	...	6.2
80		Sample J (Table II) heated 3 hr. 500°	...	4.6
85–88	E	Carbided at 235° and heated 3 hr. 500°	CO	4.7
89–90	L	Carbided at 235° and heated 5 hr. 460°	CO	4.4

ments corresponded more closely to the Fe–Fe_2C system than to the Fe–Fe_3C system.

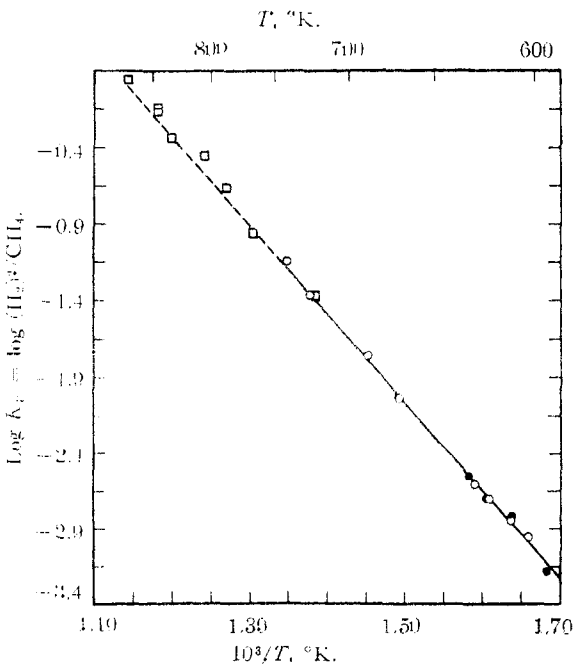


Fig. 4.—Values of the log of the equilibrium constants, log $(H_2)^2/CH_4$ for reaction 2: open circles, authors' data, equilibrium approached from the excess hydrogen side; solid circles, authors' data, equilibrium approached from the excess methane side; squares, Watase's data; dotted line, extrapolation of authors' data.

Experiments 48–54 were omitted because the first three experiments were made in the temperature range 365–389°. It was suspected that some Fe_3C may have been formed in this temperature interval. Actually, experiments 51, 52, 53 and 54 (Fig. 2) in the temperature range 318 to 353° agree very well with the final experiments on the Fe–Fe_2C system (Curve 3, Fig. 2). Experiment 55 was made after heating the carbide sample to 495° for twelve hours; the sample had apparently been partly decomposed to carbon and iron.

Experiments 83 and 84 were made on a sample carbided with carbon monoxide. Before these runs hydrogen was circulated over this sample at 327° in an endeavor to remove surface oxide which is usually formed when carbon monoxide is used as the carbiding agent, and which slows down the reaction of methane or hydrogen with the solid Fe–Fe_2C phase. Actually, the equilibrium values obtained in these two experiments are in satisfactory agreement with curve 3, and could have been included in the final data.

The final experiments on the Fe–Fe_2C–CH_4–H_2 system, the results of which are shown in Table I and Fig. 3, were made in the temperature range 296–351° using samples carbided with butane at 275°. The equilibration with samples carbided with carbon monoxide was so slow in this temperature range that only experiments 83 and 84 (Fig. 1) were attempted using Fe_2C so prepared.

The final experiments on the Fe–Fe_3C–CH_4–H_2 system are shown in Table II and Fig. 4. They were all made subsequent to the installation of grease traps above the reaction vessel as shown in

TABLE III

FREE ENERGY OF FORMATION, ΔF^0_f, AND HEAT OF FORMATION, ΔH^0_f OF $Fe_3C(\beta)$ IN THE TEMPERATURE RANGE 298.16–800°K.

	ΔF^0_f, kcal.		ΔH^0_f, kcal.	
T, °K.	Watase	Present data	Watase	Present data
298.16	4.661	4.441	5.756	5.453
400	4.174	4.000	6.428	6.028
500	3.542	3.447	6.742	6.341
600	2.93	2.85	6.839	6.446
700	2.32	2.25	6.781	6.380
800	1.72	1.68	6.514	6.122

TABLE IV

FREE ENERGY OF FORMATION (ΔF_f) OF Fe_2C

Temp., °K.	ΔF_f, kcal.
450	3.757
500	3.613
550	3.570
600	3.360
650	3.230

TABLE V

FREE ENERGY VALUES FOR THE REACTION $nFe_2C + nH_2 = C_nH_{2n} + 2nFe$

T, °K.	n	ΔF^0_f, C_nH_{2n}, kcal.	ΔF^0_f, nFe_2C, kcal.	$\Delta F^0_{react.}$, kcal.	$\log K_p = \log (C_nH_{2n})/(H_2)^n$
450	2	18.41	7.52	10.89	− 5.289
	4	26.32	15.04	11.28	− 5.478
	6	37.2	22.56	14.6	− 7.091
500	2	19.245	7.23	12.02	− 5.253
	4	29.430	14.46	14.97	− 6.543
	6	42.7	21.69	20.0	− 8.741
600	2	20.918	6.72	14.20	− 5.173
	4	35.85	13.44	22.41	− 8.164
	6	54.1	20.16	33.9	−12.350
650	2	21.80	6.46	15.34	− 5.158
	4	39.13	12.92	26.21	− 8.813
	6	60.4	19.38	41.0	−13.786

TABLE VI

FREE ENERGY VALUES FOR THE REACTION $nFe_2C + (n+1)H_2 = C_nH_{2n+2} + 2nFe$

T, °K.	n	ΔF^0_f, C_nH_{2n+2}, kcal.	ΔF^0_f, nFe_2C, kcal.	$\Delta F^0_{react.}$, kcal.	$\log K_p = \log \frac{(C_nH_{2n+2})}{(H_2)^{n+1}}$
450	2	−2.31	7.52	−9.83	4.774
	4	10.15	15.04	−4.89	2.375
	6	21.28	22.56	−1.28	0.622
	8	32.69	30.08	2.61	− 0.127
500	2	1.17	7.23	−6.06	2.943
	4	14.86	14.46	0.40	− 0.194
	6	28.46	21.69	6.77	− 2.959
	8	42.32	28.92	13.40	− 5.857
600	2	5.97	6.72	−0.75	0.273
	4	24.59	13.44	11.15	− 4.062
	6	43.18	20.16	23.02	− 8.386
	8	62.03	26.88	35.15	−12.805
650	2	8.42	6.46	1.96	− 0.659
	4	29.54	12.92	16.62	− 5.588
	6	50.66	19.38	31.28	−10.518
	8	72.03	25.84	46.19	−15.531

Fig. 1. Six of the experiments (runs 85–90) were made using Fe_3C formed by heating to 500° Fe_2C prepared by carbiding iron with carbon monoxide. The other nine experiments were on samples in which the Fe_2C was originally formed by using butane as the carbiding gas.

Discussion

Reaction (2) has been studied by Watase[12a] in the temperature range 450–603° and by Schenck[13] in the temperature range 350–850°. As can be seen from Fig. 4, Watase's data are in very good agreement with those obtained in the present work at about 500°. Furthermore, his data in the range 500 to 600° agree well with an extrapolation of our own data to the higher temperature range. On the other hand, the equilibrium values obtained by Schenck are considerably lower than the curve shown in Fig. 4, and are somewhat scattered. The cause of this disagreement with Schenck's data is not apparent.

Kelley[8] has represented ΔC_p for reaction 2 by the equation

$$\Delta C_p = 21.13 - 26.26 \times 10^{-3}T + 1.118 \times 10^5 T^{-2} \quad (3)$$

From equation (3) and the experimental data, the heat and free energy of reaction 2 may be represented by the equations[13a]

$$\Delta H^0 = 18{,}584 + 21.13T - 13.13 \times 10^{-3}T^2 - 1.118 \times 10^5 T^{-1} \quad (4)$$

$$\Delta F^0 = 18{,}584 - 48.66T \log T + 13.13 \times 10^{-3} T^2 - 0.559 \times 10^5 T^{-1} + 110.40T \quad (5)$$

The maximum deviation of the experimental points from equation (5) for free energy and heat values was 2.8%; the average deviation was 1%.

The heat and free energy of formation of Fe_3C (β) according to the reaction

$$3Fe(\alpha) + C(\beta \text{ graphite}) = Fe_3C(\beta) \quad (6)$$

may be calculated by using the heats and free energies of formation of methane as given by Rossini[14] according to the reaction

$$C(\beta \text{ graphite}) + 2H_2(g) = CH_4(g) \quad (7)$$

and equations (4) and (5). In Table III are given the calculated values for the free energy and heat of formation of $Fe_3C(\beta)$ in the temperature range 298.1–800°K., compared with values obtained from a smoothed curve through Watase's data. Obviously, the two sets of free energy and heat values are in excellent agreement.

(12a) Watase, *J. Chem. Soc. Japan*, **54**, 110 (1933).

(13) Schenck, *Z. anorg. Chem.*, **164**, 145 (1927).

(13a) ΔH^0 and I were obtained by plotting the function

$$\Sigma = -R \ln K_p + 48.66 \log T - 13.13 \times 10^{-3}T + 0.559 \times 10^5 T^{-2}$$

against $1/T$ and obtaining the best straight line through the points by the method of least squares. ΔH^0 is the slope, and I the intercept of the line so obtained. The lines drawn through the experimental points on the log K_p *versus* $1/T$ plots for reactions 1 and 2 were obtained by calculating log K_p at the various temperatures from equations (5) and (8).

(14) Rossini, "Selected Values of Properties of Hydrocarbons," Circular of the National Bureau of Standards C461, 1947.

Fe_2C.—Expressing the data for Fe_2C in the form of a free energy or heat change equation is much more difficult than it was for similar data for Fe_3C because no heat capacity data exist for the compound Fe_2C. As an approximation, it may not be unreasonable, however, to assume that the ΔC_p change for reaction 1 is the same as for reaction 2. With this assumption the data from Table I for reaction 1 then lead to the following expression for the variation of ΔF^0 with temperature

$$\Delta F^0 = 17{,}081 - 48.66T \log T + 13.13 \times 10^{-3}T^2 - 0.559 \times 10^5 T^{-1} + 113.74T \quad (8)$$

Although this equation does involve an assumption in regard to the change in heat capacity, it represents the experimental data well over the temperature range studied and presumably, therefore, can be used for short extrapolations of the experimental data.

In Fig. 5 are plots of log K against $1/T$ for both the Fe_2C and the Fe_3C systems, the K values being calculated from free energy equations (5) and (8) for the equilibria of reactions 1 and 2. As is evident from the plot, the experimental data are well represented by the equations. The calculation of Kelley[8] for the equilibrium constants for reaction 2 are shown by a dotted line.

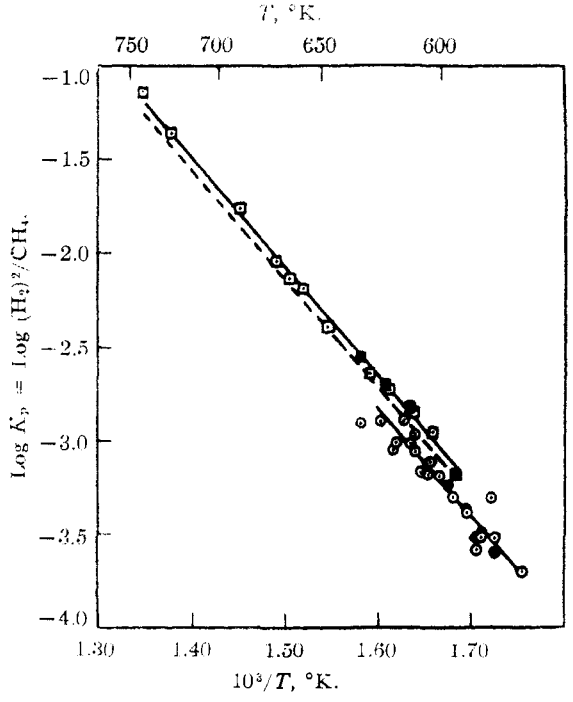


Fig. 5.—Authors' values for the log of the equilibrium constant, log $(H_2)^2/CH_4$ for reactions 1 and 2: open circles, reaction 1 equilibrium approached from excess hydrogen side; solid circles, reaction 1 equilibrium approached from excess methane side; open squares, reaction 2 equilibrium approached from excess hydrogen side; solid squares, reaction 2 equilibrium approached from excess methane side. Solid lines were calculated from equations (5) and (8). Dotted line represents equilibrium values for reaction 2 approximately as given by Kelley,[8] slight modifications of his values being introduced by employing the more recent heat of formation value for CH_4 as given by Rossini.[14]

The experimental errors involved in getting the data shown in Table I for reaction 1 are somewhat greater than those involved in getting the data for reaction 2. The maximum deviation of experimental points from those calculated by equation (8) is 4%; the average deviation was 1%. A somewhat larger error is to be expected for the values for the equilibrium constants for reaction 1 than those for reaction 2 because of the smaller partial pressures and percentages of hydrogen in the equilibrium gas mixture for the Fe_2C system compared to those for the Fe_3C system. The former were in the range 2.5 to 5% whereas the latter extended from about 3.6 to 30%. A given reading error in getting the pressure of hydrogen would therefore cause a larger percentage error in the equilibrium constants for reaction 1 than those for reaction 2.

It should be noted that for both reaction 1 and reaction 2 the equilibrium values obtained from the reduction side were in good agreement with those obtained from the carbiding side. This can be seen readily by comparing the experimental points from the two approaches in Figs. 3 and 4.

It is possible to combine the data for reaction 7 with the data for reaction 1 to yield values for the free energy of formation of Fe_2C by the reaction

$$2Fe(\alpha) + C(\beta \text{ graphite}) = Fe_2C \quad (9)$$

The results of such calculations for reaction 9 are shown in Table IV. The numerical calculations have been restricted to a temperature range that entails only a short extrapolation since, in the absence of reliable heat capacity data for Fe_2C, equation (8) ought not to be used over an extended temperature range. The numerical values shown for 500 and 600°K. are slightly different from the values of 4.070 and 3.542 kcal. previously reported[15] because of the inclusion in the present data of six additional equilibrium values, which changed slightly the slope of the line obtained by plotting log K_p against $1/T$.

Carbide Equilibrium Data and the Fischer–Tropsch Synthesis Mechanism.—In a recent paper[15] some of the results obtained for reaction 1 were used to calculate approximate values for the free energies of formation of Fe_2C. These data for Fe_2C were then employed to show that the equilibria for the reaction of hydrogen with Fe_2C to form any monoölefins according to the reaction

$$nFe_2C + nH_2 = C_nH_{2n} + 2nFe \quad (10)$$

were unfavorable over the temperature range 227 to 327°. Similarly, the formation of appreciable concentrations of the saturated hydrocarbons

(15) Kummer, Browning and Emmett, *J. Chem. Phys.*, **16**, 730 (1948).

having more than 6 carbon atoms according to the reaction

$$n\mathrm{Fe_2C} + (n+1)\mathrm{H_2} = \mathrm{C}_n\mathrm{H}_{2n+2} + 2n\mathrm{Fe} \quad (11)$$

was also shown to be thermodynamically unfavorable above about 300°. More extended calculations of the equilibrium data for these two reactions made by using the values for the free energy of formation of Fe_2C from Table IV are shown in Tables V and VI. It is apparent from these calculations, as from our previous ones, that the formation of any of the monoölefins or of the paraffin hydrocarbons having more than 6 carbon atoms according to reactions 10 and 11, respectively, is thermodynamically unfavorable at 500 and 600°K., the approximate limits of the temperature range for Fischer–Tropsch synthesis over iron catalysts. It may be safely concluded therefore that practically none of the olefin content, and of the paraffin hydrocarbons having more than 6 or 8 carbon atoms, can be produced by reactions 10 and 11 in Fischer–Tropsch synthesis.

The previously reported calculations and the present ones for reactions 10 and 11 have been purposely restricted to cases in which *all* of the carbon of the hydrocarbon would come directly from the carbide and not partly from any CO–H_2 mixture that might also be present. Because of these restrictions care was used in the previous publication[15] and must also be used here to avoid making any implication as to whether or not there are reactions by which Fe_2C could participate in the Fischer–Tropsch synthesis as an intermediate. It was fully realized and has since been pointed out by Schuman[16] that numerous reactions involving hydrogen and both Fe_2C and CO, and leading to the formation of olefins and paraffins can be written and shown to be thermodynamically favorable. One can only state from the calculations in this and in our previous paper that the reduction of Fe_2C by hydrogen over the range of temperatures and partial pressures of hydrogen employed in Fischer–Tropsch synthesis cannot lead to the formation by reaction 10 of the partial pressures of olefins actually found in such a synthesis or to the formation by reaction 11 of observed partial pressures of the higher paraffin hydrocarbons if *all* of the carbon in the hydrocarbon is assumed to come directly from the reduction of Fe_2C. The question of the extent to which the reduction of Fe_2C may furnish part of the carbon in hydrocarbon molecules by reactions such as proposed by Schuman[16] must be answered by other experimental approaches. It may be pointed out here, however, that the results of the C^{14} tracer experiments[17] indicate that, at the most, one of the carbon atoms out of every 6 to 10 in a hydrocarbon molecule comes from the reduction of the surface of any bulk Fe_2C that may be present in an iron Fischer–Tropsch catalyst.

In connection with a discussion of reactions 10 and 11 to form olefins and paraffins, some mention should be made of the possible reduction by hydrogen of Fe_3C and of hexagonal Fe_2C to form hydrocarbons. As pointed out previously, and as is evident from comparison of Tables III and IV, the free energies of formation of Fe_3C and Fe_2C differ by only a few hundred calories over the temperature range 500 to 600°K. pertinent to the Fischer–Tropsch synthesis. Accordingly, in Fischer–Tropsch synthesis over iron it is equally as impossible for Fe_3C as for Fe_2C to furnish all of the carbon for any of the olefins or for the paraffins having more than 6 or 8 carbon atoms by direct reduction by hydrogen by reactions analogous to reactions 10 and 11 above. It is more difficult to make any positive statements relative to the possible direct reduction of hexagonal Fe_2C to form olefins or higher paraffins because no equilibrium data exist on this particular carbide.[18] One can easily calculate, however, that if all of the ethylene observed in a typical fluidized Fischer–Tropsch unit operating at about 600°K. and 10 atmospheres total pressure were to be accounted for by the reduction of hexagonal Fe_2C, the latter would have to have a positive free energy of formation 4,000 to 5,000 calories higher than that of normal Fe_2C. It seems unlikely that two compounds differing only in crystal structure would have such a large difference in free energy of formation. Final conclusions on this point must, however, await additional work on this rather elusive and difficultly prepared hexagonal Fe_2C.

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Summary

Equilibrium constants for the reaction

$$\mathrm{CH_4} + 2\mathrm{Fe}(\alpha) = \mathrm{Fe_2C} + 2\mathrm{H_2} \quad (1)$$

are reported in the temperature range 295–350° and for the reaction

$$\mathrm{CH_4} + 3\mathrm{Fe}(\alpha) = \mathrm{Fe_3C}(\beta) + 2\mathrm{H_2} \quad (2)$$

in the temperature range 320–468°. Free energies of formation of Fe_2C and Fe_3C calculated from the data for reactions 1 and 2 have led to the conclusion that the formation of all monoölefins and of saturated hydrocarbons containing more than six carbon atoms by the direct reduction of Fe_2C and Fe_3C in the temperature range 450–650°K. is thermodynamically unfavorable. The results obtained for reaction 2 agree well with those obtained at higher temperatures by Watase.

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(16) Schuman, *J. Chem. Phys.*, **16**, 1175 (1948).

(17) Kummer, Dewitt and Emmett, THIS JOURNAL, **70**, 3632 (1948).

(18) Hofer, Cohn and Peebles, *ibid.*, **71**, 189 (1949).