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Equilibrium Measurements in the Ni_3C–Ni–CH_4–H_2 and Co_2C–Co–CH_4–H_2 Systems

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Equilibrium constants have been determined for the reaction $3Ni + CH_4 = Ni_3C + 2H_2$; $K_1 = (H_2)^2/CH_4$; in the temperature range 226–285° and for the reaction $2Co + CH_4 = Co_2C + 2H_2$; $K_2 = (H_2)^2/CH_4$; in the temperature range 190–444°. The free energy of formation of Ni_3C thus determined enables one to conclude that the amounts of saturated hydrocarbons and normal monoölefins which, thermodynamically, could be formed by the direct reduction of bulk Ni_3C by hydrogen, are large at 500°K., and increase with increasing molecular weight of the hydrocarbon. At 600°K. the equilibrium amounts of saturated hydrocarbons and of all monoölefins in such a reduction would be small. In the case of the reduction of bulk Co_2C by hydrogen to form hydrocarbons, the amounts of hydrocarbons having more than six carbon atoms, and of all monoölefins at both 500 and 600°K. would be quite small, as judged by the free energy of formation of Co_2C.

In order to evaluate more accurately the part played by carbides in the catalytic synthesis of hydrocarbons over Fe, Ni or Co catalysts, we have recently been measuring the free energy of formation of the carbides Fe_2C, Fe_3C, Ni_3C and Co_2C. Values for the free energies of formation of Fe_2C and Fe_3C were recently published.[1] The present paper completes this work by reporting equilibrium data for the reaction

$$3Ni + CH_4 = Ni_3C + 2H_2 \quad K_1 = (H_2)^2/CH_4 \quad (1)$$

in the temperature range 226–245° and approximate equilibrium data for the reaction

$$2Co + CH_4 = Co_2C + 2H_2 \quad K_2 = (H_2)^2/CH_4 \quad (2)$$

in the temperature range 190–444°.

Experimental

Apparatus and Procedure.—The apparatus and procedure, except for the analysis of the methane–hydrogen mixtures as described below, were the same as those described in a previous paper.[1]

Preparation of Samples.—The nickel and cobalt samples were prepared by adding a sodium carbonate solution to a mixture of nickel or cobalt nitrate and thorium nitrate, washing the carbonate precipitate until it was free of alkali, drying it at 110° and decomposing it at red heat. The metal oxide thoria samples were reduced at 350° in a stream of dry hydrogen to a constant weight. The thoria content of both the nickel and cobalt samples was about 5%. The thoria was added to retard the sintering of the metals and to increase, accordingly, the rate of carbiding with carbon monoxide, and the rate of equilibration with the methane–hydrogen mixtures.

Ni_3C and Co_2C were prepared by carbiding the metals with carbon monoxide at 220°. X-Ray patterns of the samples showed essentially complete carbonization of the nickel and 50% carbonization of the cobalt. Attempts to use butane as the carbiding agent to reduce oxygen pickup by the metal were unsuccessful, because at the higher temperature needed for carbiding with butane, the carbides of nickel and cobalt are unstable and decompose to form free carbon.

Analysis of H_2–CH_4 Mixtures.—Analysis of the CH_4–H_2 mixtures was made by means of a calibrated thermal conductivity cell. The cell had a volume of 1 cc.; about 0.07 cc. of gas was used for each analysis. Because of the small amount of gas necessary for analysis, it was possible to perform experiments at relatively low pressures (15–30 mm.), thus increasing the per cent. hydrogen at equilibrium and hence the accuracy of each determination.

The method of analysis used required that the gases be very pure, since a small amount of impurity would cause a large error in the H_2–CH_4 analysis. A small amount of oxide, apparently formed during the carbiding with carbon monoxide, was present initially in each sample. This oxide tended to react with the carbide to form carbon monoxide or carbon dioxide. In the experiments on Ni_3C, it was possible to eliminate this source of error by evacuating the sample at a temperature five to ten degrees above that at which an equilibrium experiment was to be made. The same procedure failed to eliminate complication caused by carbon monoxide or carbon dioxide formation in measurements on Co–Co_2C. In all runs, after completion of an experiment and analysis of the gas by thermal conductivity, the hydrogen was removed from the gas by combustion over copper oxide at 300°. The thermal conductivity of the resulting gas was then determined; if the value obtained corresponded to that for pure methane, it was assumed that no impurity was present in the gas.

Pure methane for calibration purposes was obtained by reducing part of the Ni_3C with hydrogen and burning the residual hydrogen over copper oxide. All of the possible impurities, such as nitrogen, carbon dioxide, carbon monoxide or hydrocarbons higher than methane, have a lower thermal conductivity than methane. Test for impurities was made by freezing the gas in a liquid nitrogen trap, and comparing the reading for the gas phase with that for the gas before freezing. Any impurities present would, during condensation and freezing in the liquid nitrogen trap, be removed from the gas phase to a different degree than methane and would cause, therefore, a change in the thermal conductivity reading. The reading for the gas finally used was such as to indicate greater purity than that of a purchased sample of "Research Grade" methane reported to be 99.57% pure.

The hydrogen used for calibration and for equilibration experiments was obtained by diffusion through a palladium tube. The purity was such that when 500 mm. was burned over copper oxide, and the resulting water removed in a Dry Ice–acetone trap, no residual pressure could be detected. Since pressures were read to 0.1 mm., the minimum purity of the hydrogen was 99.98%.

Results

In Table I are shown the data obtained for the nickel carbide system; in Fig. 1 is shown a plot of log K_1 against $10^3/T$. Since no heat capacity data are available for Ni_3C, a linear relation between log K_1 and $10^3/T$ was assumed and the best straight line through the points determined by the method of least squares.

The results for the cobalt carbide system are shown in Table II and in Fig. 1. Due to the experimental difficulties mentioned previously, only a probable range of the equilibrium constants for reaction (2) is reported. Curves were drawn through the highest values of log K_2 obtained by approaching equilibrium from the methane side and through the lowest values of log K_2 obtained by approaching equilibrium from the hydrogen side. The value at the highest temperature (443.7°) was obtained by carbiding a sample of cobalt at 220° and then raising the temperature as quickly as possible and circulating hydrogen over the sample for an additional hour after the pressure remained constant. Apparently enough carbide remained to allow equilibrium to be established, since the value of K_p obtained lies within an extrapolation of the approximate range of other values, from lower temperatures and lies below the value expected for the C–H_2–CH_4 equilibrium.

Discussion

Scheffer, Dokkam and Al[2] have studied the Ni_3C–Ni–CH_4–H_2 system in the temperature range 336–625°. Their results indicate that Ni_3C is stable

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(1) L. C. Browning, T. W. DeWitt and P. H. Emmett, THIS JOURNAL, **72**, 4211 (1950).

(2) F. E. C. Scheffer, F. Dokkam and J. Al, *Rec. trav. chim.*, **45**, 803 (1926).

TABLE I

EQUILIBRIUM CONSTANTS FOR THE REACTION
$3Ni + CH_4 = Ni_3C + 2H_2$

		Equilibrated gas			
Expt. no.	T, °C.	H_2, %	Total pressure, atm.	$Kp \times 10^6$	Approach
1	226.4	0.50	0.0126	0.319	H_2
2	227.6	.49	.0153	.369	H_2
3	236.5	.53	.0238	.670	CH_4
4	226.8	.42	.0205	.362	H_2
5	240.9	.52	.0163	.445	CH_4
6	240.3	.36	.0418	.547	H_2
7	240.3	.48	.0256	.592	CH_4
8	228.6	.36	.0224	.287	H_2
9	233.9	.40	.0196	.312	CH_4
10	247.5	.78	.0191	1.19	H_2
11	240.2	.76	.0274	1.59	H_2
12	229.0	.23	.0508	0.27	H_2
13	247.5	.66	.0408	1.79	H_2
14	253.2	.70	.0363	1.79	H_2
15	255.3	.90	.0293	2.40	H_2
16	254.7	.96	.0260	2.42	CH_4
17	255.9	.88	.0318	2.48	H_2
18	249.8	.85	.0358	2.60	H_2
19	265.8	1.52	.0227	5.31	CH_4
20	265.8	1.01	.0492	5.07	H_2
21	271.5	1.18	.0454	6.40	CH_4
22	277.9	1.48	.0550	12.23	H_2
23	272.9	1.32	.0513	9.05	H_2
24	277.4	1.46	.0458	9.89	CH_4
25	283.5	1.71	.0487	14.47	H_2
26	285.0	2.06	.0401	17.40	CH_4

TABLE II

EQUILIBRIUM CONSTANTS FOR THE REACTION
$2Co + CH_4 = Co_2C + 2H_2$

		Equilibrated gas			
Expt. no.	T, °C.	H_2, %	Total pressure, atm.	$K_p \times 10^5$	Approach
1	298.0	1.23	0.7025	10.7	H_2
2	298.0	3.40	.6286	75.4	CH_4
3	298.0	5.76	.6801	239	H_2
4	298.0	2.95	.4803	43.1	H_2
5	298.0	2.80	.4018	32.4	CH_4
6	322.0	5.17	.6068	171	H_2
7	191.0	1.08	.3003	3.50	H_2
8	190.3	2.62	.0478	3.36	H_2
9	199.9	1.60	.0683	1.77	CH_4
10	199.9	1.06	.0597	0.677	H_2
11	198.0	1.00	.0637	0.650	H_2
12	192.0	1.80	.0570	1.90	H_2
13	208.1	1.08	.0718	0.860	H_2
14	196.2	1.11	.0728	0.912	H_2
15	209.0	1.06	.0546	0.620	H_2
16	208.0	1.39	.0582	1.14	H_2
17	210.0	3.20	.0662	7.00	H_2
18	211.0	2.94	.0991	8.80	H_2
19	210.0	2.18	.0901	4.30	H_2
20	219.0	1.27	.1750	2.90	CH_4
21	230.0	0.30	.0974	0.087	CH_4
22	230.0	.30	.1406	.130	CH_4
23	230.0	.74	.0777	.420	CH_4
24	232.0	.52	.2500	.680	CH_4
25	211.0	.60	.2029	.738	H_2
26	443.7	32.9	.3582	5760	H_2

with respect to nickel and carbon at temperatures below 419°. Contrary to this, Hofer,[3] in a thermomagnetic study of Ni_3C, detected decomposition as low as 320°. Furthermore, Bahr and Bahr[4] reported decomposition of Ni_3C samples at temperatures as low as 370°, the decomposition temperature depending on the method of sample preparation. X-Ray patterns of samples of Ni_3C prepared in this Laboratory showed that the carbide completely decomposed when it was heated at 370° for 24 hours. The results of Schefer, Dokkam and Al thus disagree with the known properties of Ni_3C as well as with our equilibrium data in Table I, although the reason for this disagreement is not apparent. Their data are shown plotted in Fig. 1.

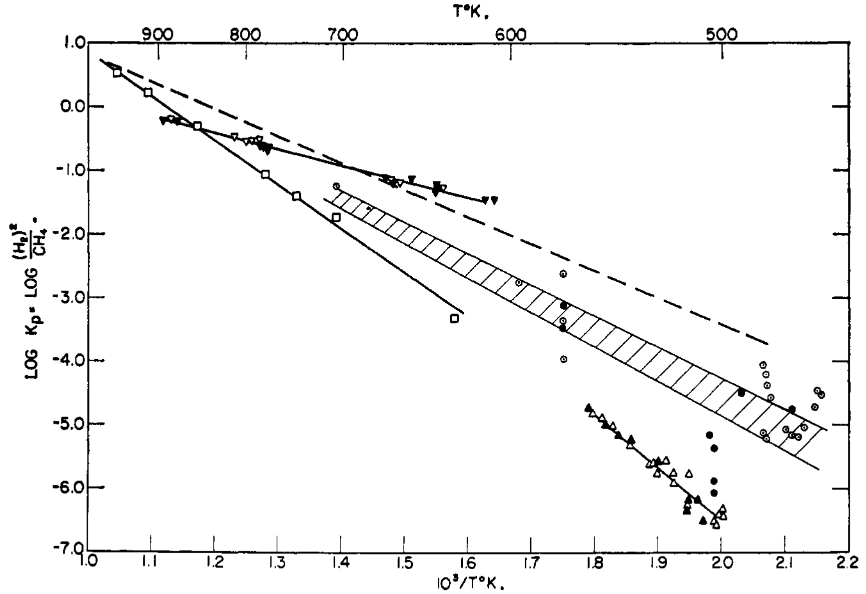

Fig. 1.—Values of the log of the equilibrium constants, log $(H_2)^2/CH_4$ for the system Ni-CH_4-Ni_3C-H_2 (reaction (1)) and the system Co-CH_4-Co_2C-H_2 (reaction (2)). Open symbols: Equilibrium approached from the excess hydrogen side. Solid symbols: Equilibrium approached from excess methane side. △, authors' data for reaction 1; ▽, Schaffer, Dokkam and Al data for reaction 1; ⊙, authors' data for reaction 2; ⊡, Schenck's data for reaction 2; ---, Rossini's values for the C-H_2-CH_4 equilibrium.

Schenck[5] has published data for the reaction

$$3Co + CH_4 = Co_3C + 2H_2 \quad (3)$$

in the temperature range 360-860°. The carbide phase was assumed to be Co_3C. However, since the existence of a cobalt carbide other than Co_2C has not been established, it is probable that Schenck's data are actually for reaction (2). Samples of Co_2C prepared in this Laboratory, however,

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[3] L. J. E. Hofer, E. M. Cohn and W. C. Peebles, *J. Phys. & Colloid Chem.*, **54**, 1161 (1950).

[4] H. A. Bahr and T. Bahr, *Ber.*, **61**, 2177 (1928).

[5] R. Schenck, *Z. anorg. Chem.*, **164**, 313 (1927).

are even less thermally stable than Ni_3C, decomposing at temperatures as low as 240° after 48 hours of heating. Either the thermal stability of the carbide is changed markedly by the method of preparation, or the rate of decomposition is such that in Schenck's work enough carbide remained at the higher temperature for equilibrium to be established. All of the conceivable errors in the present data, such as those due to thermal diffusion and to impurities in the equilibrated gas, would tend to cause an erroneously low H_2/CH_4 ratio. The one source of error which would make this ratio too high—the presence of free carbon—does not seem likely to be causing trouble, since at the lower temperatures free carbon is reduced or formed very slowly. Thermal diffusion errors in Schenck's data do not seem probable, since most of the equilibrated gas was taken for analysis. Actually, only one of Schenck's points (the one at 635°K.) disagrees with our own values to an extent that seems to be beyond experimental error. All of his other points are in reasonable agreement with an extrapolation of our lower temperature measurements. The data of Schenck for reaction (2) are shown plotted in Fig. 1.

Carbide Equilibrium Data and the Fischer–Tropsch Synthesis Mechanism.—The possibility of the formation of hydrocarbons by the reduction of bulk Ni_3C by hydrogen according to the reactions

$$n\mathrm{Ni_3C} + (n + 1)\mathrm{H_2} = \mathrm{C}_n\mathrm{H}_{2n+2} + 3n\mathrm{Ni} \quad (4)$$

$$n\mathrm{Ni_3C} + n\mathrm{H_2} = \mathrm{C}_n\mathrm{H}_{2n} + 3n\mathrm{Ni} \quad (5)$$

may be calculated from a knowledge of the free energy of formation of Ni_3C and of the hydrocarbon. From the present experimental data and the free energy of formation of methane,[6] the standard free energies of formation of Ni_3C at 500 and 600°K. are calculated to be 7,127 and 4,653 cal., respectively. Combining these results with the free energies of formation of the various hydrocarbons,[6] values for the standard free energy change for reactions (4) and (5) as shown in Tables III and IV were obtained. As can be seen from the tables, the amounts of saturated hydrocarbons at 500°K. at equilibrium are quite large, while the amounts of unsaturated hydrocarbons formed according to reaction (5) become larger with increasing values of n. At 600°K., however, the same conclusions that were reached in the case of the iron carbides can be applied to Ni_3C, namely, that the formation of appreciable quantities of saturated hydrocarbons containing more than six carbon atoms, and all normal monoölefins by the direct reduction of bulk Ni_3C with hydrogen is thermodynamically unfavorable.

The same calculations applied to the formation of hydrocarbons by the reduction of Co_2C are even less favorable than in the case of the iron carbides. Thus, at 500°K., the approximate free energy of formation of Co_2C is 2,400 cal./mole, and the free energies of reaction of normal Co_2C with hydrogen to form hexane and ethylene are 15,300 and 14,400 cal., respectively.

Table III

Free Energy Change for the Reaction

$n\mathrm{Ni_3C} + (n + 1)\mathrm{H_2} = \mathrm{C_2H}_{2n+2} + 3n\mathrm{Ni}$

T, °K.	n	$\Delta F°_f$, $n\mathrm{Ni_3C}$, kcal.	$\Delta F°_f$, $\mathrm{C}_n\mathrm{H}_{2n+2}$, kcal.	$\Delta F°$, reaction, kcal.
500	2	14.254	1.168	−13.086
	4	28.508	14.868	−13.640
	6	42.762	28.460	−14.302
	8	57.016	42.320	−14.696
600	2	9.306	5.970	− 3.336
	4	18.612	24.590	5.978
	6	27.918	43.180	15.262
	8	37.224	62.030	24.806

Table IV

Free Energy Change for the Reaction

$n\mathrm{Ni_3C} + n\mathrm{H_2} = \mathrm{C}_n\mathrm{H}_{2n} + 3n\mathrm{Ni}$

T, °K.	n	$\Delta F°_f$, $n\mathrm{Ni_3C}$, kcal.	$\Delta F°_f$, C_nH_{2n}, kcal.	$\Delta F°$, reaction, kcal.
500	2	14.254	19.245	4.991
	4	28.508	29.430	0.922
	6	42.762	42.700	−0.062
600	2	9.306	20.918	11.612
	4	18.612	35.850	17.238
	6	27.918	54.100	26.182

It should be recognized in a discussion of the role of the carbides in the Fischer–Tropsch synthesis that a surface carbide, if formed, would undoubtedly be more important than the bulk carbide. The results obtained for the bulk carbide, however, give some information as to the properties a surface carbide must have in order to serve as an intermediate in the Fischer–Tropsch synthesis. In the case of iron, for example, such a carbide would have to be more unstable than Fe_2C to the extent of 5,000–6,000 cal. before the amounts of higher hydrocarbons actually observed in Fischer–Tropsch synthesis could be accounted for by the mechanism of direct reduction of the carbide. Such a surface carbide would obviously tend to form bulk carbide. The C^{14} tracer studies made by Kummer, DeWitt and Emmett[7] indicate that no surface carbide or bulk carbide capable of existing at synthesis temperatures for longer than two to three minutes can be an intermediate in the formation of more than 10 to 15% of the hydrocarbon product of Fischer–Tropsch synthesis over iron or cobalt catalysts. The above conclusions do not, however, preclude the possibility of a surface carbide such as might be formed from a CO–H_2 mixture acting as an intermediate in the synthesis, the carbide so formed being almost instantaneously hydrogenated to hydrocarbons. Neither do they preclude the possibility of some of the carbon atoms coming from the carbide, provided the remainder and major portion of the carbon in each hydrocarbon molecule comes directly from the carbon monoxide.

Pittsburgh, Penna. Received October 11, 1951

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[6] F. D. Rossini, *et al.*, Circular of the Bureau of Standards C461, 1947.

[7] J. T. Kummer, T. W. DeWitt and P. H. Emmett, This Journal, **70**, 3632 (1948).