

KINETICS OF THE FISCHER-TROPSCH SYNTHESIS ON IRON CATALYSTS

This section reports kinetic studies made with 6- to 8-mesh particles of catalyst D3001 in the reduced and the nitrided states (31). Experiments with the reduced catalyst were difficult because catalytic activity decreased with time. The activity was checked at frequent intervals by short tests at "standard" conditions, and the catalyst was replaced when significant changes in activity were observed. The nitrided catalyst showed only minor variations in activity during periods of operation as long as 6 months. On this basis enough tests were made on reduced catalysts to demonstrate that the results from reduced and nitrided catalysts were essentially the same in most respects, and thereafter all tests were made with nitrided catalysts. Data are given for the change in rate with space velocity, feed gas composition, temperature, and pressure. Then changes in selectivity are considered, followed by an account of the influence of water vapor, carbon dioxide, and diluents on the rate of synthesis. Finally, the kinetic data are summarized and a semifundamental rate equation is proposed and tested.

EFFECT OF SPACE VELOCITY, FEED COMPOSITION, AND TEMPERATURE

Data were obtained at 21.4 atmospheres with synthesis gas having H_2 -CO ratios of 1.0 and 2.0 at 240° C and 255° C for reduced catalysts and with H_2 -CO ratios of 0.25, 0.7, 1.0 and 2.0

for nitrided catalysts at 225° C and 240° C. Gas flows were varied to obtain conversions of H_2 +CO from about 0.05 to 0.85.

Data for a typical experiment with nitrided iron catalyst computed from the inlet and outlet flows are shown in table 1. Plots of data of this type as a function of reciprocal space velocity, S^{-1} , for reduced catalysts with $1H_2+1CO$ feed gas at 240° C are given in figure 2. Similar graphs for nitrided catalysts are presented in figures 3 and 4. The upper portions of these graphs show plots of conversion of H_2 +CO, x ; space-time-yield, xS ; and differential reaction rate, $r=dx/d(1/S)$, as determined by two graphical differentiation methods. The lower portions of these graphs show plots of mole fractions of the major components of the exit gas as a function of reciprocal space velocity. To demonstrate the influence of gas composition and the general consistency or experimental results from tests with nitrided catalysts, all of the rate data are plotted on a logarithmic scale in figure 5. This plot expands the scale to show the relationship of experimental points at low values of S^{-1} more clearly.

The data in figures 2 and 3 indicate that the kinetics of the Fischer-Tropsch synthesis are qualitatively similar for reduced and nitrided catalysts despite large differences in selectivity. Results for tests with $0.25H_2+1CO$ gas are probably complicated by the carbon-forming reaction $2CO=CO_2+C$, as the conversion ex-

TABLE 1.—Basic data as computed from gas flows and compositions. Nitrided catalyst with $1H_2+1CO$ gas at 240° C

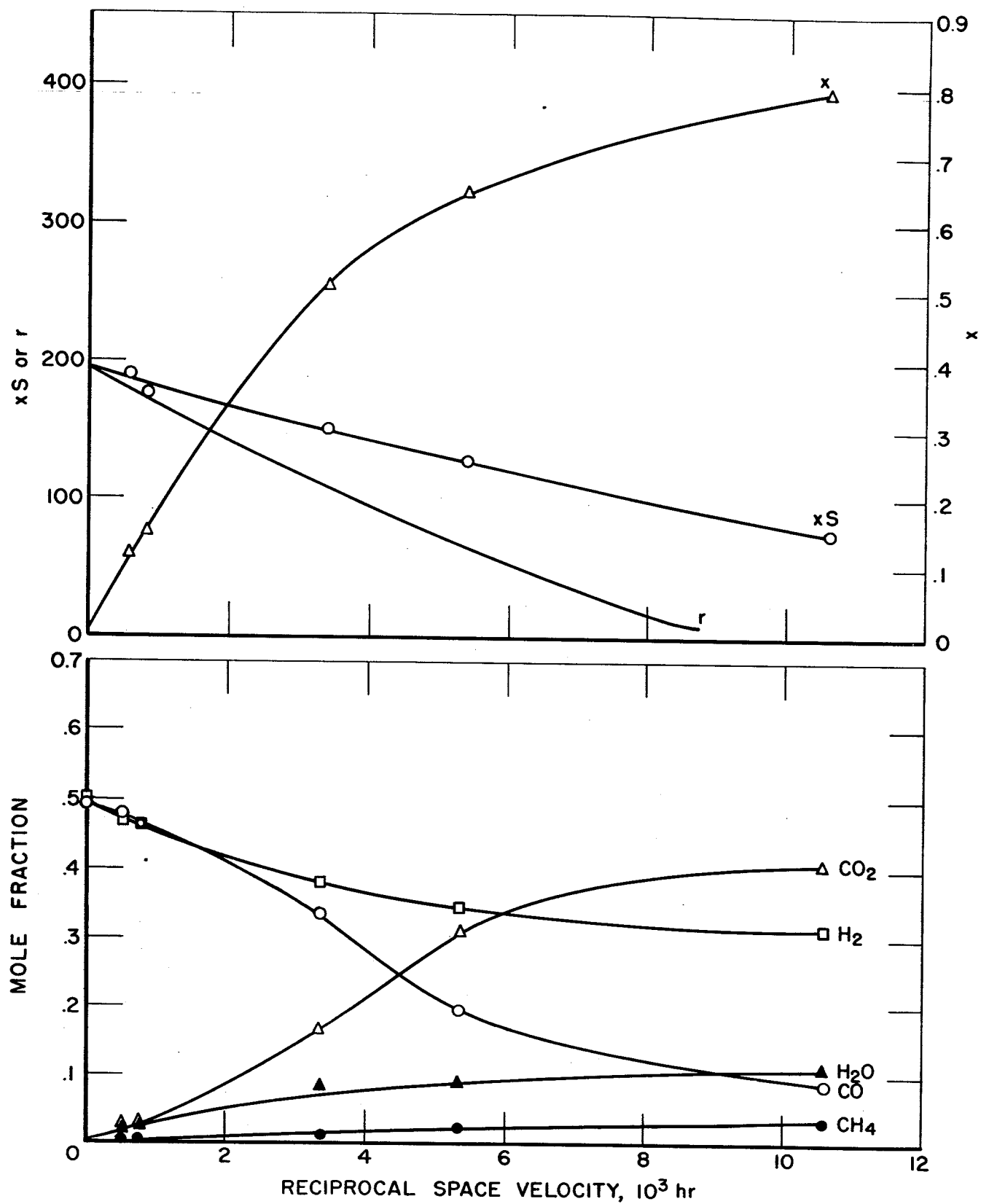
Hourly space velocity	S_e/S^*	Conversion, percent	Reaction † rate, hour ⁻¹	Partial pressures of exit gas atmospheres						
				p_{H_2}	p_{CO}	p_{CO_2}	$p_{H_2O}†$	p_{CH_4}	p_{C_2}	$p_{C_3+C_4}$
Feed gas§	1.00	(0)	293	10.68	10.68	0.02	0	0.02	0	0
1,834	.904	16.3	264	10.16	9.60	.77	0.46	.19	0.10	0.12
1,177	.870	22.6	247	9.86	9.14	1.25	.51	.31	.13	.20
903	.831	28.4	233	9.54	8.89	1.70	.60	.38	.13	.13
607	.766	38.5	204	8.97	8.35	2.50	.85	.52	.18	.08
325	.610	64.9	126	8.02	4.78	5.43	1.39	1.14	.31	.31
222	.530	79.2	49	6.84	1.99	8.42	1.40	1.70	.56	.47
112	.472	88.2	—	5.41	.50	10.12	1.96	2.32	.67	.44

* Ratio of outlet flow S_e to inlet flow S . Outlet flow includes H_2O , CO_2 and C_1 - C_4 hydrocarbons.

† Computed using the half-order empirical equation.

‡ Computed by difference from oxygen balance assuming that no oxygenated molecules other than CO_2 and H_2O are formed.

§ Corresponds to infinite space velocity or zero conversion.

FIGURE 2.—Evaluation of Data for $1\text{H}_2+1\text{CO}$ Feed Gas at 240°C , Reduced Catalyst.

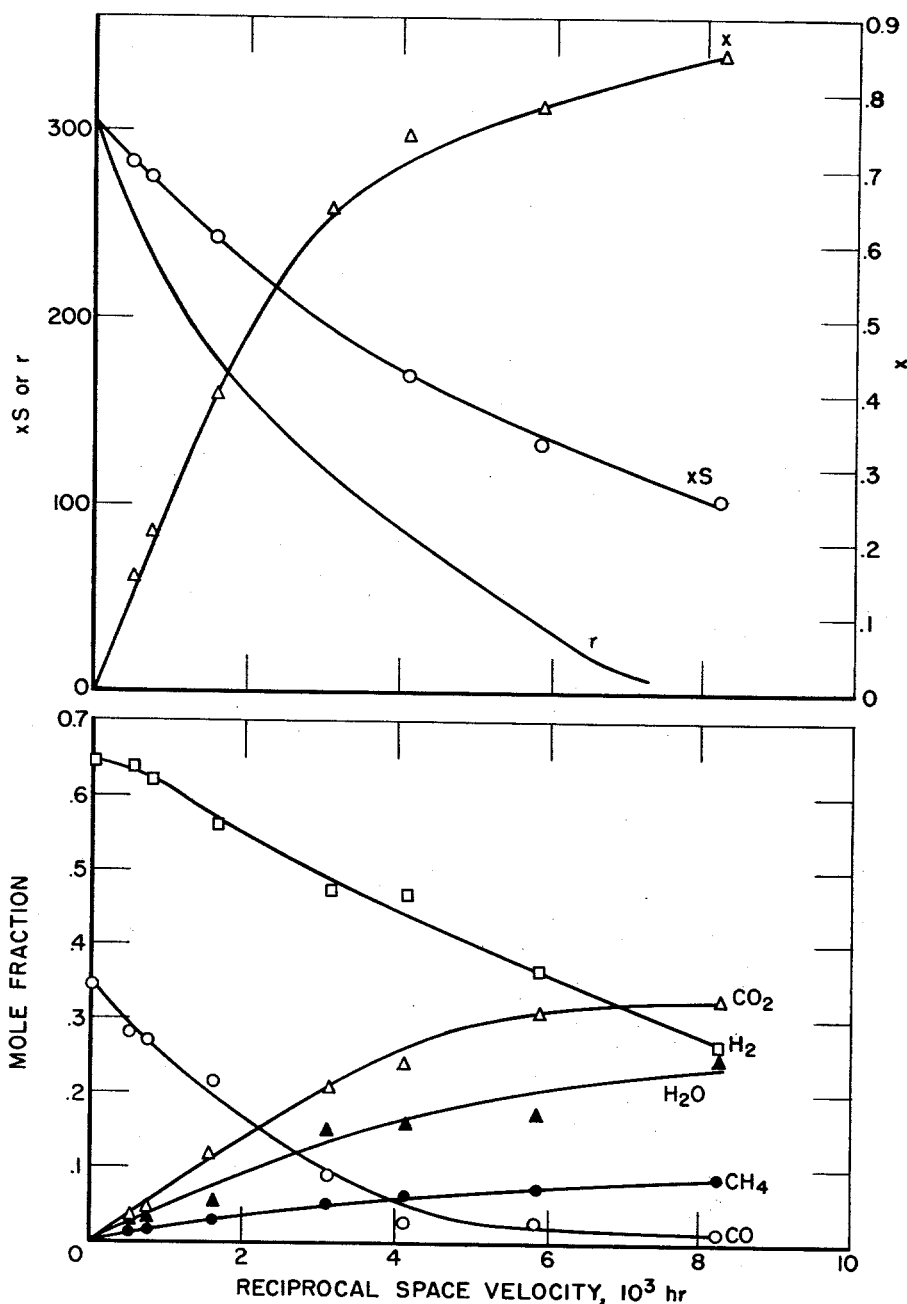


FIGURE 3.—Evaluation of Data for $2\text{H}_2 + 1\text{CO}$ Feed Gas at 240°C , Nitrided Catalyst.

ceeds the maximum allowable according to equation (1). Figure 5 indicates that the rate of synthesis increases with hydrogen content of the feed gas, possibly to a maximum between 50 and 67 percent hydrogen.

The differential reaction rates at zero conversions r_0 were estimated by extrapolating the xS curves to $S^{-1}=0$, and by empirical equations. First or half order equations of the type $r=k(1-x/x_e)^n$, where $n=1$ or $1/2$, $k=r_0$, and x_e is a constant, were used. As previously reported the first-order empirical equation with $x_e=1$ in the integrated form, $-\ln(1-x)=k/S$, fits the kinetic data satisfactorily up to $x=0.4$,

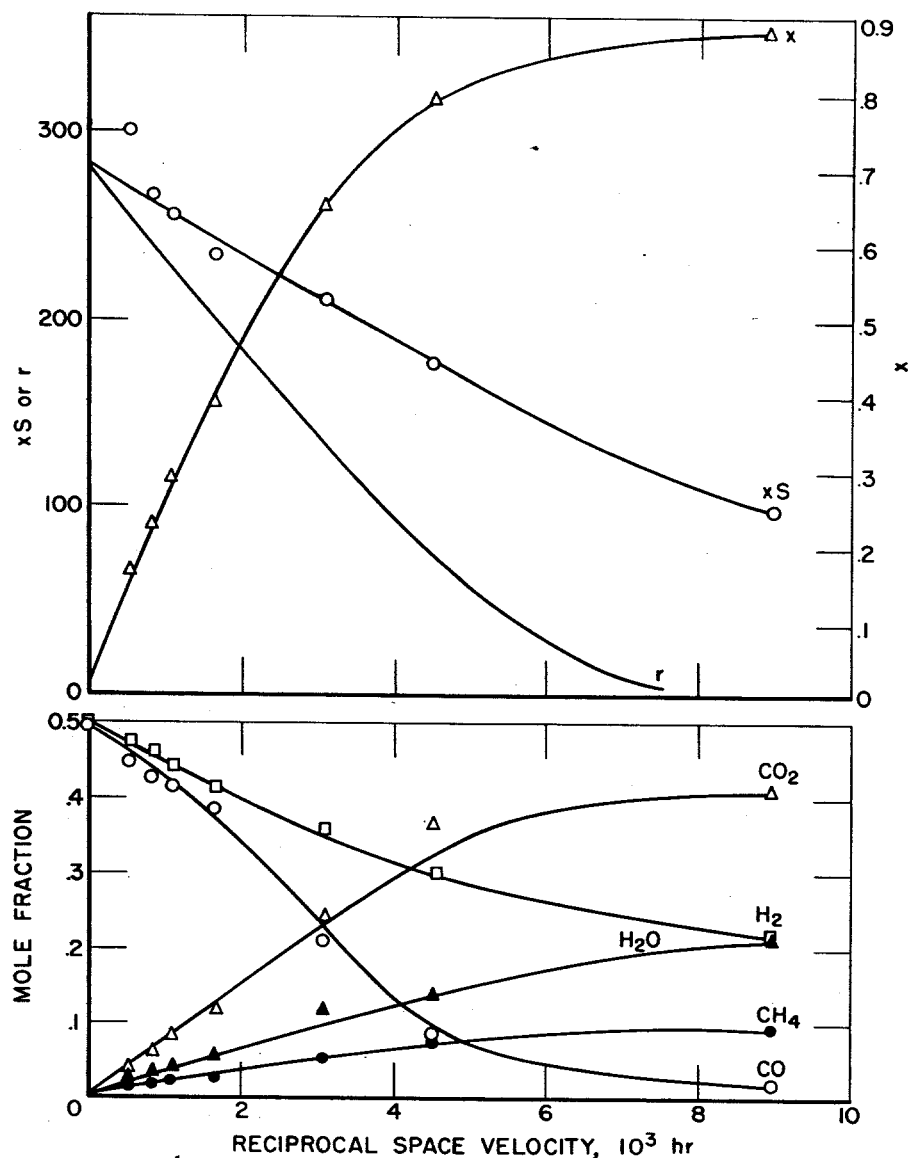
as shown in figure 6, and in some cases up to $x=0.6$ or 0.7 . If x_e is taken as an adjustable constant, the half-order empirical integrated equation

$$xS = k - k^2/(4x_e S) \quad (8)$$

provides a satisfactory representation of the data up to conversions of 0.7 or 0.8 .⁴ This equation also was used to compute the differential reaction rate r_0 . These values, shown in table 1, are in good agreement with those

⁴ The fact that first- and half-order empirical equations give reasonably good descriptions of the same data is not surprising. Plots of x against S^{-1} for first- and half-order equations deviate less than the usual experimental errors up to values of x of 0.3 or 0.4 . Compare reference 49.

FIGURE 4.—Evaluation of Data for $1\text{H}_2+1\text{CO}$ Feed Gas at 240°C , Nitrided Catalyst.



obtained by graphical differentiation. Values of r_0 obtained by various methods and overall activation energies computed by the Arrhenius equation are given in table 2.

Activation energies of the overall synthesis may also be obtained by comparing values of xS at constant conversion; activation energies computed in this way are given in table 3 for conversions of 0, 0.15, 0.30, 0.45, and 0.60.

The experimental results indicate that the kinetics of the synthesis are essentially the same for reduced and reduced-and-nitrided fused iron catalysts despite the rather large differences in selectivity of these catalysts. As the activity of nitrided catalysts remained essentially constant for long periods, the results from nitrided catalysts will be largely used to interpret the kinetics of the Fischer-Tropsch synthesis. Although the experiments were carefully made and the best available analytical methods were

employed, the final kinetic results have a moderate degree of uncertainty. Data for tests with $0.25\text{H}_2+1\text{CO}$ gas at moderate to high conversions should not be regarded as significant, as carbon forming and other reactions probably occur.

The simple first-order type rate equation $r=k(1-x)$ is very useful for examining the overall characteristics of the synthesis and for evaluating and correlating data of catalyst testing experiments and studies in larger reactors. It must be inferred that the overall reaction is greater than first order with respect to partial pressures of H_2+CO , as these partial pressures decrease less rapidly with increasing x than the quantity $(1-x)$. Equally good or better representation of the data is obtained by a half-order equation.

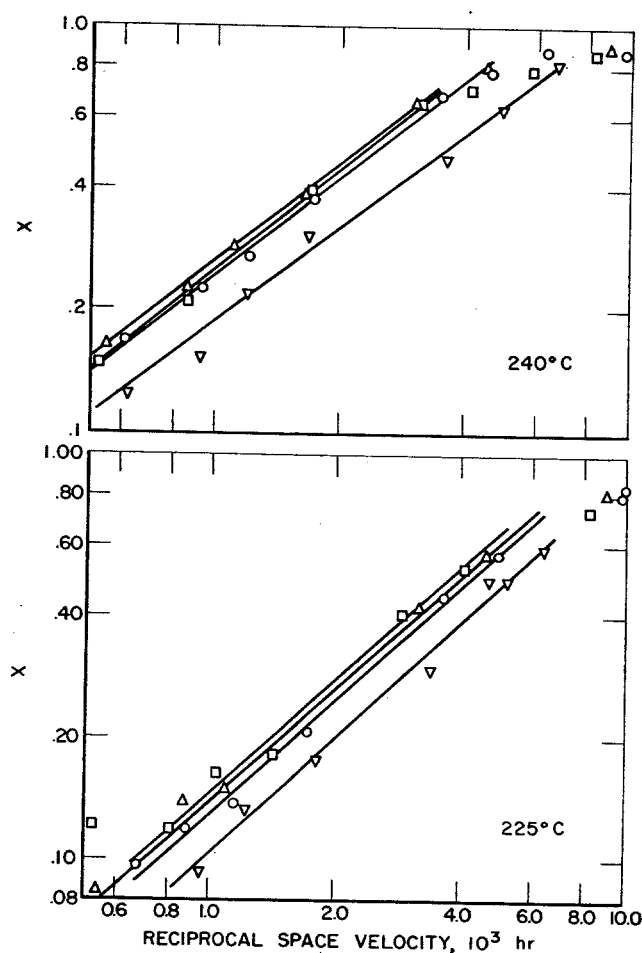
For nitrided catalysts the apparent overall activation energies computed from the varia-

TABLE 2.—Values of initial reaction rate, r_0 .

Synthesis gas, H_2/CO	r_0 at 240° C				r_0 at 255° C				Activation § energies
	A *	B †	C ‡	Average	A *	B †	C ‡	Average	
Reduced catalysts:									
2/1-----	191	182	186	186	324	330	-----	327	20.4
1/1-----	193	190	190	191	315	314	-----	314	17.9
	r_0 at 225° C				r_0 at 240° C				
Nitrided catalysts:									
2/1-----	181	161	161	168	315	289	291	298	19.5
1/1-----	169	146	157	157	303	282	293	293	21.2
0.7/1-----	134	130	140	135	279	272	262	271	23.7
0.25/1-----	114	98	112	108	207	205	204	205	21.8

* From equation $-\ln(1-x)=k/S$.† Extrapolation of values of xS to $S^{-1}=0$.

‡ From half-order empirical equation.

§ From Arrhenius equation using average values of r_0 .FIGURE 5.—Logarithmic Plot of Rate Data for Nitrided Catalysts. \square represents $2H_2+1CO$; Δ , $1H_2+1CO$; \circ , $0.7H_2+1CO$; ∇ , $0.25H_2+1CO$.

tions of r_0 increase with carbon monoxide content of the feed gas up to $0.7H_2+1CO$, and the magnitude of the increase seems to be greater than experimental uncertainties. This trend is also shown by activation energies computed by comparing values of xS at constant x in table 3. The fact that relatively constant activation energies are obtained by this method, as well as by the empirical equation, suggests that the rate equation can, to at least a first approximation, be separated into the form $r=f(T)g(x)$. Activation energies for reduced iron catalysts reported by British researchers (23,24) varied in the same way with gas composition. Their values were 14.5, 18, 22.3, and 27.5 kcal/mole for feed gases with H_2 -CO ratios of 3, 2, 1.12, and 0.67, respectively.

If the extrapolation to zero values of S^{-1} is correct, values of r_0 may be properly related to the feed gas composition. A rate equation

$$r_0 = ap_{H_2}^{1-n} p_{CO}^n \quad (9)$$

which will be considered in detail subsequently, was rearranged to

$$r_0 = aP_i f^{1-n} (1-f)^n \quad (10)$$

$$r_0/f = aP_i [(1-f)/f]^n \quad (11)$$

where a is a constant, p_{H_2} and p_{CO} are the partial pressures of H_2 and CO , respectively, n is a constant less than 1, P_i is the system pressure, and f is the mole fraction of H_2 in the feed gas. A double logarithmic plot of r_0/f against $(1-f)/f$ should give a straight line with a slope of n , and approximately linear plots were obtained as shown in figure 7. For nitrided catalysts, values of n of 0.32 and 0.36 were

TABLE 3.—Activation energies from ratios of xS values at constant values of x for nitrided-iron catalysts

Conversion, x	Activation energies for different feed gases, kcal/mole			
	$2\text{H}_2+1\text{CO}$	$1\text{H}_2+1\text{CO}$	$0.7\text{H}_2+1\text{CO}$	$0.25\text{H}_2+1\text{CO}$
0	19.5	21.2	23.7	21.8
0.15	21.5	21.7	22.4	19.2
.30	17.6	20.0	20.8	19.9
.45	18.8	19.5	20.9	
.60	17.8	19.5	18.6	

obtained at 225° and 240° C, respectively, and the initial reaction rate can be represented by

$$r_0 = ap_{\text{H}_2}^{0.66} p_{\text{CO}}^{0.34} \quad (12)$$

This equation approximates the data for reduced catalysts to within the experimental uncertainties.

PRESSURE DEPENDENCE OF RATE

Studies on pressure dependence were made with 6- to 8-mesh nitrided iron catalyst D3001 with $1\text{H}_2+1\text{CO}$ gas at 240° C (32). At each pressure the conversions of H_2+CO and exit gas composition were determined as a function of space velocity. Tests were made in the order: 21.4, 14.6, 11.2, and 7.8 atmospheres. To maintain the period of operation relatively short, fewer experimental determinations were made than in the previous work to avoid progressive changes in catalytic activity; nevertheless, the activity increased slightly in the course of the experiments.

Plots of exit gas composition and conversion of H_2+CO , x , against reciprocal space velocity were similar to those reported in the previous section from $1\text{H}_2+1\text{CO}$ gas on nitrided iron catalyst at 240° C. Plots of the first-order empirical equation,

$$-\ln(1-x) = kS^{-1}, \quad (13)$$

where S is the space velocity and k is a rate constant which is equal to the differential reaction rate at zero conversion, r_0 , were linear over a wide range of conversions as shown in figure 8. If the rate equation can be separated into the form $r = g(x)h(P)$, where P is the system pressure, then $(xS)_x = k'h(P)$, where $(xS)_x$ are values of xS determined at constant values of

x as pressure is varied, and $k' = x / \int_0^x [1/g(x)] dx$, a function only of x . Logarithmic plots of $(xS)_x$ against P are presented in figure 9 for values of x of 0, 0.2, 0.4, and 0.6. The limiting values of xS as $x \rightarrow 0$ are obtained from the slopes of the curves of figure 8. The plots for constant conversions can be approximated by

a straight line. Slopes of the lines, as determined by least squares methods, were 0.95, 0.92, 0.97, 0.94 for values of x of 0, 0.2, 0.41, and 0.6, respectively, and averaged 0.94. Thus $h(P) \approx P^{0.94}$.

Data are presented in the appendix (p. 45) for pressure dependence of synthesis up to 103 atmospheres. For nitrided catalysts the rate increased with operating pressure to the 0.74 to 0.84 power in the range 21.4 to 103 atmospheres. Fragmentary evidence for reduced catalysts suggests a pressure exponent of about 0.5.

Figure 10 presents logarithmic plots of the differential reaction rate ($r = dx/dS^{-1}$) determined by graphical differentiation for the pressure-dependence series as a function of the sum of the partial pressures of H_2+CO for conversions ranging from 0 to 0.81. In the course of tests at each pressure the rate varies approximately as $(p_{\text{H}_2} + p_{\text{CO}})^{1.7}$ as the partial pressure is decreased by conversion. The apparent contradiction between this expression and the linear dependence of rate on operating pressure when compared at constant conversion as well as the empirical first-order equation results from two factors: (1) The reaction is inhibited by reaction products; (2) the partial pressure of synthesis gas, $p_{\text{H}_2} + p_{\text{CO}}$, decreases less rapidly than $(1-x)$ as conversion x is increased, according to the approximate equation which ignores the production of gaseous hydrocarbons

$$p_{\text{H}_2} + p_{\text{CO}} = (p_{\text{H}_2,0} p_{\text{CO},0}) + (1-x)/(1-0.67x) \quad (14)$$

where the subscript 0 denotes partial pressure at $x=0$.

Previous studies have disclosed that the rate of synthesis on reduced iron catalysts is approximately proportional to the operating pressure (7, 25). This relationship holds for nitrided iron catalysts in the present paper, and the results may be expressed in the form $r = g(x)p^{0.94}$. Comparison of the differential reaction rate with the partial pressure of H_2+CO showed that the rate decreased more rapidly with increasing conversion than the partial pressures of H_2+CO . Thus, the rate

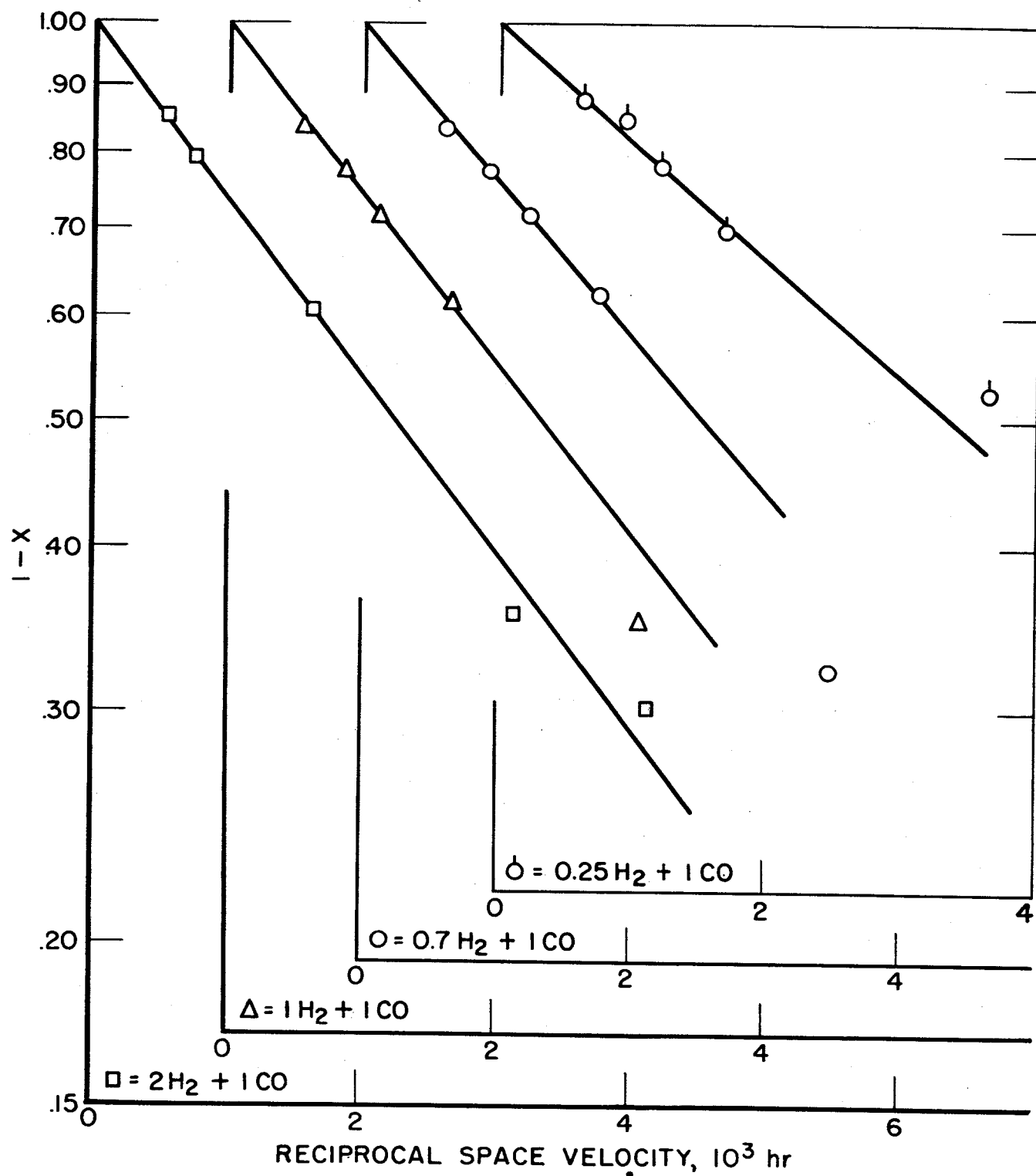


FIGURE 6.—Data for Nitrided Catalysts at 240° C According to Empirical Equation.