

MEASURING THERMAL EFFECTS IN CATALYTIC REACTIONS

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As a part of investigations on processes for converting coal to gaseous and liquid hydrocarbons, a unique catalyst configuration has been devised for measuring catalyst temperatures in the hydrogenation of carbon monoxide on iron and nickel catalysts. The catalyst, promoted fused iron oxide or Raney nickel, as a 150- to 200-mesh powder, was sprayed on the cylindrical surfaces of 0.95-cm. diameter cylinders of copper or aluminum. Each cylinder contained a 0.32-cm. thermocouple well and temperature differences between the central well and the Dowtherm bath were determined at corresponding positions along the length of the reactor. The average excess temperature of the catalyst, determined from the temperature profiles, was a linear function of the rate of reaction of $H_2 + CO$ per unit area of cylinder. Data from several iron and nickel catalysts were plotted and could be represented by a single straight line, the slope of which corresponds to an over-all heat transfer coefficient of $4.79 \times 10^{-3} \text{ cal. sec.}^{-1} \text{ cm.}^{-2} \text{ }^\circ\text{C}^{-1}$. Activation energies for the synthesis on iron were determined using the observed temperature profiles and the first-order empirical rate equation that has been shown to represent the kinetics in tests where overheating is not important. An activation energy of 28 kcal. per mole was obtained.

IN AN EXOTHERMIC catalytic reaction using a packed bed, catalyst temperatures at the gas-solid interface are difficult to measure. Since the capacity of a unit may be limited by the rate of heat removal, accurate temperature observations and heat transfer coefficients are desirable. A new catalyst configuration permits the measurement of temperatures approaching those of the catalyst surface. A thin layer of catalyst is prepared on the surface of a massive metal cylinder which contains a 0.32-cm. central well of stainless steel and a movable thermocouple for measuring temperature. From kinetic studies using packed beds of iron catalysts, apparent activation energies of 19 to 28 kcal. per mole were obtained for the Fischer-Tropsch synthesis (1, 3). The activation energy increased from 19 to 28 kcal. per mole as the particle size was decreased. If catalyst temperatures are significantly higher than the reactor temperature, activation energies determined by the Arrhenius equation will be erroneous. Damkohler (4) estimated that the excess catalyst temperature in the Fischer-Tropsch synthesis on cobalt catalysts was 3°C . The purpose of the present investigation was to determine catalyst temperature in the Fischer-Tropsch synthesis, to estimate heat transfer coefficients, and to check the values of activation energies determined previously.

Experimental

Catalyst assemblies were made by coating with catalyst aluminum or copper cylinders of 0.95-cm. outside diameter, 31, 20, or 10 cm. long. The apparatus and the general procedure for testing catalysts have been reported (2). The catalytic materials were fused iron oxide catalyst D3001 and Raney nickel.

	Catalyst D3001		Raney Nickel
Fe, %	67.4	Ni, %	42
MgO, %	4.61	Al, %	58
Cr ₂ O ₃ , %	0.65		
K ₂ O, %	0.57		

Each catalyst was crushed to a particle size of 150- to 200-mesh and hot-sprayed onto the cylinder by metallizing techniques (5) using oxygen-hydrogen for Raney nickel and oxygen-acetylene for iron oxide. Aluminum cylinders were used for iron preparations and copper for Raney nickel. Before coating, the cylinder was roughened by a blast of 50- to 80-mesh steel particles. The coatings were confined to the cylindrical surface, and were 0.001 to 0.007 cm. thick for D3001 and 0.03 cm. for Raney nickel as determined by a micrometer caliper and checked by weight gain of the cylinder. The following sprayed catalysts were prepared and tested:

Experiment	Sprayed Material		Length of Catalyst, Cm.
	Type	Weight, g. ^a	
Z281	D3001	0.75	31
Z294	D3001	0.40	20 ^b
Z305	D3001	1.00	10
Z300	Raney nickel	7.00	30

^a Weight gain as D3001 in original oxidized form or Raney alloy.

^b Catalyst assembly composed of 4 segments, each 5 cm. long and separated by distance of 2.5 cm.

Before use each iron catalyst was reduced in place at 400°C . with hydrogen at a linear velocity of 3 cm. per second at atmospheric pressure. The Raney nickel catalyst was treated with a 20% aqueous solution of potassium hydroxide until half of the aluminum had been dissolved, then washed with water and positioned in the reactor.

The catalyst assembly was suspended by the thermocouple well in the 1.39-cm. inside diameter reactor tube of a conventional Fischer-Tropsch unit with a boiling Dowtherm bath. Figure 1 is a diagrammatic sketch of the reactor, showing the relationship between catalyst and thermocouples. With this type of catalyst all heat of reaction is generated at the surface of the supporting cylinder.

Tests of iron catalysts were made with $1H_2 + 1CO$, and of nickel with $3H_2 + 1CO$. Synthesis pressure was 21.4 atm. in all tests. Gas flows were 5 to 120 liters (STP) per hour, corresponding to linear velocities of 0.10 to 2.45 cm. per second at operating pressure. The calculated Reynolds numbers

indicated that the flows were piston-type in all tests. The temperature profiles and over-all rates of gas conversion were determined at several bath temperatures between 267° and 330° C. and at several feed gas rates. In each experiment, the temperature profiles were measured at intervals of 2.5 cm. or less in both the catalyst thermowell and Dowtherm bath using single and differential Chromel-Alumel thermocouples. The average temperature differentials were computed by means of Simpson's rule.

In Figures 2 to 5, flow of synthesis gas is given as hourly space velocity (h.s.v.), volumes (STP) per volume of reactor occupied by the catalyst cylinder per hour. For example, the volume of reactor space for the 31-cm.-long cylinder is 47.2 cc. The hourly space velocity multiplied by 0.0051 equals the flow rate expressed as cubic meters (STP) per hour per square meter of geometrical surface area of catalyst layer. Conversion is expressed as the fraction of $H_2 + CO$ reacted.

Temperature Profiles and Over-All Heat Transfer Coefficients

Figures 2 to 5 present examples of the temperature differential profiles along the catalyst supports. Each point represents the temperature difference between the catalyst well and the Dowtherm bath at the same vertical position. Large temperature differentials were found only within the limits of the catalyst zones. For iron (Figure 2) the differential temperature increased rapidly near the gas inlet and decreased rapidly in the outlet portion of the sprayed cylinder. For the segmented iron-coated cylinder (Figure 3) the temperature profile followed the same pattern, except that the temperatures measured between segments were lower than at adjacent positions. For the short cylinder (Figure 4) the temperatures were nearly constant over the length of the catalyst. The nickel-coated cylinder (Figure 5) had lower activity than expected, and the temperature profile was unusual, the differential temperature increasing with length. Possibly the low activity is related to interaction of nickel with the copper substrate.

Data from all catalyst assemblies have been combined in Figure 6, in which the mean temperature differentials are plotted against rate of conversion of $H_2 + CO$ per unit external area of catalyst—i.e., the geometrical area of each cylinder. The data for all catalysts may be approximated by a single straight line passing through the origin. The slope of the line

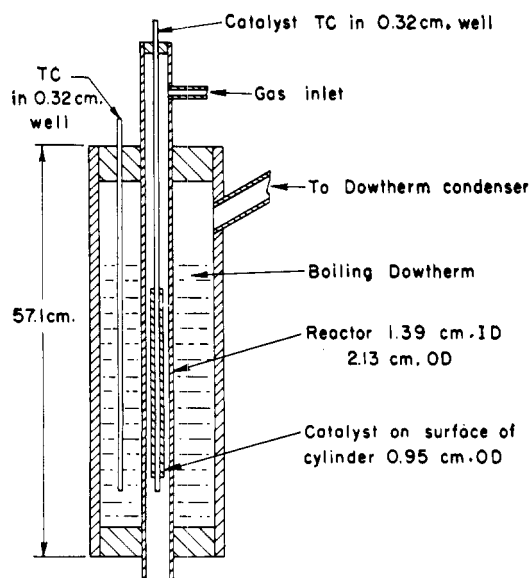


Figure 1. Thermocouples and catalyst bed

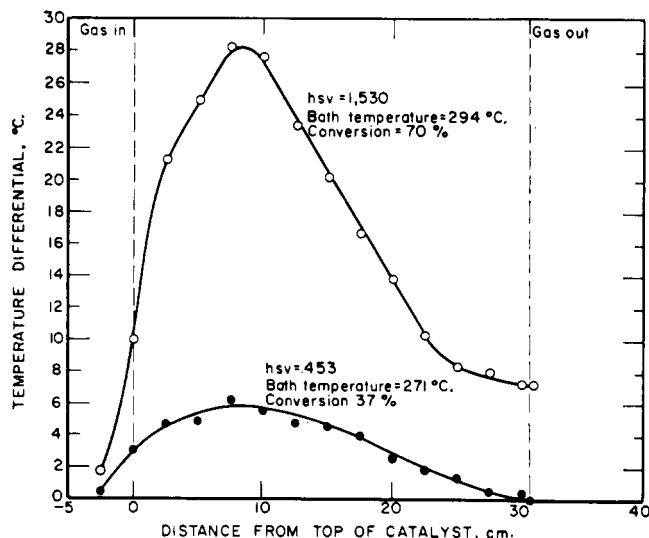


Figure 2. Observed temperature differentials as a function of bed length

31-cm. cylindrical catalyst, fused magnetite

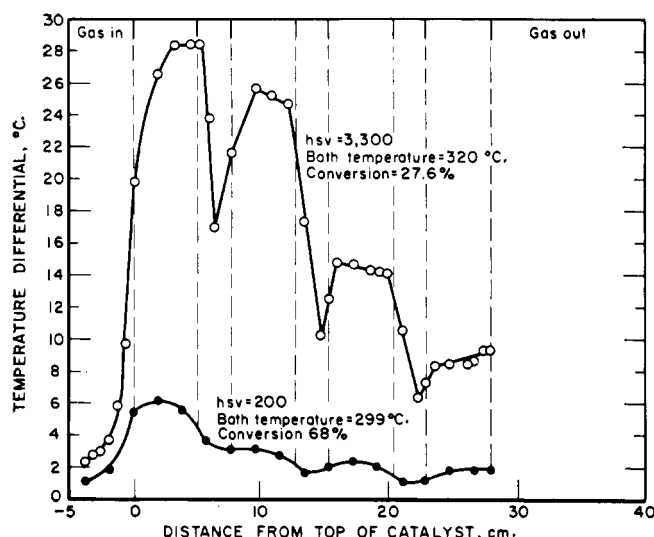


Figure 3. Observed temperature differentials as a function of bed length

Cylindrical catalyst consisting of four sections 5 cm. long with 2.5-cm. separations, fused magnetite

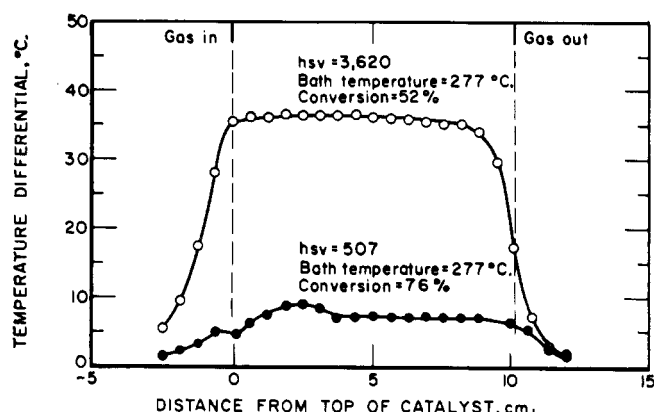


Figure 4. Observed temperature differentials as a function of bed length

10-cm. cylindrical catalyst, fused magnetite

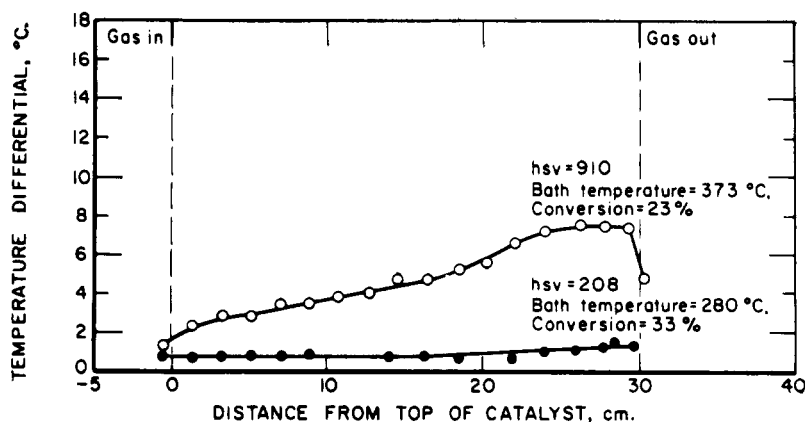


Figure 5. Observed temperature differentials as a function of bed length
30-cm. cylindrical catalyst, Raney nickel

in Figure 6 was determined by least squares. A single over-all heat transfer coefficient can be calculated as follows:

$$\text{Heat generated} = \text{heat removed} = (U)(A)(\Delta T)$$

where U is the over-all heat transfer coefficient, A is the geometric area of the catalyst, and ΔT is the average of the temperature differences between the thermocouple reading in the catalyst well and in the Dowtherm well. Heat generated can be determined from the heat of reaction of the gas synthesis and the volume of $\text{H}_2 + \text{CO}$ converted per unit time [see Table I and (12)]. As detailed analytical data were not available, an approximate heat of reaction was chosen on the basis that over-all reaction on iron produces about 3 moles of CO_2 per mole of H_2O and only moderate yields of gaseous hydrocarbons, and on nickel produces predominantly H_2O and CH_4 . The value selected, 13 kcal. per mole ($\text{H}_2 + \text{CO}$) is probably within 10% of the actual values. From the slope of Figure 6 a conversion of 0.297 cu. meter (STP) of synthesis gas per hour

per square meter of cylinder surface is accompanied by a 1°C . rise in the catalyst temperature. This value can be converted into an over-all heat transfer coefficient of $4.79 \times 10^{-3} \text{ cal. sec.}^{-1} \text{ cm.}^{-2} \text{ }^\circ \text{C.}^{-1}$.

In the present experiments the heat generated on the cylindrical catalyst surface is lost principally by transfer through the gas, except for small end losses, and the principal heat transfer surface is the geometrical area of the coated cylinder. The temperature profiles in Figures 2 and 3 show that heat is not generated evenly over the surface and is not conducted along the length of the cylinder fast enough to equalize temperatures. To avoid inaccuracies due to using average temperature differentials the iron-catalyst cylinder was shortened to 10 cm. (Figure 4). The temperature differentials measured along this cylinder were essentially constant. However, the inaccuracies caused by averaging temperature differences proved unimportant, because data for tests using all catalyst configurations fall on essentially the same straight line in Figure 6.

Losses of heat by the thermocouple well are small, as the ratio of cross-sectional area of well to the area of the cylinder is only 0.06. Losses from the uncoated ends of the cylinders are small, as the areas of the ends are only 1% of the cylindrical surfaces. The gain in sensible heat of the gas flowing over the catalyst is sufficient to remove about 1% of the heat of reaction. All remaining heat must be removed through the annular space 0.22 cm. wide and the reactor wall into the boiling Dowtherm reservoir. The annular space is filled with gas (typical composition 35% H_2 , 28% CO , 22% CO_2 , 7% CH_4 , and 7% water)

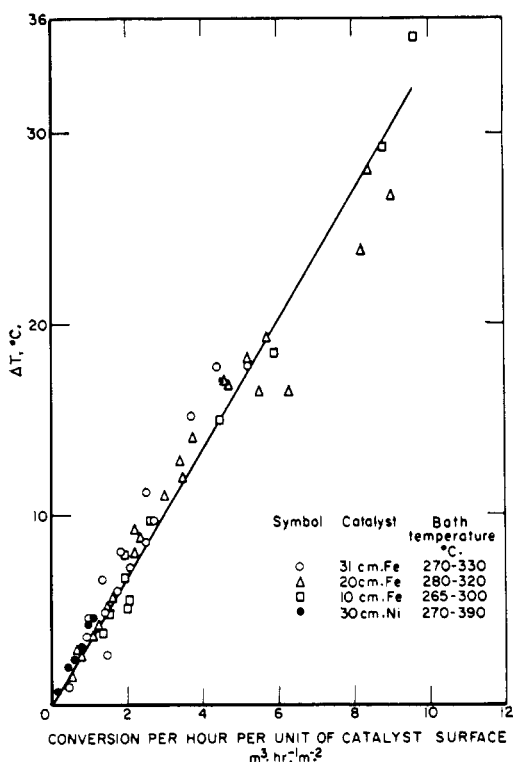


Figure 6. Observed temperature differentials as a function of gas conversion per unit of catalyst

Table I. Heats of Reaction per Mole of Gas Consumed during Hydrocarbon Formation at 300°C .

Moles of $\text{H}_2 + \text{CO}$ Required	Product Formed	Heat of Reaction, Kcal./Mole of $\text{H}_2 + \text{CO}$	
		By-product H_2O	By-product CO_2
4	CH_4	12.9	15.1
6	C_2H_4	9.0	12.0
7	C_2H_6	12.7	15.1
9	C_3H_8	10.6	13.5
10	C_3H_6	12.4	15.1
12	C_4H_8	10.8	13.8
13	C_4H_{10}	12.6	15.4
18	C_6H_{12}	11.3	14.4
19	C_6H_{14}	12.6	15.5
60	$\text{C}_{20}\text{H}_{40}$	12.3	15.3
61	$\text{C}_{20}\text{H}_{42}$	12.5	15.4

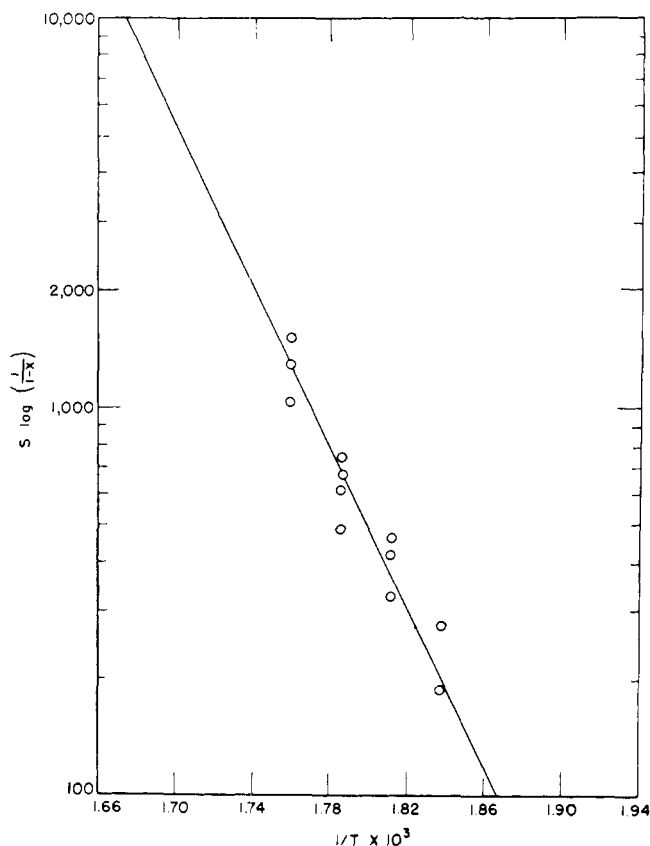


Figure 7. Rate as a function of bath temperature on a 31-cm. iron catalyst

in streamline flow at 21.4 atm. which would have a thermal conductivity of about 1.5×10^{-3} cal. $^{\circ}\text{C}^{-1}$ sec. $^{-1}$ if static. Gas flow and vertical temperature differentials in the gas would increase this coefficient. Other authors (7, 8, 11, 13) have reported heat transfer coefficients from catalyst surfaces through gas barriers and reactor walls. Conditions were similar to the present work except for catalyst configuration, packed beds of pellets or granules. This arrangement usually led to less precise temperature measurements and estimated distances for heat transfer. Over-all heat transfer coefficients for the dimensions of the special reactor used in the present work were calculated from published data.

Computed from Data of	Over-All Heat Transfer Coefficient, U , Cal. Sec. $^{-1}$ Cm. $^{-2}$ $^{\circ}\text{C}^{-1}$
Hougen (8)	4.6×10^{-3}
Yoshida (13)	3.8×10^{-3}
Ogino (11)	2.9×10^{-3}
Gupta (7)	2.7×10^{-3}
Present work	4.8×10^{-3}

Activation Energy for Fischer-Tropsch Synthesis on Iron

If a catalyst bed is not essentially isothermal, the problem of deducing the kinetics of the reaction is greatly complicated. For the present data on iron catalysts reasonably reliable temperature profiles for the catalyst are known; therefore, the results were used to determine the activation energy using an empirical first-order rate equation. If the activation energy is known, the differential reaction rate in increments of cylinder length can be corrected for excess temperature to give a rate corresponding to the bath temperature. As the activation energy is not known for the present catalyst system, a value

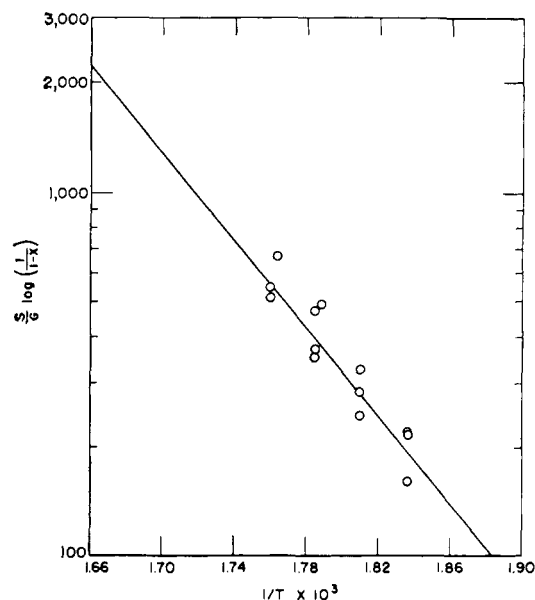


Figure 8. Rate adjusted for temperature profile as a function of bath temperature on a 31-cm. iron catalyst

was assumed, and the validity of the assumed value was subsequently tested.

For the first-order equation used in this work and certain other simple kinetic expressions, the temperature correction factors may be integrated numerically over the length of the cylinder to give an average correction factor which may be introduced into the integral rate equation. From the dependence of the corrected constant of the kinetic equation on bath temperature, an activation energy was determined. If the assumed and determined activation energies are not equal, the calculations may be repeated using a new assumed activation energy between the original assumed and calculated values, until assumed and calculated values become equal.

For these calculations, the empirical rate equation was used

$$-\ln(1-x) = (A/S)e^{-E/RT} \quad (1)$$

where x is the fraction of $\text{H}_2 + \text{CO}$ reacted, A is a constant, S is the hourly space velocity, and E is the apparent activation energy. Equation 1 has been shown to represent data satisfactorily for the Fischer-Tropsch synthesis in packed beds, at least for $0 < x < 0.6$, and temperatures below 270°C . (9). According to Equation 1, the differential reaction rate, r , is given by

$$r = dx/d(1/S) = A(1-x)e^{-E/RT} \quad (2)$$

For a nonisothermal catalyst bed, Equation 2 may be integrated in the form

$$-S \ln(1-x) = \frac{A}{l} \int_0^l e^{-E/RT_l} dl \quad (3)$$

in which the activation energy of the surface process, E , must be assumed and the actual temperatures observed at distance l from the inlet end of the cylinder, T_l , are employed. The expression can be arranged to

$$-S \ln(1-x) = A e^{-E/RT_0} (1/l) \int_0^l \frac{e^{-E/RT_l}}{e^{-E/RT_0}} dl = G A e^{-E/RT_0}$$

where $G = (1/l) \int_0^l e^{-E/RT_l} / e^{-E/RT_0} dl$ and T_0 is the bath tem-

perature. An Arrhenius plot of

$$-(S/G) \ln(1-x) = Ae^{-E/RT_0} \quad (4)$$

should give the activation energy, E , that was assumed in evaluating the quantity, G , if a correct value of activation was chosen for calculating G .

For the data from tests with the 31-cm. cylinder, Arrhenius plots of Equation 1 using bath temperatures are shown in Figure 7. The slope of the line passed through the points corresponds to an activation of 48 kcal. per mole. If Equation 4 is used with $E = 28$, the points in the Arrhenius plot do fit a line corresponding to an activation energy of 28 kcal. per mole as shown in Figure 8. Therefore, we may conclude that the apparent activation energy for the synthesis on thin layers of iron catalysts was about 28 kcal. per mole. The use of Equation 4 was not very effective in decreasing the spread of points in the Arrhenius plot, which suggests that catalyst activity changed moderately from point to point, or that the empirical rate equation is not valid. As the current experiments were made at bath temperatures from 271° to 294° C. over a period of several weeks, moderate changes in activity may be expected to have occurred from point to point (6).

In previous tests of iron catalyst D3001 in packed beds, the activation energies increased from 19 kcal. per mole for 4- to 6-mesh particles to 27.6 kcal. per mole for 28- to 32-mesh particles, and the activation energy of the surface process, without complications by diffusional resistance, was estimated to be 28 kcal. per mole (7). The thickness of the layer of iron on the 31-cm. cylinder, if spread evenly, was calculated to be 0.002 cm., which is smaller than the diameter of 28- to 32-mesh particles, 0.02 cm.; therefore, the activation energy of 28 kcal. per mole for the sprayed catalyst is in accord with previous work.

In kinetic studies on fixed beds of catalyst D3001 reported from this laboratory (7, 9, 10), the temperatures were lower

and the amount of synthesis gas reacted per unit time-weight of catalyst was smaller. Temperatures measured within the bed were usually less than 1° C. higher than the bath. These results were confirmed using the over-all heat transfer coefficient reported in the present paper. For example, for a bed of 6- to 8-mesh particles operating at an hourly space velocity of 300 and a conversion of $H_2 + CO$ of 65%, the average temperature differential from particle to bath was calculated to be 0.5° C. On this basis we may conclude that the temperature of the catalyst in previous fixed-bed studies did not exceed the bath temperature substantially.

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EFFECT OF GAS FLOW RATE ON THE KINETICS OF REDUCTION OF IRON OXIDE PELLETS WITH HYDROGEN

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PREVIOUS investigators who studied the kinetics of iron oxide reduction observed that the rate of reduction increases with increasing flow rates (7, 4), and that there appears to be a "critical" flow rate above which the rate of reduction is constant. To eliminate this variable, these workers conducted their studies using flow rates that were believed to be above the observed "critical" value. It is believed that no detailed study of the effect of flow rate on reduction kinetics has been made. Many ore-reduction processes are operated under conditions where process kinetics are affected by gas flow. Therefore, information obtained from such studies might be useful in analyzing the performance of these processes.

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The kinetics of reduction were studied by measuring the weight loss as a function of time of single spherical iron oxide pellets in a stream of pure hydrogen. The physical and chemical properties of these oxide pellets were kept as uniform as possible. Temperature and rate of gas flow were the only variables.

Materials and Experimental Procedure

The apparatus used in this study is shown in Figure 1. The reactor consisted of a 2-inch i.d. Inconel tube packed with alumina balls to a height of 1 foot to facilitate heat transfer to the gas. A wire basket, suspended from a beam balance located directly above the reactor, held the pellet at the center of the tube. A calibrated Cr-Al thermocouple was placed at approximately the same level and about 1/2 inch from the pellet.