# INTERPRETATION OF KINETIC EXPERIMENTS IN A FLOW SYSTEM

In investigations of catalytic kinetics the primary experimental problem is the determination of the differential reaction rate, the quantity of reactant consumed or product formed per unit quantity of catalyst per unit time on a small quantity of catalyst in which the change of concentration of reactants and products is negligible. The differential reaction rate can be obtained by direct measurements using a "differential" reactor (30); however, experiments of this type often are difficult or inconvenient and in some cases undesirable. The differential reaction rate may also be obtained by differentiating integral rate data, or integral rate data may be compared with integrated rate equations. The second object in kinetics is the establishment of suitable equations relating the differential reaction rate to experimental parameters such as composition of the fluid in contact with the catalyst, operating pressure, and temperature. A fundamental rate equation consistent with the mechanism of reaction is preferred; however, empirical equations, for example, relating rate to conversion are often of great utility, especially because they are mathematically simpler than most fundamental rate equations.

The investigator must choose a suitable component or components of the reactants or products to serve as an index of the forward progress of the reaction. For a reaction of simple and constant stoichiometry the problem is simple; for example, in the ammonia synthesis, $3H_2+N_2 \rightarrow 2NH_3$, the rate could be equally well expressed in terms of moles H_2, N_2, or H_2+N_2 consumed or NH_3 produced. For the Fischer-Tropsch synthesis which may be expressed approximately as

$$(1+y)H_2+(2-y)CO = 1/n(CH_2)_n$$
$$+ yH_2O + (1-y)CO_2 \quad (1)$$
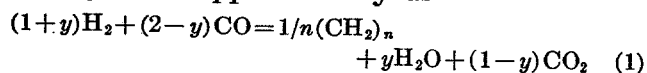
where y may vary from -1 to $+2$ and n is an average of the carbon numbers of a spectrum of hydrocarbons, the choice is more difficult. According to equation (1), 3 moles of H_2+CO react to form $1/n(CH_2)_n$. This quantity is not influenced by the water-gas-shift reaction, which is apparently a secondary process. On this basis in the present paper, the reaction rates will be based on the moles of H_2+CO converted, a quantity that is proportional to the weight of total hydrocarbons produced.

For complicated reactions such as the Fischer-Tropsch synthesis, the choice of components on which the differential reaction rate is based may be arbitrary, and a detailed examination of the data may suggest that other choices would be preferable. In the present work the overall rate is expressed in terms of total moles of reactants consumed and the formation of specific products or groups of products are presented as moles or weights of these components produced per mole of H_2+CO consumed.

For reactions involving gaseous reactants, space velocity is a useful quantity, and it may be expressed in terms of total feed or components of feed, as volumes (STP) fed to the reactor per unit volume of catalyst space per hour.

In the Fischer-Tropsch synthesis, if space velocity, S, is expressed in terms of H_2+CO fed to the reactor and x is the fraction of H_2+CO reacted, the integral reaction rate (space-time-yield) is xS and the differential reaction rate

$$r = dx/d(1/S). \quad (2)$$

This definition of differential reaction rate was derived by Hougen and Watson (30) by the flow balance method, but is identical to equations derived by the contact time method (10). However, the contact time approach has led to complicated and incorrect expressions that can be found in the literature, and in the present paper the notion of contact time will be avoided.

For all of the kinetic derivations presented in this paper, it is assumed that the temperature of the catalyst bed remains constant, and the experiments reported were arranged so that excess temperatures in the bed due to overheating would be avoided. Similarly, concentration gradients from the exterior of the catalyst particles to the gas stream were assumed to be zero. As the amount of reaction and heat generated per unit external area of the particles was maintained relatively low, these assumptions are valid, and they have been confirmed by estimates made from approximate working rules proposed by Yoshida, Ramaswami, and Hougen (71). For any valid set of kinetic data the activity of the catalyst must remain constant throughout all of the experiments that are compared. The general procedure in this work was to obtain data at a number of

3

different space velocities with the feed composition, operating pressure, and temperature held constant. In the present experiments the space velocity was changed by changing the feed rate to a constant catalyst volume; however, similar results should be obtained if space velocity was changed by changing the volume of catalyst with the feed rate held constant.

The rate equation

$$r = f(p_A, p_B \cdots p_R, p_S, p_X \cdots T) = g(x, T) = dx/d(1/S) \quad (3)$$

can be integrated to give

$$1/S = \int_0^x [1/g(x, T)]dx = G(x, T). \quad (4)$$

In equation (3), $p_A, p_B \ldots$, are partial pressures of reactants, $p_R, p_S \ldots$, partial pressures of products, and $p_X \ldots$, partial pressures of extraneous components that may influence the reaction rate. In equations (3) and (4), $g(x, T)$ and $G(x, T)$ are functions only of conversion x and temperature T. For the Fischer-Tropsch synthesis, integral 4 is too complicated to be useful, and rate equations were tested using differential reaction rates obtained by numerical differentiation of the rate data.

Valuable information on the general characteristics of the kinetics of the process can be obtained by comparing the space velocity required to produce a given conversion as the temperature or pressure is changed, especially if the rate equation can be separated as shown below into functions of conversion, pressure, and temperature:

$$dx/d(1/S) = \alpha(x)\beta(P)\gamma(T). \quad (5)$$

Then for constant values of P and T

$$1/S = \int_0^x \frac{dx}{\alpha(x)\beta(P)\gamma(T)} = \frac{1}{\beta(P)\gamma(T)} \int_0^x \frac{dx}{\alpha(x)}. \quad (6)$$

Therefore, for comparison at constant values of x for which $\int_0^x \frac{dx}{\alpha(x)}$ is constant,

$$S = \text{constant} \cdot \beta(P)\gamma(T). \quad (7)$$

In porous catalysts diffusion in catalyst pores may be an important factor in the overall kinetics. Concentration gradients produced by reactions at the catalyst surface are the driving force for diffusion into or out of pores. Solutions of differential equations for diffusion coupled with reaction at the surface have been obtained for idealized pore structures and simple rate equations (19, 61, 65, 66, 68, 69). These solutions are usually relatively complicated and difficult to apply to experimental data. In a number of these solutions, as diffusional resistance increases, the dependence of rate on operating pressure approaches first power, and the measured activation energies decrease to one-half of values on a freely accessible surface. As at least a first approximation, diffusional resistance (in pores) may be assumed to make small changes in the exponents of partial pressure terms but not to change the general form of the rate equation.

The simplest way of testing for diffusional resistance is to determine the rate as a function of particle size. The rate per gram of catalyst will increase with decreasing particle size for particles of sufficient size for diffusional resistance to be important.

Fundamental rate equations should be developed from a valid model of the reaction mechanism and should be of the proper mathematical form to represent the kinetic data accurately. Constants of the equations should have reasonable values and certainly the proper sign. Finding a suitable fundamental kinetic equation provides a critical test of the reaction mechanism on which it is based and of the ingenuity of the investigator. To emphasize the difficulty in proving that a given kinetic equation uniquely and unambiguously represents the kinetics of a given reaction process, we may paraphrase the statement of Burwell (18) on reaction mechanisms: "A successful mechanism is the residuum left after the elimination of other conceivable mechanism by any kind of information." Few reaction mechanisms and probably fewer fundamental kinetic equations meet this criterion; for example, the kinetics and mechanism of the ammonia synthesis has probably not yet reached a unique and unambiguous form; see, for example, Ozaki, Taylor, and Boudart (47).

EXPERIMENTAL

APPARATUS

The apparatus described previously was used with only minor changes (7, 8, 59). The reactor held about 75 cu cm of catalyst in a half-inch, schedule 40, steel pipe (inside diameter 1.58 cm) surrounded by an electrically heated bath of boiling Dowtherm.[3] The temperature of the bath was maintained by regulating the pressure on the boiling Dowtherm. The flow of synthesis gas, which was premixed in cylinders, was controlled by a geared needle valve and measured by calibrated capillary flowmeters held at 35° C by a thermostat. Synthesis gas was passed down through the catalyst bed, and most of the water and C_5^+ hydrocarbons were condensed in the wax trap and the refrigerated trap. Pressure was reduced by a back-pressure regulator, and the gas was passed through a carbon dioxide scrubber (41) and a water-

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[3] Reference to specific brands is made to facilitate understanding and does not imply endorsement of such items by the Bureau of Mines.

saturating vessel and measured in a water-filled wet test meter.

CATALYST COMPOSITION AND PRETREATMENT

In most of the present experiments, 6- to 8-mesh particles of fused ammonia synthesis catalyst D3001 were used. The raw catalyst contained, Fe, 67.42 weight-percent; SiO_2, 0.71; Cr_2O_3, 0.65; MgO, 4.61; K_2O, 0.57; and oxygen combined with iron, 26.04. Physical properties and behavior of this catalyst during reduction, pretreatment and synthesis have been described in previous papers (4, 9, 28, 29, 55, 56), and in a subsequent section (p. 30).

The catalyst was reduced in hydrogen at an hourly space velocity of 2,500 at 450° C for 40 hours and at 500° C for 8 hours in a metal-block reactor (9). Nearly complete reduction (98.3 to 98.6 percent) was achieved in this treatment. Nitrides were prepared by treating the reduced catalyst with anhydrous ammonia at an hourly space velocity of 1,000 at 350° C for 12 hours. This treatment converted the catalyst to an ε-nitride with an atom ratio of N to Fe of about 0.47.

SYNTHESIS TESTS

The pretreated catalysts were transferred to the synthesis unit by methods that prevented exposure to air (9) and $1H_2+1CO$ gas was introduced at 21.4 atmospheres and an hourly space velocity of 300. For reduced catalysts the temperature was increased rapidly to 220° C and then slowly increased to 255° C; at this temperature the flow was adjusted to give an apparent contraction of 65 percent. This flow rate and temperature were used as reference conditions to test reproducibility of catalyst charges and variation of activity with time. For nitrided catalysts reference conditions were similarly established at 240° C.

For each experimental point with a given feed, the temperature and flow were set at the desired values, and the reactor was operated long enough for the contraction to become constant, indicating that reaction products from the previous condition had been flushed from the system. The time required for reaching steady-state conditions varied inversely with space velocity. Flows of gas into and from the reactor were then determined over a 2-hour period, and a sample of exit gas was collected for mass spectrometric analysis. At the end of the test period, carbon dioxide was determined on an exit-gas sample with a Haldane apparatus.

Gas samples were collected beyond the back-pressure regulator for Haldane carbon dioxide

analyses and for mass spectrometric analyses. The latter samples were collected by withdrawing mercury from the sample bulb at a constant rate over a period of an hour or more. The mass spectrometric analysis for H_2, CO, CO_2, CH_4, and C_2 to C_4 saturated and unsaturated hydrocarbons accounts for all components except water present in sizable amounts in the gas phase at synthesis temperature. Water was estimated from an oxygen balance, assuming that all the oxygen in the products was present as carbon dioxide or water. An attempt was made to remove exit gas directly from the outlet of the reactor into an evacuated vessel at total pressure less than the vapor pressure of water. Mass spectroscopic analyses of these gases could not account for a substantial fraction of the water vapor, and hence the method was discontinued.

In special experiments water was added to the feed stream by the apparatus shown in figure 1. Water was displaced by nitrogen from the calibrated glass tube, entered the top of the reactor, and was evaporated and mixed with synthesis gas in a bed of inert solids. The flow of water was controlled by the pressure differential on the water column at a given setting of the needle valve. Reasonably constant rates in the range of 1 to 16 cu cm per hour were possible. At times deviations of rates as great as 15 percent from the designated value occurred at the lower flows; however, the actual quantity of water introduced was measured by the graduated tube. Smaller variations were observed at higher flows.
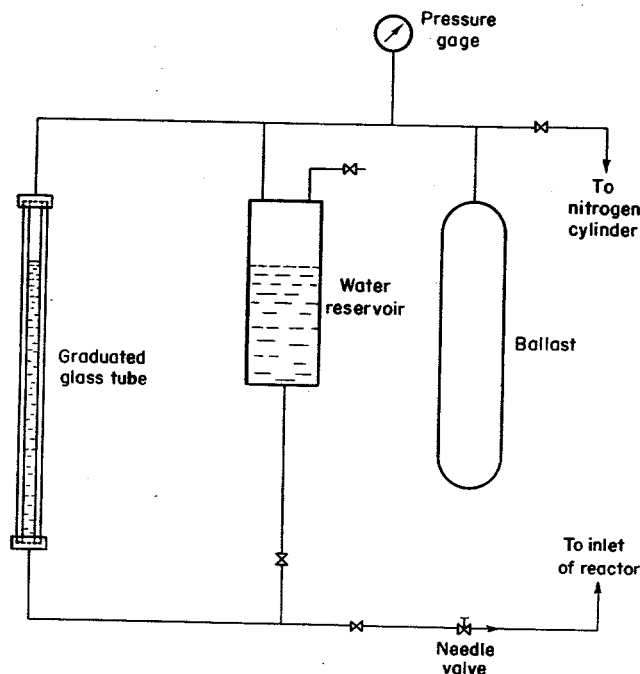

FIGURE 1.—Water Feed System.