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Surface Combustion of Hydrogen:
Part I. On Platinum-Coated Alumina

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It is well known that combustion of hydrogen, carbon monoxide, methane, and other gases can occur in the gas phase and on the surface of catalytic materials. The latter is referred to as *surface combustion.* Surface reactions are usually carried out industrially at temperatures high enough to obtain rapid rates of reaction. If the object of the reaction is the transformation of chemical species, to make a product or to destroy fumes, economy dictates high rates. If the object is heat generation, again, rates of reaction must be high to obtain a sufficiently rapid heat release. The surface combustion of hydrogen was chosen for this study as a representative reaction, without complications such as byproducts, hazards due to toxicity, or problems of chemical analysis.

The purpose of this investigation was to determine the rate behavior of surface combustion of hydrogen on the surfaces of a very active and a moderately active catalyst in the temperature range of industrial applications. To permit study of the rate of the surface reaction alone the homogeneous gas-phase reaction was suppressed with cold hydrogen-air feeds and dilute mixtures. To minimize the effects of boundary-layer diffusion on the rate measured high flow rates were used. A tubular reactor configuration was employed to simplify mathematical description of fluid and heat flow phenomena and to facilitate description of the active surface. The experimental setup was designed to permit maintenance of constant temperature and, in later phases of the work, constant total pressure for different flow rates. Gas samples were obtained through a movable water-cooled probe which also contained a high-velocity thermocouple. Sampling at various positions allowed separate study of sections of the reactor in which only surface reaction occurred.

BACKGROUND

Research on surface combustion started in 1817 when Sir Humphrey Davy (*5*) discovered that a warm spiral of platinum wire brought about the ignition of hydrogen. Later nineteenth-century investigators, such as Dulong and Thenard, William Henry, Graham, Faraday, Mendeleev, and De la Rive, studied the accelerating effect of surfaces on the combustion of hydrogen in an attempt to explain the phenomenon qualitatively. Bodenstein (*1*) attempted the experimental measurement of reaction velocities, and the complexity of the phenomenon was soon apparent from his work. In 1906 Bone and Wheeler (*3*) published the results of their rate studies on surfaces such as porous porcelain, silver, and nickel gauze. Bone's (*2*) work and that of his co-workers dealt with applications.

In the 1920's a group of chemists began to study the heterogeneous oxidation of hydrogen because of interest in the fundamentals of catalysis. The hydrogen-oxygen reaction appeared easy to study since its progress could be followed by observing the drop in pressure with time in a closed recirculating system. These investigators were interested in the rate law and not in the absolute values of the rate constants. Three reviews of their work are given in Advances in Catalysis (*6*), in Emmett's (*7*) and in Schwab's (*17*) books on catalysis. A recent review of the catalytic reaction on platinum or palladium in the pres-

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sure range of 0.01- to 5-mm. mercury and in the temperature range of −100° to 200°C. is given in a paper by Krilov and Roginskii (*13*). The rate laws which are presented usually differ markedly. They were obtained for different catalysts and different ranges of concentration, temperature, and pressure. The various investigators frequently obtained data over limited and different ranges of variables; concentrations were usually near stoichiometric or higher in hydrogen, and temperatures were relatively low. The few high-temperature data available often represent a diffusion-controlled regime, as for example those of Langmuir (*14*) and Garber and Peebles (*8*).

Economic factors seemed to have generated a great deal of development closer to the possible range of application in the Soviet Union following World War II. These results are summarized in "Surface Combustion" by M. B. Ravich (*15*). Experiments were reported for various surfaces at pressures of 1 and 100 mm. Hg and at temperatures up to 950°C. No rate constants or activation energies are given. The orders of the reaction are not known, and surface areas can be estimated only roughly. The bulk of the Russian papers on heterogeneous oxidation of hydrogen, especially in recent years, has been concerned with basic problems in heterogeneous catalysis. Only a 1953 paper by Boreskov (*4*), reporting an activation energy of 11 kcal./mole for bulk platinum in the temperature range of 100° to 180°C., merits mention; a more complete review is given in references 9 and *10*.

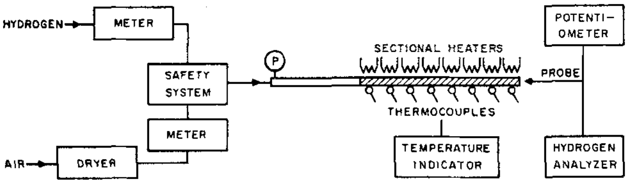

Fig. 1. Schematic diagram of reactor and accessories.

APPARATUS AND PROCEDURE

The apparatus employed included a tubular catalytic reactor, input system for reactants, reactor temperature and flow metering and control systems, a movable probe for determining gas temperatures and obtaining samples inside the reactor, a continuous hydrogen analyzer, plus exhaust and safety systems, Figure 1. The flow of reactants and the surface temperature could be varied and set at desired values. The equipment was designed for residence times ranging from 0.0004 to 0.1 sec.

The reactor tube was wound externally with eight sectional heaters to provide surface temperature control zones. Each heater was connected to an autotransformer to permit variation in power input to individual sections of the reactor wall. Reactor-wall temperatures were measured by means of 13% rhodium-platinum, 0.016-in. diameter thermocouples imbedded in the reactor wall approximately at the midpoint of each heater winding and connected to a multipoint indicating potentiometer.

Two reactor tubes were used to obtain different surfaces: a vitreous alumina tube coated internally with platinum and a smooth, grade A nickel tube of similar dimensions. The results and data analysis for the platinum-coated reactor are presented herein. The accompanying paper treats the reaction on nickel.

The vitreous alumina reactor tube (38 × 0.46 in. I.D. × 0.73 in. O.D.) was made of 96% alumina. This material has high service temperature and thermal conductivity and a low coefficient of expansion. Uniform internal platinum coating of the outlet 24.8 in. was achieved as follows. The inlet 13.2 in. of the tube were coated with a solution of paraffin wax in iso-octane. Then the tube was filled with a measured volume of 10% platinum chloride solution, and the solution was agitated for half an hour by rotating the tube. The unabsorbed solution was collected and weighed to determine the amount taken up. The tube was slowly heated to 800°C. to decompose the platinum chloride so that the inside of the tube appeared to be uniformly black. The complete coating process was repeated to ensure uniform platinum distribution. A total of 0.0773 ± 0.005 g. or 3.12 mg. of platinum per inch of tube was deposited. After sixty-one runs had been made with this catalyst the tube was recoated in place to determine effects of catalyst concentration and aging.

The movable sampling probe consisted of a water-cooled sampling tube through which the sample was drawn by a vacuum pump. The water jacket served to quench the sample rapidly, minimizing reaction occurring after the sample left the test location. The rate of flow of sample through the probe was approximately 140 ft./sec. for atmospheric pressure at the inlet. A chromel-alumel thermocouple in a chamber at the probe inlet was used to measure the gas temperature.

The reacting systems were mixtures of air and hydrogen in which the hydrogen content was usually maintained below the lower explosive limit. The air passed from compressors through traps to drying towers packed with activated alumina. The relative humidity of the air supplied to the reactor was maintained in the range 20 to 30%. No attempt was made to further dry the air, because a greater change in relative humidity would then result as the reacting mixture passed through the reactor. The air flow to the reactor was measured by calibrated rotameters.

Electrolytic hydrogen was supplied to the reactor from cylinder storage through calibrated rotameters. Both reactants passed through magnetic check valves into a mixing chamber upstream of the reactor.

The procedure for making runs was simple, but maintenance of a steady state reaction at desired conditions required constant check of flows and temperatures and periodic adjustment of Variacs controlling the heater inputs. At the beginning of each run the air flow was adjusted to the desired value and heaters turned on and adjusted to give a surface temperature somewhat below the desired value. Then the hydrogen flow was adjusted to the proper value. If appreciable reaction occurred, the surface temperature rose rapidly. The heaters were then readjusted so that the surface temperature varied by less than 20°F. along the length of the reactor and held constant for at least 15 min.

The probe was positioned near the tube outlet at the beginning of each run to determine outlet gas temperature and concentration. During the run the inlet and outlet gas compositions and temperatures were determined for each 4-in. section of the reactor by moving the probe into the tube 4 in. at a time. The hydrogen content of the samples obtained at various points in the reactor tube was measured by a continuous thermal conductivity analyzer. The calibration of the analyzer was checked before and after each run by sampling the reactor feed, for which the composition was known from the flow rates, and also by sampling the incoming air.

METHODS OF DATA ANALYSIS

Kinetics in a Flow System

Consideration of the kinetics in the tubular reactor properly begins with the continuity equations for total mass and species *i* for monodirectional flow, which are, when one neglects longitudinal diffusion

$$\frac{\partial \rho}{\partial \tau} + \frac{\partial (\rho v)}{\partial L} = 0 \tag{1}$$

$$\frac{\partial (\rho Y_i)}{\partial \tau} + \frac{\partial (\rho v Y_i)}{\partial L} = -r_i' M_i \tag{2}$$

For steady state substitution of Equation (1) into (2) yields

$$(\rho v)\frac{dY_i}{dL} = -r_i' M_i \tag{3}$$

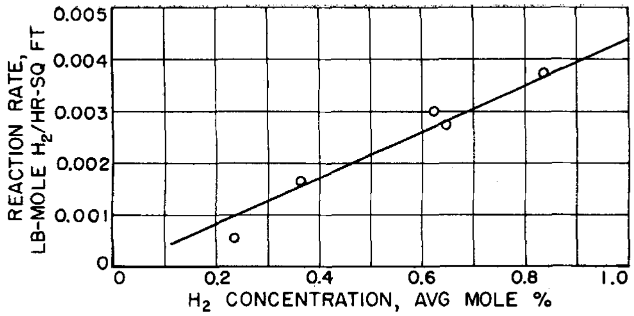

Fig. 2. Rate of combustion of hydrogen at 300°F. (Run 7, 469 std.cu.ft./hr., 3 to 23 in.).

For surface reactions the overall rate of reaction is proportional to the active-surface area. In a complete description of flow through a tube with chemical reaction on its inner surface and axial symmetry the rate will appear as a boundary condition for the two-dimensional equations describing the concentration changes. In this case however the rate is inserted in Equation (3) directly. The basis of Equation (3) can be changed by use of Equation (4), which equates the rate of disappearance of a given species for a given increment of reactor length based on the surface area to the rate of disappearance based on the reactor volume for the same incremental length of reactor

$$r'\Delta V = r\Delta S \tag{4}$$

The above conversion will hold for the tubular reactor for turbulent flow beyond the mass transfer entrance length for relatively smooth concentration changes. With this modification the defining rate equation becomes

$$\left(\frac{GA}{M_i}\right) dY_i = -r_i dS \tag{5}$$

If n moles of species i are reacted per mole of feed, of initial mole fraction n_o and a mean molecular weight M_{mo}, Equation (5) then becomes a definition of reaction rate

$$\left(\frac{GA}{M_{mo}}\right) dn = r_i dS \tag{6}$$

The mole fraction of species i is given by

$$y = \frac{n_o - n}{n_t} \tag{7}$$

where n_t is the total number of moles per mole of feed. For small changes in total moles with reaction this quantity approaches unity. For the reaction of hydrogen with oxygen the stoichiometric balance shows that $n_t = 1 - 0.5n$.

Rate Constant Calculations on Platinum

Analysis indicated the rate law for oxidation of hydrogen on platinum is of first order with respect to hydrogen for the ranges of concentrations and surface temperatures studied. In the data analysis the longitudinal pressure drop through the platinum-coated alumina tube had to be taken into account, because the pressure measurements were made upstream from the reaction site and the flow rates used were high. It was observed that increasing the total pressure increased the hydrogen conversion. The rate law for a first-order reaction and ideal gas behavior can be stated as

$$r = K_p P_t y \tag{8}$$

Substitution of this rate law into Equation (6) and integration for constant $K_p P_t$ for the range of concentrations concerned gives

$$\frac{(2\pi R\Delta L)(M_{mo}K_pP_t)}{GA} = \ln\frac{n_o}{n_o - n} - 0.5\left(n_o \ln\frac{n_o}{n_o - n} - n\right) \tag{9}$$

Conversion to mole fractions and elimination of terms negligible for systems with low hydrogen concentrations and incomplete conversion yields

$$\ln\frac{y}{y_o} = -\frac{(2\pi R\Delta L)(M_{mo}K_pP_t)}{GA} \tag{10}$$

Equation (10) or its expansion in a truncated Taylor's series was used to calculate the rate constants presented in this report, since it was verified that the reaction could be characterized as first order for the range studied. The order of the reaction was verified by observing that K_p did not change with y.

A recently published numerical solution of longitudinal and radial concentration distributions in turbulent flow with a first-order reaction at the tube wall by Wissler and Schechter (*19*) shows that beyond the mass transfer entrance length ratios of mixing cup concentrations are equal to ratios of center-line concentrations at any two axial positions (see Wissler and Schechter, Figures 2 and 3). This shows that the authors' formula (*10*) gives the same rate constant as would be obtained from measurements of mixing cup concentrations in the rate-controlled region.

DATA

Data Obtained

Only a few runs were made for surface temperatures of less than 400°F., Figure 2, to show that the rate of reaction below this temperature is low. The order of the reaction is near unity. At 140°F. no conversion was detected, while at 228°F. the value of K_p was 0.1 lb. moles hydrogen/hr.-sq. ft.-atm. These values were measured

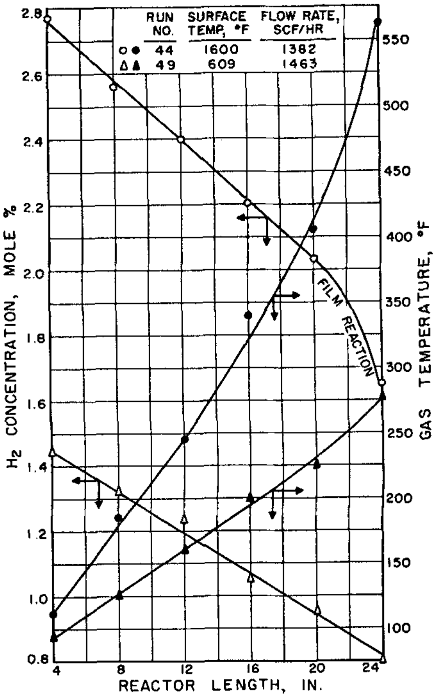

Fig. 3. Typical concentration and temperature profiles for high flow rates.

over essentially the complete coated reactor section, that is 3 to 23 in.

All other data were obtained for surface temperatures of 400° to 1,600°F., primarily above 600°F. Two typical runs for a high flow rate, one at a low and the other at a high surface temperature, are shown in Figure 3. It can be seen that for the reactor section 20 to 24 in. there is an excessive concentration decrease accompanied by a large temperature rise, especially noticeable for the high surface-temperature run.

Reaction Rate Behavior

The rate data have been interpreted as follows. Figure 4 shows the rate of combustion of hydrogen corrected to atmospheric pressure vs. the average mole fraction of hydrogen. The best lines were defined visually instead of statistically owing to the complexity of the weighing factors. There is significant difference between sections (determined by variance analysis). Some of this difference was apparently caused by nonuniform roughness of the alumina reactor tube used, as explained later. Since interest is in overall rate data for this reactor, the rate constants for the reactor section 4 to 20 in. have been calculated. These give essentially the same values as the average for the four sections, since by adding logarithms of the ratios of concentrations the intermediate concentrations cancel out. This results because the time parameter is constant and the pressure profile is relatively flat. The rate constants, with a first-order reaction assumed, are given in Table 1, and since they do not vary with concentration, the reaction is first order in the range determined. The concentrations are known to within 7% with a few exceptions, mostly at very low concentrations.

The rate constants were measured as a function of flow rate for approximately equal initial concentrations to determine whether and to what extent diffusion through the film affects the rate of surface combustion. Four such sets of runs were made. The results for three such sets are shown in Figure 5. The rate constants for the last reactor section, section 20 to 24 in., are well above all others at high flow rates. This is the section having the highest gas temperature, as well as the highest temperature rise generally, although the driving force for heat transfer had decreased. This would occur if there were some extra reaction taking place either in the film or in the bulk, if the heat transfer coefficient for this section were for some reason unusually high, or if there were

TABLE 1. RATE CONSTANTS FOR REACTOR SECTION 4 TO 20 IN., LB. MOLE H_2/HR.-SQ. FT.-ATM.

Run No.	Std. cu. ft./hr.	Inlet mole % H_2	Exit mole % H_2	Average mole % H_2	T, °F.	K_p
49	1485	1.445	0.952	1.199	609	6.40
50	1,478	0.976	0.668	0.822	593	5.81
51	1,473	0.630	0.417	0.524	605	6.29
52	1,470	0.476	0.308	0.392	601	6.64
53	1,467	0.268	0.178	0.223	597	6.30
54	1,465	0.122	0.077	0.100	603	7.02
56	1,501	2.99	2.17	2.58	1,204	4.48
57	1,493	2.51	1.81	2.16	1,206	4.65
58	1,483	1.857	1.313	1.585	1,200	4.80
59	1,474	1.300	0.919	1.1095	1,205	4.82
60	1,466	0.756	0.542	0.649	1,213	4.61
61	1,461	0.311	0.453	0.382	1,170	5.26

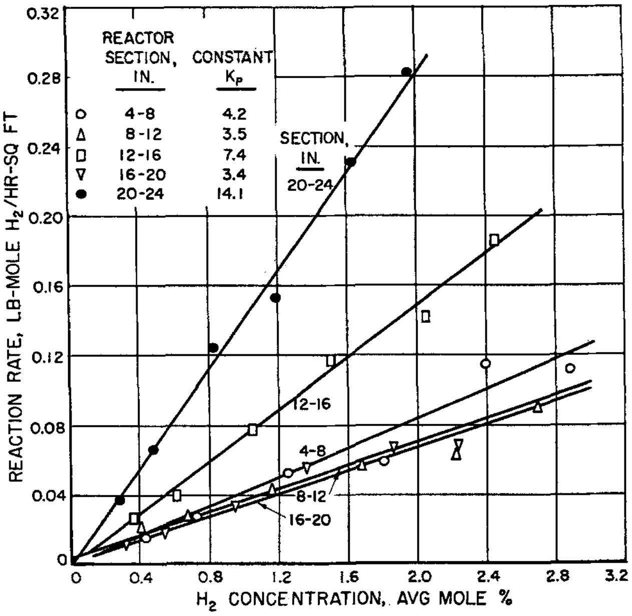

Fig. 4. Rate of combustion of hydrogen at 1,200°F. (Runs 56 to 61, 1,500 std.cu.ft./hr.).

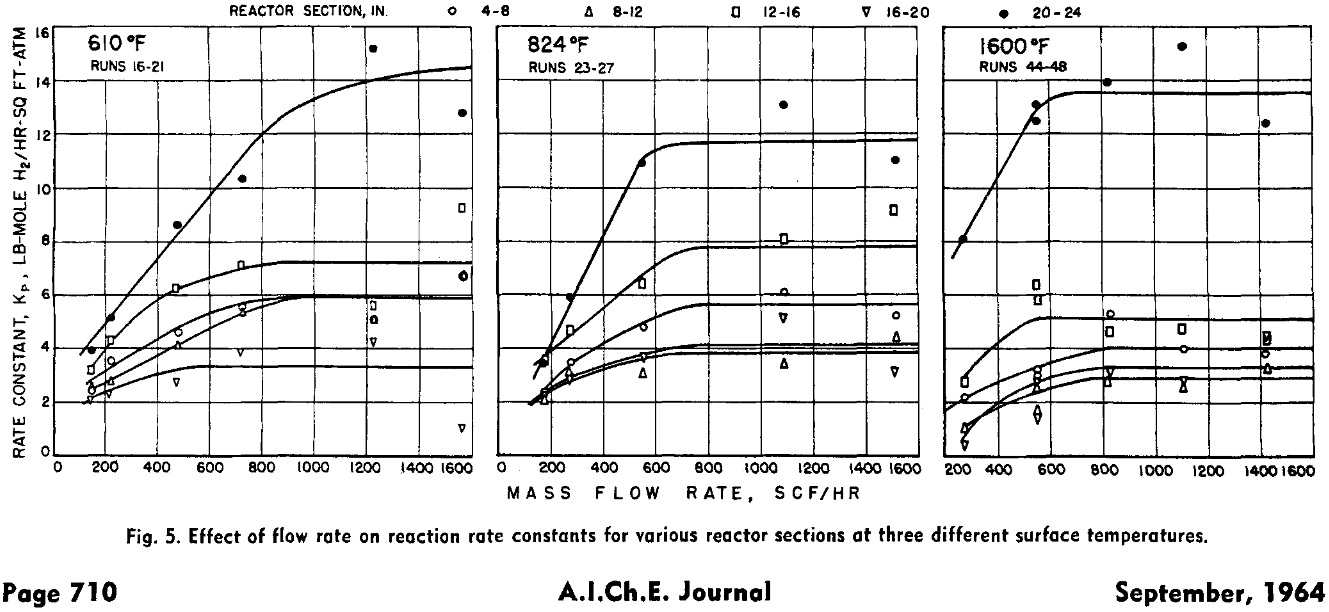

Fig. 5. Effect of flow rate on reaction rate constants for various reactor sections at three different surface temperatures.

more surface reaction due to different physical or chemical conditions.

It can also be seen that at low flow rates for the last section as well as all others there is a marked drop in reaction rate constants, while at higher flow rates there is no such trend. This indicates that above flow rates of roughly 700 to 800 std. cu. ft./hr. the reaction is not affected by diffusion, while below this diffusion slows down the rate. The various film theories show that the thickness of the film will vary with the flow rate, and hydrogen must diffuse through that film to get to the reactive surface. The variation of rate constants with flow rate, or the lack of variation, can be clearly seen from logarithmic plots of rate constants for the combined section 4 to 20 in. shown in Figure 6. The constants, as explained previously, are close to the average value of the rate constants for the first four sections. The last section was not considered because of the extra reaction. The average of the five, however follows the same trend.

The data are plotted on logarithmic coordinates, since this method shows directly the per cent change and because diffusion-controlled rate constants or mass transfer coefficients are known to vary to some fractional power of the mass rate of flow. The expression for the mass transfer coefficient as a function of the rate of flow can be deduced from the Reynolds analogy, the *j*-factor equivalence, or other analogies. The plot using the *j*-factor analogy and the heat transfer data obtained with pure air for this reactor at 600°F. is also shown in Figure 6. The mass transfer coefficients were calculated with equality of *j* for mass and heat transfer assumed. A familiar correlation for mass transfer in pipes is the one obtained by Sherwood and Gilliland for wetted wall columns. In each case one finds that the mass transfer coefficient varies approximately to the 0.8 power of the mass velocity. For combustion of carbon spheres Tu, Davis, and Hottel (*16*) obtained a straight line on logarithmic paper when they plotted specific rate vs. flow rate, although they do not show their data points.

In the present case it is found that in the range affected by velocity the slopes of the inclined lines, if forced through the points, are considerably different from 0.8. They are 0.45 at 612°F., 0.45 at 825°F., and perhaps 0.9 at 1,600°F. This probably indicates that operation is not completely in the diffusional region but is in a transition region where both the reaction and the mass transfer are important. It is however quite possible that the slope should be different from 0.8 for the present situation even in the completely diffusion-controlled region. The slope may change with surface temperature and ratios of surface to gas temperatures. Figure 6 however shows how remarkably close the simple heat mass transfer analogy predicts the mass transfer coefficient at 600° to 800°F. in the low flow rate range where it is expected that the process will be completely diffusion controlled.

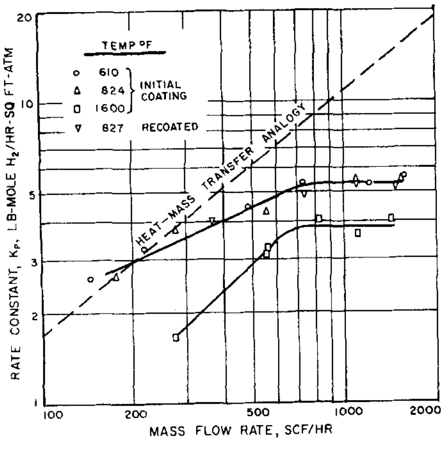

Fig. 6. Effect of flow rate on the overall rate constants.

Heat Transfer Behavior

Heat transfer coefficients for pure air were determined to find how they compared with the heat transfer coefficients in the reactor with surface combustion of hydrogen and to see whether there is a difference from section to section. An inspection of rate data showed that for a given change in conversion there seemed to be a corresponding change in gas temperature, which could not always be attributed to a homogeneous or a film reaction.

The heat transfer coefficients were calculated on the basis of the usual definition of *h*, where the rate of heat transfer was calculated from the rise of gas temperature. The physical properties were evaluated, with the data in National Bureau of Standards Circular 564, at the arithmetic average film temperature. A Dittus-Boelter correlation was used. To correct for high surface-to-gas temperature ratios, according to Humble, Lowdermilk, and Desmon (*12*), it is necessary to multiply the Reynolds number in the correlation by the ratio of bulk gas temperature to a temperature midway between gas and surface temperatures. Figure 7 shows a simple Dittus-Boelter correlation for the overall heat transfer coefficients. The constant is 0.014. This number agrees with the usual value when the correction for the surface to gas temperature is included.

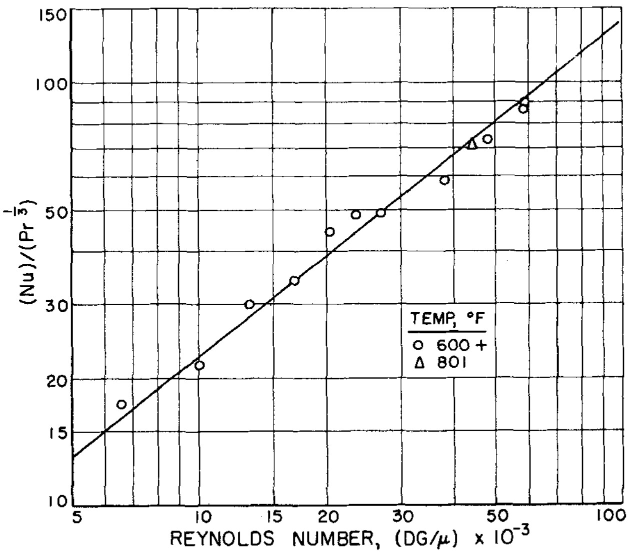

Fig. 7. Heat transfer correlation for the alumina reactor at 600°F.

Sectional Comparison of Reaction and Heat Transfer Rates

Figure 8 shows that the sectional heat transfer coefficients vary with length in the same way —intermediate, low, high, very low, very high—as the rate constants. Curves *a* and *b* of Figure 8 show that the heat transfer data vary in the same way as the reaction rate data along the length of the tube. Each point of curves *a* and *b* is an average transfer coefficient over a length of 4 in. The last point on curve b, at 22 in., is excessively high owing to extra reaction in the film, as will be explained. It is interesting to note that since the temperature and concentration gradients from the wall to the bulk are in the opposite

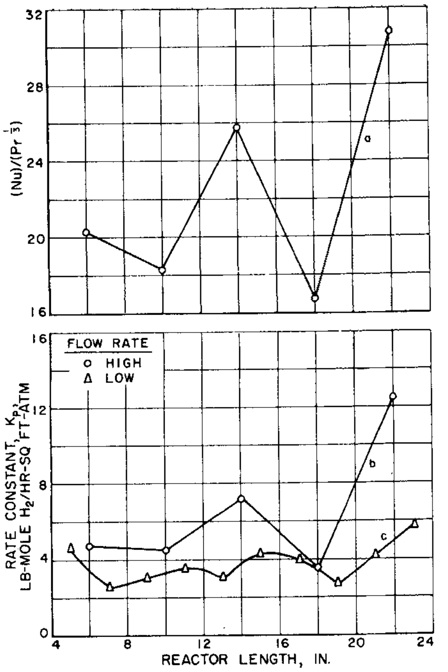

Fig. 8. Variation of heat transfer and rate constant with reactor length.

direction, a slight radial displacement of the probe would affect mass and heat transfer in opposite directions, so that this cannot be a cause of the consistent variation. Curve *c* shows the rate constant or mass transfer coefficient for Run 12A at a low flow rate, 232 std. cu. ft./hr., determined every 2 in. This run was near the completely diffusion-controlled region, and still the same general trend is preserved. From Figure 5 it can be observed that the pattern is not changed in the region where the rate constant decreases with mass velocity, 700 std. cu. ft./hr. and down. In the low-velocity region however the difference between the sectional rate constants seems to decrease somewhat. For section 20 to 24 in. the decrease compared with other sections is obvious. Bulk-phase reaction cannot be appreciable in this section, otherwise the coefficients would not decrease with velocity increase, especially since there is a tendency for higher gas temperature at lower air rates.

Differences in heat transfer coefficients and rate constants are due to either some longitudinal changes in the bulk stream or to longitudinal differences at the surface of the alumina tube. To determine whether the first possibility could have been the cause for the sectional differences observed longitudinal heat transfer rates from a hot-wire anemometer in midstream were measured. The heat transfer rates were found to vary with length less than 1% of the change in flow rate. There is therefore no change with length in resistance to transfer processes in the bulk stream. To determine whether the probe could have been responsible for the differences observed a Teflon plug was attached to the hot-wire anemometer and pushed through the reactor tube to simulate the probe used in the previous determinations. No changes were observed. The sectional differences must therefore occur at the surface. Since the differences are at the surface, probable cause could be a nonuniform roughness along the length of the inside surface of the alumina tube. This would give a nonuniform surface area and a nonuniform rate of reaction, since the rate is proportional to the surface area. This roughness effect would also give varying heat transfer rates. The method of manufacture of the alumina tube makes one suspect that roughness could not be the same throughout the length of the tube. Visual inspection indicates some differences. It should also be observed that the thickness of the laminar sublayer falls approximately between 0.0005 and 0.004 in. for the range of data involved. Judging from the texture of the surface the height of the protrusions could easily exceed the thickness of the laminar sublayer and cause local differences in heat transfer coefficients due to nonuniform distribution of the protrusions. Variation of 1-in. transfer coefficients with length is such as one might expect from a randomly rough surface.

Thus considerable evidence supports the conclusion that roughness was the cause of the sectional variation of heat transfer coefficients and rate constants. No evidence was found to contradict this conclusion. Because of this evidence the inner surface of the second reactor was smoothed to within 0.0002 in. This was well within the thickness of the laminar sublayer in the range of available flow rates. There should have been little variation from section to section. The results (see Part II) show that there was little variation from section to section compared with the variation obtained in the alumina tube.

Temperature Dependence of Reaction Rates

Figure 9 shows the variation of the rate constants, for the range unaffected by mass rate of flow, as a function of surface temperature. The rate constant for 300°F. was evaluated from the slope of the line in Figure 2, while the constant for 228°F. represents a single experiment. The rate constants for 600° and 1,200°F. were obtained by averaging the slopes of the lines such as in Figure 4 for the first four sections. These values compare with the arithmetic averages, respectively, for the section 4 to 20 in. given in Table 1 as follows: for 600°F., 6.26 vs. 6.41; and for 1,200°F., 4.63 vs. 4.76. The rate constants for 612°, 824°, 827°, and 1,600°F. were obtained by averaging the first four sections of velocity-independent runs at each temperature. The data for 401°F. were slightly diffusion controlled, and so the rate constant was slightly increased with the velocity variation of the other runs used as the basis. The surface temperature in Figure 9 represents the average of eight temperature readings for eight heating zones separately controlled to within 15°F. of each other.

Figure 9 shows a maximum in the rate constant at about 600°F. Such behavior, although at first unexpected, is not strange. O. A. Hougen *(11)* back in 1951 reviewed the theory of reactions catalyzed by solid surfaces and discussed this possibility for exothermic irreversible reactions. C. N. Satterfield and R. S. C. Yeung *(16)* recently observed a maximum in the rate constant for hydrogen peroxide vapor decomposition on platinum at about 650°F. They have also cited examples of other surface reactions with maxima in true rate constants.

From the rate constants in Figure 9 two activation energies can be obtained, one for reaction below 450°F. and one for the reaction between about 450° and 1,600°F.

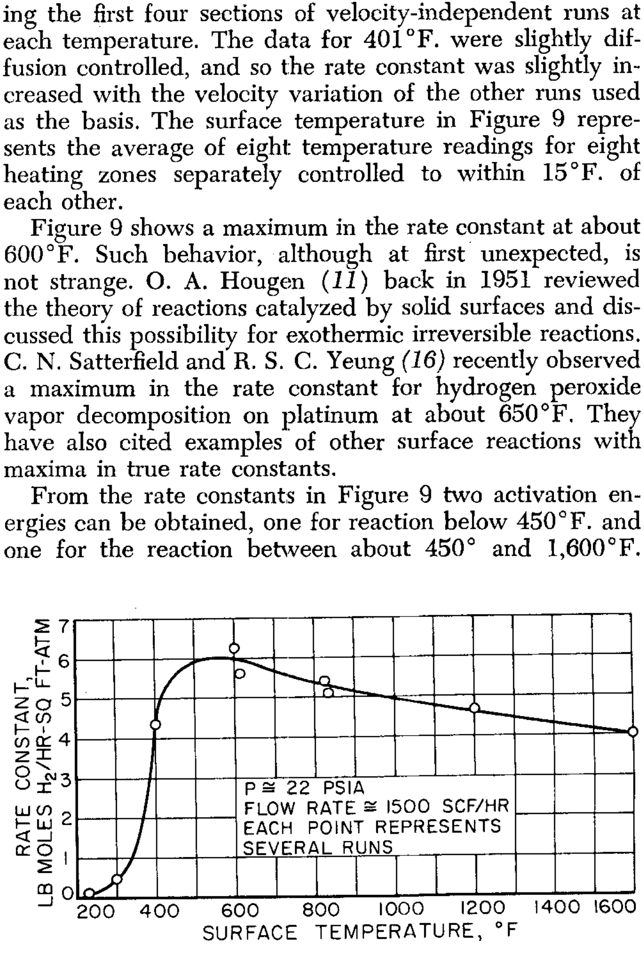

Fig. 9. Effect of surface temperature on hydrogen oxidation reaction rate.

The rate constants are first transformed to the classical basis, that is into concentration units, by multiplying the rate constants in Figure 9 by the ideal gas law constant and by the surface temperature. Then the activation energy above 450°F. is 0.66 kcal./g.-mole; below 450°F. it is 17.

Effect of Catalyst Concentration

The reactor was recoated after a series of runs to determine whether the different surface activities observed along its length were due to an uneven coating. Originally the reactor was coated as already described. After sixty-one runs had been made with this catalyst the tube was recoated in place to obtain a better platinum distribution. The 10% platinum chloride solution was concentrated to half its volume, brushed on with a sponge, cut to fit into the tube tightly, and continuously fed with the solution. The tube was dried and heated to 1,600°F. The process was repeated. The second coating did not change the rate of reaction. The sectional rate constants at a surface temperature of 827°F. in the diffusion independent regime were 4.9, 4.1, 7.9, 3.4, and 14 for sections 4 to 8 in. up to 20 to 24 in., respectively. These numbers can be compared with those in Figure 5. Therefore catalyst concentration was at its maximum throughout the length of the reactive section after the initial coating. Different sectional rates were not due to an uneven coating.

Boundary-Layer Reaction

It has been observed that there was an excessive rise in gas temperature in the last reactor section where the gas temperature is highest. In all other sections the specific rise in gas temperature, as measured by the heat transfer coefficient, was the same for heating of air and for combustion of hydrogen. For example at a flow rate of 1,450 cu. ft./hr. and at a surface temperature of 610°F. the sectional heat transfer coefficients in British thermal units per hour per square foot per degrees Fahrenheit are 42, 40, 61, 39 for heating of air vs. 46, 44, 60, 37 for surface combustion of 1% hydrogen. The coefficients refer to four consecutive 4-in. sections of the reactor starting at the section labeled 4 to 8 in. In the last section section 20 to 24 in., the heat transfer coefficient with surface combustion is 91 vs. 65 for heating of pure air. The heat transfer coefficients did not appreciably change with hydrogen concentration. For example for the last reactor section they are 109, 100, 98, and 99 for average hydrogen concentrations of 0.07, 0.28, 0.61, and 0.88 mole %.

Since the heat transfer coefficients with and without surface combustion are the same for the first four sections, the extra rise in gas temperature in the last section must be due to heat liberation in the gas phase. The reaction how ever cannot be proceeding throughout the gas phase because the rate constant decreased sharply with flow rate and did not increase appreciably with gas temperature, as shown in Figure 5. Therefore the additional conversion of hydrogen must be confined to the boundary layer. It is neither truly homogeneous nor truly heterogeneous. Such behavior was not observed in the case of combustion of hydrogen in a nickel oxide reactor (Part II).

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NOTATION

A = cross-sectional area, sq.ft.
G = mass rate of flow per unit cross-sectional area, lb./(hr.)(sq. ft.)
K_p = first-order reaction rate constant for reaction on platinum, lb. mole hydrogen/(hr.)(sq. ft./atm.)
L = length coordinate, ft.
M_i = molecular weight of species i, lb. i/lb. mole i
M_{mo} = mean molecular weight of feed, lb. feed/lb. mole feed
n = moles of species under consideration per mole of feed
n_o = moles of species i entering per mole of feed, or mole fraction of i in feed
n_t = total number of moles in system at any time per mole of feed
P_t = total pressure, atm.
R = inside tube radius, ft.
r = net molar rate of consumption of species i per unit surface area by chemical reaction, lb. mole i/(hr.)(sq. ft.)
r' = net molar rate of consumption of species i per unit reactor volume by chemical reaction, lb. mole i/(hr.)(cu. ft.)
S = surface area, sq.ft.
SCFH_i = std. cu. ft. of i/hr. at 70°F., 14.70 lb./sq.in.
V = volume, cu.ft.
v = linear velocity of fluid, ft./hr.
Y_i = weight fraction of species i, lb. i/lb. mixture
y = mole fraction of controlling specie, lb. mole i/lb. mole mixture
y_o = mole fraction of controlling specie in feed
Δ = differences at two axial positions
ρ = density of fluid, lb./cu.ft.
τ = time, hr.

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