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A Fast Response, Local Gas-Sampling System for Studies of Catalytic Reactions at 1–10^3 Torr; Application to the H_2–D_2 Exchange and H_2 Oxidation Reactions on Pt

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An experimental system designed for studies of catalytic reactions at pressures of 1–10^3 Torr is described. Special features of the system are the local sampling of gas close to the catalyst and the small response time (~50 msec). The gas is sampled locally in space at a distance of ~0.1 mm from the catalyst by a specially prepared quartz tube orifice leak. Gas analysis is made by mass spectrometry. The design reduces several of the problems connected with studies of mass-transfer-limited reactions and rapidly varying reaction rates such as, for example, ignition phenomena and chemical oscillations. Results for the H_2–D_2 exchange and H_2 oxidation reactions on polycrystalline Pt at 990 Torr are used to illustrate the performance of the experimental system.

1. INTRODUCTION

The simultaneous development of ultra high vacuum techniques and surface sensitive methods has had a tremendous importance for our understanding of the elementary steps in adsorption, desorption, and catalytic reactions at surfaces. The low pressures attainable offer not only a way of preparing clean surfaces but also a way of studying monolayer formation on a time scale compatible with the response times of the experimental probes.

Most of the surface-sensitive spectroscopies require pressures $<10^{-5}$ Torr for their proper operation. However, it is desirable to translate the knowledge gained in low-pressure studies to the much higher pressures where practical catalysis is performed. Recently, several attempts have been made to bridge this gap (*1*). Such translation is very far from trivial, however, because new physical and chemical processes start to play a role at the higher pressures and because the relative importance of the various possible processes at high and low pressures may be drastically different. The population of an adsorption state with a small binding energy, for example, may be effectively zero at say 10^{-6} Torr and very close to unity at 1 atm. This adsorption state may still be observed at the lower pressure by lowering the catalyst temperature, but the participation of molecules in that adsorption state in a reaction may then be prevented by a too high activation energy.

Two new effects of importance at higher pressures are that reactions may be strongly influenced by limited mass and heat transfer. Finite mass transport rates may create great problems in the determination of real, rather than apparent, rate laws in catalytic reactions at pressures >10 Torr (*2–4*). For a given geometry and pressure the problem becomes increasingly

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more severe with increasing reaction rate, and the partial pressures of the reactants just outside the catalyst surface may be very different from those in the original gas mixture. Since derived rate laws are usually expressed in terms of the latter, great care must then be exercised if even qualitatively correct results are to be obtained. The limited mass transfer rate is an obstacle also in the study of rapidly varying reaction rates as, for example, in ignition phenomena (*2, 5, 6*) and chemical oscillations in heterogeneous catalysis (*7, 8*). A similar class of problems is caused by inefficient heat transfer (*2, 9*) in exothermic reactions where temperature gradients may prevent accurate determination of the gas and catalyst temperatures.

The experimental system described here was designed to reduce or eliminate some of these problems. The gas is sampled at a position very close to the catalyst surface by a quartz tube orifice leak. The design and performance of the equipment are discussed and results from studies of the H_2–D_2 exchange and H_2 oxidation reactions on polycrystalline Pt at atmospheric pressure are used to demonstrate the capabilities of the equipment.

Hori and Schmidt described a system (using mass spectrometry for gas analysis) with an overall time constant of a few seconds (*10*). They also commented on the lack of experimental investigations with sufficient resolution for studies of transients in catalytic reactions. Matsumoto and Bennett studied the CO/H_2 reaction on iron in a flow system with a time constant of ~12 sec (*11*). In most other experimental systems, however, the overall time constant is about half a minute or more. Since diffusion processes are slow a reduction of the time constant at high pressures requires a very short distance between the catalyst and the gas sampling system, and a small response time of the gas analyzer.

2. EXPERIMENTAL SYSTEM

The experimental system is shown schematically in Fig. 1. Four different gases can be injected into the reaction cell (C) via four precision needle valves (A). The different gases enter the cell in a small mixing volume (B) through closely spaced, narrow ($\phi = 0.1$ mm) channels. The close spacing and the rather high speed of the entering gas ensures a good gas mixing. Heating is achieved either by the external heating coil (D), or by resistive heating of the catalyst wire or foil (E). The catalyst is mounted in a four-point probe arrangement allowing simultaneous heating and temperature determination via the temperature-dependent resistivity of the catalyst. When supported catalysts are studied, the temperature is measured with a thermocouple. The length and diameter of the cell (Pyrex or quartz) is 30 cm and 15 mm, respectively. The cell is connected to the inlet and outlet systems by vacuum tight Viton O-rings. The pressure in the cell is kept constant by a variable relief valve at (G), and the absolute pressure is determined by a capacitance manometer connected via the valve (F). The gas flow is controlled by the calibrated leak valves and by rotameters. With the valves (G) and (A) closed the cell can be evacuated by the roughing or diffusion pumps of the vacuum system, connected via the valve (H).

A small fraction of the flowing gas mixture is leaked into the vacuum system through a specially prepared quartz tube orifice leak (I) (*12*) mounted in the holder (K). Sealing is achieved by Viton O-rings. The tip of the quartz leak can be positioned at any desired position on the cell axis, thereby ensuring a local measurement of the gas concentration. The gas introduced into the vacuum system is continuously analyzed by a quadropole mass spectrometer (Vacuum Generators, Q7B) equipped with an electron multiplier for ion detection. By a mass selection unit up to 8 preset mass numbers can be repeatedly displayed in sequence on a strip chart recorder or a multichannel analyzer. The mass spectrometer is housed in an oil-diffusion-pumped,

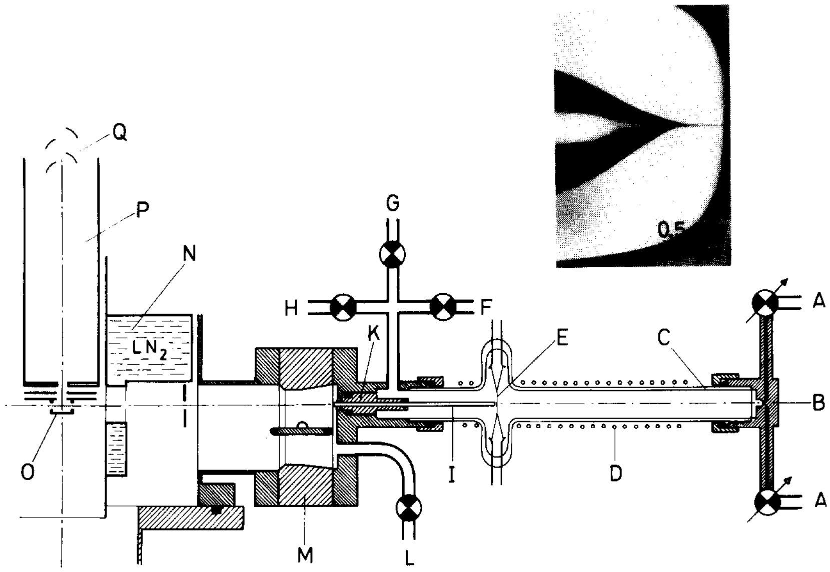

FIG. 1. Experimental set-up. The gas mixture is injected into the reaction cell C via the needle valves A and the narrow channels at B. The catalyst E is mounted in a "four-point probe" arrangement allowing accurate temperature measurements. A small fraction of the gas is injected into the vacuum system for mass spectrometric analysis. The injection is achieved by the quartz tub orifice leak, I, which has a narrow constriction ($\phi \approx 0.006$ mm) at the tube tip (shown in the insert). This arrangement allows gas sampling close to the catalyst (~0.1 mm) with a small response time (~50 msec). D, External heating element; F, capacitance manometer; G, gas outlet; H, connection to vacuum pumps; K, O-ring sealed adaptor for the quartz tube leak; L, evacuation tube for butterfly valve volume; M, butterfly valve; N, liquid nitrogen dewar; O, ion source of mass spectrometer.

all-metal (except for a few Viton O-rings) vacuum system with a liquid nitrogen cold trap. The effective pumping speed with the trap uncooled is 100 liters/sec and the base pressure after bake out is in the low 10^{-9} Torr range.

Temperature measurements. The catalyst wire is mounted as part of a four-point probe in order to make accurate temperature measurements of the catalyst possible. The contact leads, spot-welded to the catalyst wire, are made from the same wire as the catalyst. This design is necessary to minimize temperature gradients across the wire, which cause errors in the temperature determination. The outer ends of the electrical leads are spot-welded to tungsten feedthroughs. The error in the temperature measurements is estimated to be about ±10 K, mainly due to a low accuracy in the resistance measurement and thermal gradients.

At low reaction rates, when the dissipated chemical power is negligible, the four-point probe arrangement simply serves as a thermometer measuring the catalyst temperature. In studies of exothermic reactions proceeding at high rates the chemical power may be large and the device may then be used as a crude calorimeter yielding data complementary to those obtained by the mass spectrometer. The measured temperature of the catalyst is in such cases produced by a combination of chemical power dissipation, external heating, cooling by convection, and heat conduction. The two latter are corrected for by running calibration runs with the carrier gas alone. The wire is then heated only resistively and the catalyst temperature is recorded as a function of electrical power at the used flow speeds and pressures of the carrier gas. Knowing the exothermicity of the particular reaction studied, it is then possible to obtain the overall rate of the reaction. Gravelle (*13*) has recently reviewed the use of calorimetric measurements in heterogeneous catalysis.

Gas sampling. The quartz tube orifice leaks have been described elsewhere (*12*), but a short recapitualtion is appropriate. The leak was made from a 10-cm-long quartz tubing with inner and outer diameters of 1 and 2 mm, respectively. The tip of the tubing was heated in an oxygen–hydrogen flame until a constriction was formed that gave a gas flow through the tube at 1 atm inlet pressure of about 10^{-4} Torr · liter/sec. The tube tip then had the appearance shown in the insert of Fig. 1. The width and length of the narrow constriction at the tube tip were determined to be about 0.006 and 0.15 mm, respectively.

3. RESULTS

Figure 2a shows the mass spectrometer (MS) mass 40 signal as a function of the argon pressure in the reaction cell. This curve serves as a correction diagram when results obtained at different cell pressures are to be compared. For small variations in cell pressure the signal can to a good approximation be assumed to vary linearly with inlet pressure. Over the whole range of experimental points the signal varies approximately as $P^{1.35}$ which is intermediate between the linear and square dependences expected for pure molecular and viscous flow, respectively.

The MS signal varied also with the temperature of the gas at the probe tip (at constant pressure) due to the variation in gas density with temperature. Figure 2b shows the variation in the mass 40 signal at constant argon pressure in the cell when the cell temperature was varied in the range 295–530 K. The heating was achieved by the external heating coil and the gas temperature was determined from the resistivity of the Pt-wire (E in Fig. 1). The MS signal decreases as $T^{-1.25}$ with increasing temperature. It is thus of vital importance to know the gas temperature at the probe tip in order to obtain the true partial pressures of the reactants and the reaction products. The gas temperature may in fact be derived from the MS signal for the carrier gas, since changes in the latter are mainly due to temperature changes when the total pressure is kept constant.

The system response time for measurements of variations in the partial pressures at the tip of the quartz leak was found to be ~50 msec at 1 atm total pressure. This value was obtained by recording the argon signal rise time when a high-speed, chopped argon beam was directed towards the tube tip. The effective time constant, τ, of the system is composed of several contributions. The inherent response time of the mass spectrometer and the transport time from the vacuum side of the quartz leak to the MS ion source are negligibly small, while the time constant of the vaccum system is estimated to be about 20 msec from the ratio of the system volume (2 l) and

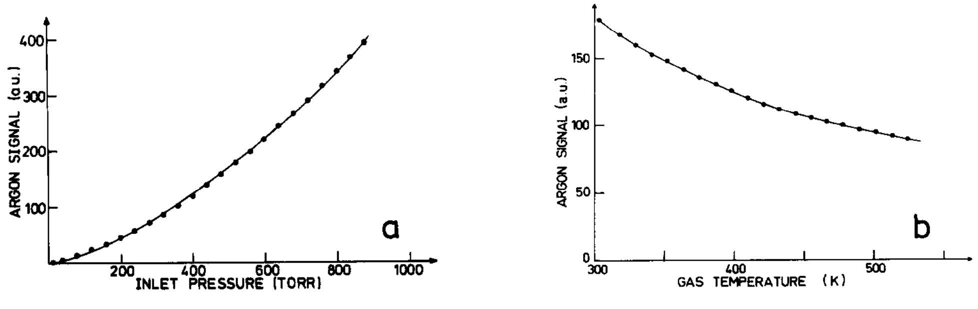

FIG. 2. Dependence of the mass spectrometer signal for argon(a) on the argon pressure in the reaction cell and (b) on the argon gas temperature at constant pressure.

the pumping speed (100 liter/sec). An important contribution comes from the gas transport from the catalyst to the quartz leak inlet. We call this contribution τ_{leak}. At large catalyst-leak distances, d, τ_{leak} is determined by the gas diffusion speed or the gas flow speed through the cell. In the latter case τ_{leak} varies linearly with d. At sufficiently small distances (the actual case) τ_{leak} is determined by the volume of gas sampled per unit time, and varies as d^3. An estimate is obtained by calculating the time required to sample a gas volume with linear dimension d. Assuming the volume to be half spherical with radius $d = 0.1$ mm and using the known leak rate and pressure, $1 \cdot 10^{-4}$ Torr · liter/sec and 760 Torr, respectively, we obtain $\tau_{\text{leak}} \approx 15$ msec. From these considerations an overall time constant of about 50 msec seems very reasonable, in spite of the neglect of diffusion effects and of the finite size of the catalyst.

Figure 3 shows the result of an experiment performed to illustrate the local sampling achieved by the quartz leak. The diagram shows the nitrogen partial pressure at the tube tip as a function of time caused by an N_2 pulse introduced at the gas inlet at A in Fig. 1. The N_2 pulse was injected during approximately 1 sec into the oxygen carrier gas, flowing through the cell at constant speed. The three N_2 concentration curves shown were obtained with three different O_2 flow speeds. The qualitative features of the curves are the expected ones. (The vertical scale is different for each run.) With a smaller flow speed it takes a longer time before the nitrogen gas reaches the quartz leak and the N_2 signal is seen over a longer time period. The asymmetry of each N_2 peak is due to the combination of the unidirectional flow of the carrier gas and the isotropic diffusion of N_2 into the O_2 gas. On the low t side the signal rises more rapidly since both the flow and the diffusion then tend to drive the gas toward the quartz leak. On the high t side, however, the signal decreases more slowly because the flow away from the leak is partly compensated by the diffusion against the flow direction. With increasing flow speed the N_2 peak becomes narrower because the broadening in space due to diffusion is smaller and because the N_2 "cloud" passes the sampling position in a shorter time. A calculation of the N_2 peaks assuming a gaussian distribution developing in time gave a fair agreement with the experiment and reproduced the form of the N_2 curves very well. However, the control on the N_2 injection was not good enough to extract the N_2 diffusion constant in O_2.

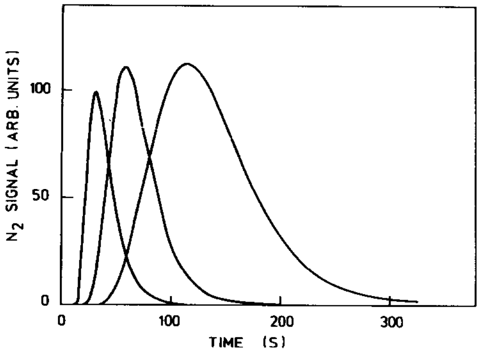

FIG. 3. Variation in the mass spectrometer signal for N_2 with time when a small pulse of N_2 was injected at $t = 0$ into the O_2 carrier gas at B (see Fig. 1). The three curves were obtained for three different flow speeds of the O_2 carrier gas (0.19, 0.38, and 0.77 cm/sec, respectively).

H_2–D_2 Exchange

As a model reaction we studied the H_2–D_2 exchange reaction on polycrystalline Pt wire. The reactant gas was a mixture of ~2% of each of H_2 and D_2 in argon at 1.3 atm absolute pressure. The H_2, D_2, and HD signals were recorded as a function of time when the temperature of the gas and the Pt catalyst (99.99% purity, Ø = 0.127 mm) was continuously raised by the external heating coil. The gas flow was 30 ml/min, corresponding to a flow speed of 0.4 cm/sec. The catalyst had been pretreated by running the $H_2 + 1/2\ O_2 \rightarrow H_2O$ reaction at about 800 K for a few minutes. This treatment had been found to produce an active catalyst for the

H_2 oxidation reaction (see below and Ref. *14*).

The filled circles in Fig. 4a are the experimental points recorded by the mass spectrometer. The background signals for H_2 and D_2 in the vacuum system have been subtracted but no correction for the relative sensitivities of the MS for H_2 D_2, and HD has been made. It is seen that the HD exchange rate becomes appreciable around 200°C and that the equilibrium ratio $H_2:HD:D_2$, 1 : 2 : 1 is approached as the temperature is increased. An Arrhenius plot of the HD curve (Fig. 4b) yielded a straight line in the temperature range 440–570 K. Following the analysis given by Lu and Rye (*15*) we obtained an activation energy of 17 kcal/mol, which is close to the desorption energy for H_2 on Pt (*15, 16*), but far from the quoted activation energies for the exchange reaction on a Pt surface (*15, 17*). We thus conclude that the rate-limiting step in the mentioned temperature range is the desorption of hydrogen molecules from the Pt surface.

H_2 Oxidation on Pt

As the second example we show some

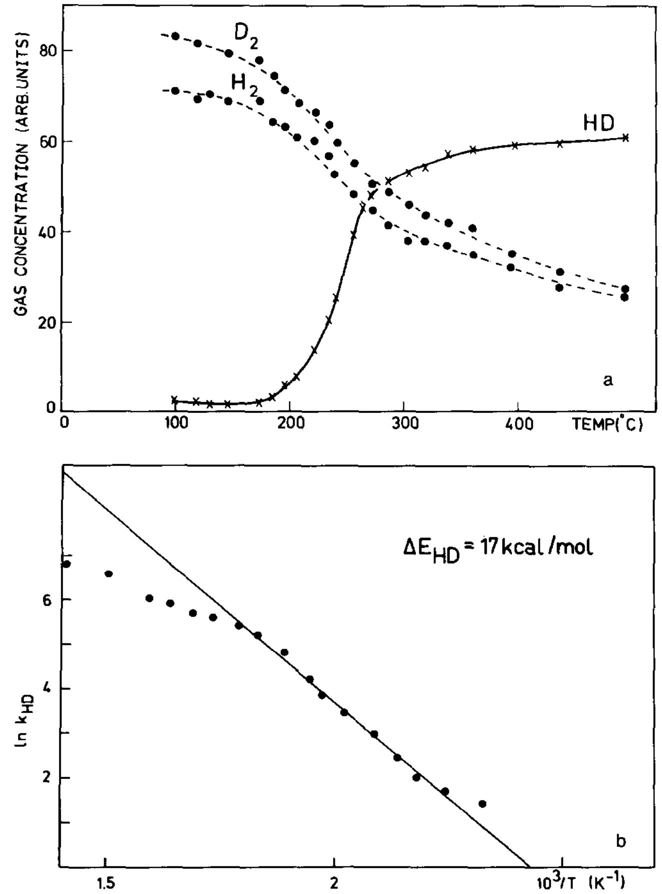

FIG. 4. H_2–D_2 exchange on Pt. (a) The diagram shows the H_2, D_2, and HD mass spectrometer signals as a function of temperature (gas + catalyst) when a mixture of ~2% H_2 and 2% D_2 in argon at 990 Torr was flowing at constant flow speed through the reaction cell. The catalyst was a 10-mm-long Pt wire, diameter 0.127 mm. (b) Derivation of an activation energy for the H_2–D_2 exchange using the results of Fig. 4a and following the analysis in Ref. (*12*). k_{HD} = [HD]/0.5Σ − [HD], where [HD] is the HD concentration and Σ the sum of the H_2, D_2, and HD concentrations.

results from the oxidation of H_2 on Pt in a 3.6% mixture of H_2 in synthetic air at 1.3 atm. The catalyst was the same as in the H_2–D_2 exchange experiments and the gas flow was 30 ml/min. The catalyst was cycled several times in the temperature range 295–500 K in the reaction mixture until reproducible results were obtained. Figure 5 shows the concentrations of H_2, O_2 and H_2O and the catalyst temperature as a function of time when the catalyst was heated by continuously increasing the heating current. The system background levels have been subtracted, but no correction for the MS sensitivities has been made and the scale on the abscissa is different for each gas. The production of H_2O (and consumption of H_2 and O_2) increases slowly with increasing temperature up to about 420 K. At this temperature the reaction rate and temperature both increase rapidly ("ignition") until a steady state is established. The temperature rise above 150°C is solely caused by the increased chemical power dissipation. The H_2 curve shows that after ignition there is very little unreacted hydrogen at the position of the tip of the quartz leak (~0.1 mm from the Pt wire). In this situation the reaction rate is limited by the transport of H_2 to the catalyst. The small overshoot in the temperature curve is attributed to the larger concentration of reactants available at the moment of ignition compared to later times when there is a depletion of reactants close to the catalyst and large concentration gradients are set up.

The results of Fig. 5 were very reproducible when the catalyst was cycled in the temperature range 295–500 K. A characteristic feature was the ignition temperature of About 420 K for the reaction mixture mentioned above. However, this state of the catalyst was not the most active. The most efficient activation was obtained by running the reaction at temperatures > 800 K at a high gas flow and then switching off the reaction with argon. After this treatment ignition temperatures as low as 320 K were observed. The ignition temperature then steadily increased to the asymptotic value of 420 K (each new run starting at 295 K) is the highest temperature was kept below 700 K.

No clear identification of the cause of this behavior was made. The two most likely causes are: (i) poisoning by an impurity in the reactant mixture, and (ii) a change in the composition of the catalyst caused by the reactants. At first sight (i)

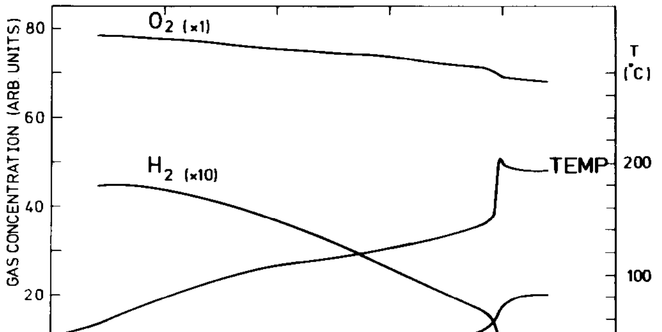

FIG. 5. Oxidation of H_2 on a Pt wire catalyst (diameter 0.127 mm) in a gas mixture of 3.6% H_2 in synthetic air at 990 Torr. The H_2, O_2, and H_2O mass spectrometer signals are shown as a function of time when the catalyst was slowly increased in temperature (right vertical axis) by resistive heating. At 150°C ignition occurs and the temperature increases spontaneously solely due to the increasing chemical power dissipation.

seems very likely, since extremely small amounts of impurities could contaminate the surface (with a sticking coefficient of unity an impurity of 1 in 10^9 would saturate a monolayer in 1 min). However, the high reproducibility of the data on nonactivated catalysts is somewhat in conflict with this explanation. Cause (ii) could for example involve a change in the oxidation of the Pt surface. It has recently been demonstrated that strongly bound, nonreactive oxygen on Pt is most probably sitting below the outermost Pt layer (*18*). Although this oxide-like structure is formed only at temperatures >1000 K in pure oxygen, it might be formed at lower temperatures under reaction conditions.

Guided by the high reaction probability (of order unity) for H_2 oxidation on clean polycrystalline Pt under UHV conditions (*19*) we suggest that the activated catalyst is metallic Pt. (A remarkable result in this context is that a supported Pt–Rh automobile exhaust catalyst was found to oxidize H_2 very efficiently even at 200 K and 1 atm under conditions identical to those described above.) A distinction between (i) and (ii) or a possible other cause must await a spectroscopic characterization at the catalyst in the various stages of activity.

Under certain conditions catalytic reactions run into oscillatory states (*7*). Figure 6 illustrates this for the H_2 oxidation reaction on Pt. The phenomenon may be regarded as a periodic series of ignition–extinction sequences or, equivalently, periodic transitions between surface-kinetic-controlled and mass-transport-controlled reaction conditions. Such oscillations have been studied extensively in the past by temperature measurements (*16*). In our system we additionally obtain an instantaneous recording of the oscillations in the concentrations of reactants and reaction products. The oscillations shown in Fig. 6 cease after five periods. However, the periodic oscillatory behavior could often last for hours with period times from one half to several minutes. No detailed investigation was made of the conditions for which oscillations appeared but one qualitative observation may be important. We never managed to initiate the oscillations when the reaction cell was heated by the external heating coil. This may indicate that the cooling of the catalyst by the reactant gas is an important factor for this kind of oscillation. In our view, the large period times are indications that the mass and heat transport are of major importance. The reaction conditions are such that the gas temperature, T_g, as well as the partial pressures, P_i, of the reactants and reaction products are functions of time and of the space coordinates

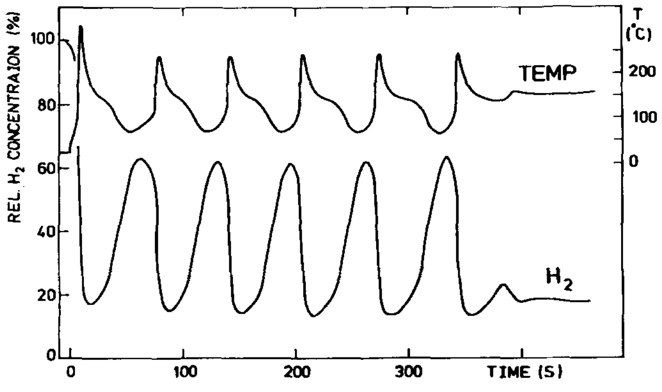

FIG. 6. Chemical oscillations in the H_2 oxidation reaction on Pt. The upper curve shows the oscillations in the catalyst temperature and the lower curve the oscillations in the H_2 concentration close to the catalyst. The latter curve measures the H_2 consumption and thus the reaction rate.

(due to gradients). Furthermore, the coverages of the reactants and the catalyst temperature are also functions of time, coupled to $T_g(t)$ and $P_i(t)$. It is not surprising if this set of five or more coupled differential equations have oscillatory solutions. The analysis of these data is in progress and the results will be presented elsewhere (*14*).

4. DISCUSSION

The local gas sampling has several important advantages over averaging measurements at the outlet of the reaction cell. Due to the small time constant, rapid variations in reaction rates may be stuided. The sampling close to the catalyst surface increases the sensitivity in comparison with sampling at a more distant position. Catalysts with very small mass and area (and thus small thermal mass) may then be studied, which is an advantage for the control and measurement of catalyst temperature. The small size of the quartz leak and the negligible amount of sampled gas ($\sim 10^{-7}$ cm^3/sec) guarantees a minimum of perturbation of the gas flow around the catalyst. The high temperature stability of the quartz leaks make them useful even at temperatures >1000 K (*12, 20*).

Finally, we consider some drawbacks, limitation, and possible improvements of the experimental system.

An inherent drawback with an MS is that its background levels and thus the sensitivity depend on the conditions of the vacuum system in which it is housed. In the present system the total background pressure is around $5 \cdot 10^{-9}$ Torr, which together with exchange reactions on the chamber walls and "memory effects" (particularly bothersome with H_2O and CO_2) produce background levels which vary in time and which thereby reduce the accuracy in the measurements or require time-consuming control of the backgrounds. These problems may be much reduced by use of a more sophisticated UHV system for the mass spectrometer, by increasing the pumping speed, and by extending the vacuum end of the quartz leak into the ion source of the MS so that the relative pressure of the "direct beam" increases. By such improvements the signal-to-noise ratio may probably be improved by one to two orders of magnitude.

The advantage of the local gas sampling is not fully utilized in the present set-up. Even over the small distance ($\sim$0.1 mm) between the catalyst and the quartz leak a significant concentration gradient may exist when the reaction rate is large. If the reaction cell, instead of being rigidly fixed at the ends, were mounted by flexible bellows and attached to an x,y,z-manipulator the sampling position could be systematically moved, and concentration gradients mapped out.

5. CONCLUSIONS

The particular advantage of the experimental system described here over one based on, for example, a gas-chromatographic detection is the local gas sampling in space and time, which reduces the experimental problems with concentration gradients common at high reaction rates. The time resolution of $\sim$50 msec makes it possible to study rapidly varying reaction rates.

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