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Mercury Adsorption, Catalyst Poisoning, and Reactivation Phenomena on Metal Catalysts

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Mercury adsorption measurements, using a radioactive tracer method, have been made on evaporated films of nickel and on a 5% nickel-on-pumice catalyst prepared by reduction in hydrogen. Evidence has been obtained for at least two types of uptake which have been ascribed to chemisorption and physical adsorption. The similar behavior of the films and supported catalyst suggests that this physical adsorption takes place on top of the chemisorbed mercury and not elsewhere on the supported catalyst. Hydrogen displacement during the adsorption of mercury has been observed. Poisoning and reactivation studies have been made using mercury and a palladium-pumice catalyst. The results of the adsorption, hydrogen displacement and catalytic studies are discussed in relation to one another.

INTRODUCTION

Considerable interest has been shown in the use of mercury as a catalyst poison (*1, 2, 3*) because of its simple monatomic form and its selective poisoning action for certain catalyzed reactions. For this reason, studies of the manner by which mercury is adsorbed by metals are of value. This investigation extends our knowledge both of the behavior of mercury adsorbed on nickel films and on supported nickel catalysts. Conclusions deduced from this have been applied to the interpretation of poisoning effects observed with a supported palladium catalyst in the hydrogenation of cyclopropane.

EXPERIMENTAL

Nickel films. The films were evaporated from a filament of 0.02-inch diameter pure nickel wire supplied by Johnson, Matthey and Co. Ltd. This filament was connected across two 1-mm tungsten leads sealed into a 25-mm diameter Pyrex vessel. Inside the vessel, surrounding the filament, was a piece of Pyrex tubing open at both ends. To degas the film vessel and its connecting tubing it was maintained under high vacuum at 500°C for several hours. Meanwhile, a current of 4.0 A was passed through the filament. During the last 5 min of this degassing procedure the filament was raised to the evaporation temperature by increasing the current to 6.5 A, and a film was allowed to form on the internal tube which surrounded the filament. The vessel was sealed off at a previously degassed constriction and inverted so as to cause the internal tube to slide clear of the filament. On once again passing a current of 6.5 A through the filament, a nickel film was formed on the walls of the vessel itself. During deposition the temperature of the walls was maintained at about 15°C in water.

The vessel was connected to the apparatus for the adsorption studies by means of a break-seal.

Radioactive mercury. Radioactive mercury was produced by neutron irradiation of natural mercury at the AERE, Harwell. ^{197}Hg and ^{203}Hg activities were present, but the short-lived isotope (^{197}Hg, $t_{\frac{1}{2}}$ 65h) was allowed to decay before the ^{203}Hg ($t_{\frac{1}{2}}$ 47d) was used. The mercury was diluted with natural mercury to reduce the activity to a convenient value, and then purified by distillation.

Adsorption of mercury on nickel films. Radioactive mercury vapor was allowed to pass into the vessel containing the nickel film at 24°C, but the source of mercury was kept at some lower temperature to prevent transfer by a process of condensation rather than adsorption. The arrival of mercury on the film was detected and measured by a γ-ray counter arranged parallel with the vessel. The apparatus and the method by which the observed count rates were related to the weights of mercury is described in a previous paper (*4*). The weight of nickel in the film was estimated colorimetrically by dissolving the film in 10*M* nitric acid after the adsorption measurements had been completed, and converting it to the water-soluble nickel(III) dimethylglyoxime complex. The highly sintered nickel film formed during the bake-out was not included in this estimation.

Supported nickel catalyst. A 5% nickel-on-pumice catalyst was prepared as follows: 120-mesh pumice was purified by being boiled with concentrated hydrochloric acid. This was repeated with fresh acid until, on settling, the supernatant liquid was no longer yellow. The acid was then decanted and the pumice treated with two changes of boiling distilled water, and finally washed with distilled water until the washings were neutral. Twenty five grams of this purified pumice was slurried with 60 ml of distilled water; 18.6 g AnalaR nickel nitrate in 25 ml of distilled water was added. The slurry was dried and the nickel nitrate decomposed to nickel oxide by ignition at 350°C in a muffle furnace for 15 hr. Five-gram batches of this were reduced to nickel as required by heating them to 480°C for 10 hr in a stream of hydrogen. The reduced catalyst was allowed to cool in hydrogen. Before use, the catalyst was activated *in situ* for 2 hr at 250°C in hydrogen at a pressure of 200 torr.

Measurement of adsorption of mercury on supported nickel. The catalyst, 0.2 g, was placed in a 4 cm long porcelain boat and inserted through a B14 joint into a horizontal Pyrex tube (Fig. 1). A source of radioactive mercury was placed in a sidearm connected to this tube through a stopcock, and shielded with lead. The rate of arrival of mercury on the catalyst was measured with a γ-ray G.M. counter parallel to and above the tube containing the catalyst boat. Hydrogen displaced from the catalyst was measured with a McLeod gauge. In those experiments in which the mercury vapor pressure was measured a quartz absorption cell was attached to a second sidearm by means of a B10 joint sealed with Apiezon W wax. A thermostat, shaped to fit the cell compartment of the spectrophotometer, surrounded part of the apparatus, as shown in Fig. 1.

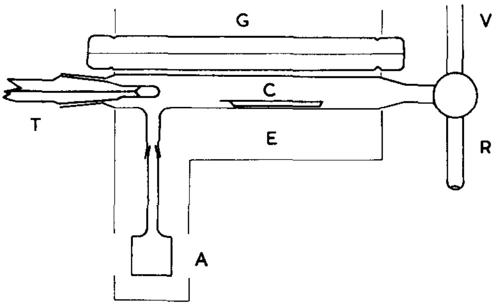

FIG. 1. Apparatus for the study of mercury adsorption on supported nickel: C, nickel catalyst; G, γ-ray counter; A, quartz absorption cell; E, thermostated enclosure; R, radioactive mercury source; T, thermometer; V, connection to vacuum apparatus. Lead shielding is not shown.

Measurement of mercury vapor pressure. The vapor pressure of mercury in the system was measured by absorption of 2537-Å mercury resonance radiation in the mercury vapor contained in a 2-cm quartz cell attached to the adsorption vessel. A Hilger Uvispec spectrophotometer was used to measure absorption, but an external mercury resonance lamp (Philips Electrical Ltd. T.U.V. 6 W) was used as the light source to produce a narrow 2537-Å line. This was an inert gas-filled low-pressure mercury arc lamp, which showed collision-broadening to a tolerable extent. Its energy output at 2537 Å was 85 mW. The monochromator system of the spectrophotometer was able to discriminate against other wavelengths emitted by the lamp.

Preliminary experiments showed that the presence of hydrogen along with the mercury vapor resulted in collision-broadening of the absorption line, as a consequence of which the absorption was a function of both the hydrogen and the mercury pressures. Hydrogen at 17.5 torr was therefore admitted to the system initially to swamp the

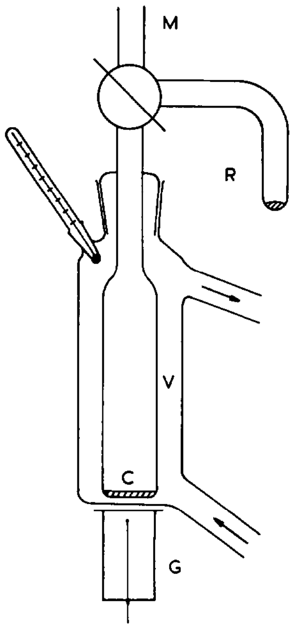

FIG. 2. Diagram of the reaction system for the hydrogenation of cyclopropane: C, palladium catalyst; G, Geiger-Müller counter; V, ethanol-vapor jacket; R, radioactive mercury; M, connection to manometer, gas storage, and vacuum apparatus. Lead shielding around mercury source and counter is not shown.

effect of hydrogen subsequently returned to the gas phase by displacement as the mercury adsorption proceeded. A series of measurements with the mercury source at different temperatures enabled a calibration curve of optical density against vapor pressure to be constructed.

Cyclopropane hydrogenation on supported palladium. An equimolar mixture of cyclopropane and hydrogen was used. Hydrogen was purified by allowing it to pass through a heated palladium thimble. Anesthetic grade cyclopropane, supplied by British Oxygen Co., was purified by distillation. Its purity was verified by GLC.

A 5% palladium-on-pumice catalyst was prepared from palladium chloride supplied by Baker and Co., and which was stated to contain 60% palladium; 2.016 g of this material was dissolved in 2 ml of conc. hydrochloric acid and 15 ml of distilled water and made into a slurry with 25 g of purified pumice. The slurry was then dried. The catalyst was reduced and activated *in situ* in hydrogen at 100°C.

A diagram of the apparatus is shown in Fig. 2. A 240-mg sample of the catalyst was distributed over the flat bottom of the reaction vessel. The vessel was maintained at 78°C in an ethanol vapor bath during the hydrogenation reactions. Radioactive mercury could be admitted through a stopcock from a sidearm containing a source of mercury at 20°C. An end-window G.M. tube (Mullard MX 148), fitted with a piece of lead foil of thickness 87 mg/cm^2, to increase the count rate by the photoelectric effect with the γ-radiation, was placed below the catalyst vessel. The rate of reaction was measured by noting the total pressure as a function of time.

RESULTS

Mercury adsorption on clean nickel films. The adsorption of radioactive mercury on nickel films was studied with the film at 24°C and the mercury source at 14° ± 1°C. The vapor pressure of the mercury relative to its saturated vapor pressure (p/p_0) was 0.41 under these conditions (*5*). The relationship between the amount adsorbed and the time for which the adsorption had proceeded is shown in Fig. 3. On Film 27, adsorption proceeded at a rate which gradually decreased until after 1900 min no adsorption occurred during a further 600 min. This adsorption corresponded to 4.43×10^{17} atoms of mercury per mg of nickel. Under the same conditions, the adsorption of mercury on Film 32 reached a limit of 4.52×10^{17} atoms of mercury per mg of nickel, in good agreement with the value obtained with Film 27. When this steady state had been reached, the temperature of the mercury source was increased to 22°C to result in a change in the p/p_0 value to 0.85. Further adsorption took place and continued for 12,000 min without reaching a saturation value, although the rate of adsorption did diminish with time.

A previous study showed that the average amount of hydrogen adsorbed by nickel films deposited in vacuum at 25°C was 1.94×10^{17} atoms/mg, and that when displacement was complete 1.21 mercury atoms

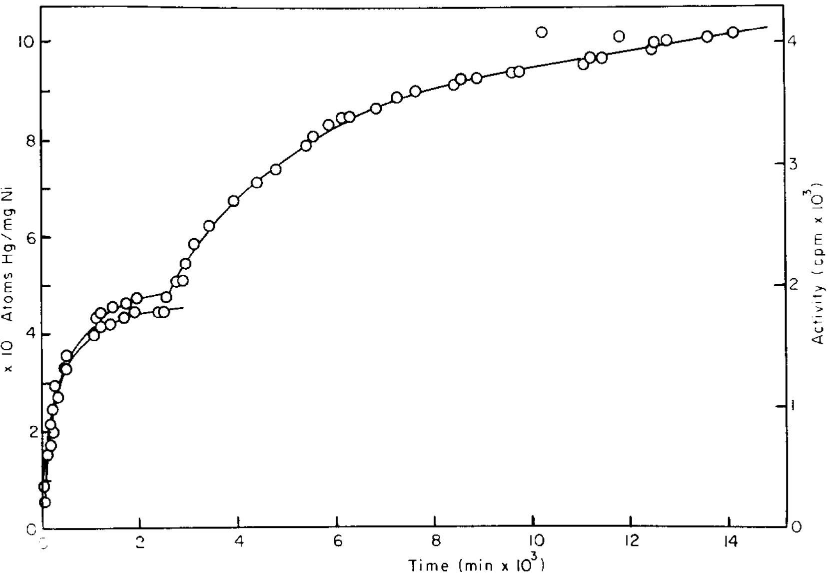

FIG. 3. Adsorption of mercury on clean nickel films. Film 27 (lower curve), $p/p_0 = 0.41$. Film 32 (upper curve), $p/p_0 = 0.41$ and 0.85.

were present for each hydrogen atom which had been displaced (*4*). The amount of mercury necessary to remove all the displaceable hydrogen was thus 2.34×10^{17} atoms/mg nickel.

Mercury adsorption on reduced supported nickel catalysts. Mercury adsorption was studied using 5% nickel on pumice for five values of p/p_0. The statistical error on the counting measurements was ±5 cpm. Stepwise adsorption with respect to relative pressure was observed, but a saturation adsorption was reached at each p/p_0 value below 0.59. This is shown in Fig. 4. A separate experiment indicated that the transition between adsorption which showed saturation and adsorption which did not occurred at a p/p_0 value of 0.64 ± 0.04. Displacement of hydrogen occurred throughout the first step during which p/p_0 reached the value 0.38. No further hydrogen was released when p/p_0 was increased to higher values, showing

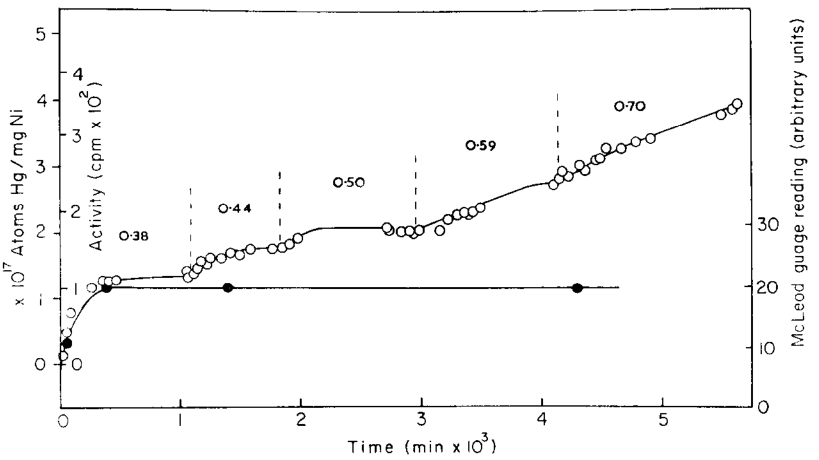

FIG. 4. Adsorption of mercury on 5% nickel on pumice at the various values of p/p_0 indicated. The right-hand scale and lower curve represent hydrogen displaced from the catalyst.

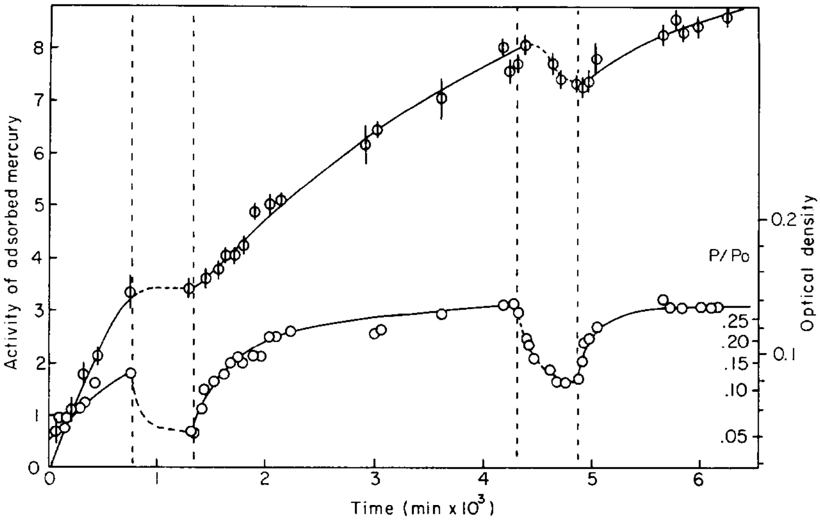

FIG. 5. Mercury adsorption on 5% nickel on pumice (upper curve), with simultaneous measurement of mercury vapor pressure (lower curve). Access of mercury was interrupted during the time intervals defined by the broken lines.

that displacement was complete as a result of mercury adsorption which was possible at $p/p_0 < 0.38$.

To identify more precisely the conditions for hydrogen displacement, a further experiment was carried out at $p/p_0 = 0.11$ by maintaining the vessel containing the catalyst at 24°C, and having the mercury source at 0°C. A graph similar in shape to the first plateau of Fig. 4 was obtained, but the saturation value corresponded to 0.98×10^{17} atoms mercury/mg nickel. Hydrogen displacement continued until 0.88×10^{17} atoms mercury/mg nickel were present.

The manner in which the pressure of mercury vapor, measured by UV absorption, varied with the amount adsorbed during the approach to the steady state was the subject of further investigation. The catalyst was maintained at a temperature of 26°C and the mercury source at 22°C, so that the maximum to which p/p_0 could rise was 0.71. On two occasions during the adsorption, the access of mercury vapor was interrupted for

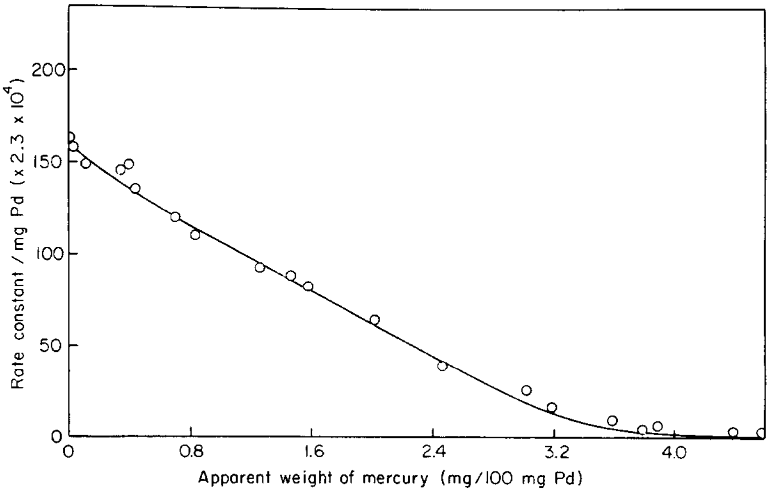

FIG. 6. The poisoning effect of mercury for cyclopropane hydrogenation on palladium.

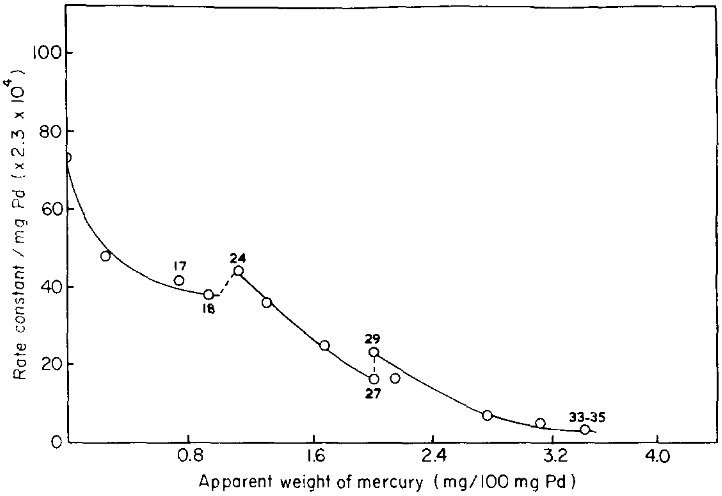

FIG. 7. Reactivation phenomena on a partially poisoned palladium catalyst.

periods of about 9 hr. Figure 5 shows the manner in which the amount of adsorbed mercury and the optical density and vapor pressure varied with time. The broken curve indicates the time intervals during which the mercury source was isolated.

Mercury poisoning of cyclopropane hydrogenation. Reproducibility of reaction rate between successive runs could not be achieved in the hydrogenation of cyclopropane with a nickel catalyst. Using palladium, it was found to be necessary to perform several preliminary hydrogenation runs, after which the catalyst settled down to reproducible behavior. When this had been achieved, the catalyst was exposed to mercury vapor between subsequent runs. First order rate plots of the results showed good linearity, and the slope of these was used as a measure of the catalytic activity. The form of the relationship between the amount of mercury present and this catalytic activity is shown in Fig. 6.

A partially poisoned catalyst was found to exhibit a curious reactivation phenomenon, and it is this aspect of the behavior of the poison which we wish to emphasize because of its similarities with the adsorption phenomena described in the previous section. Results obtained from a catalyst exhibiting this phenomenon are shown in Fig. 7. Runs 18 to 24 were carried out without the admission of further amounts of mercury vapor to the partially poisoned catalyst; the catalyst was allowed to stand for 20 min under vacuum between each run. In spite of this, an increase in the count rate was observed which was statistically significant. Simultaneous with this, reactivation occurred to an extent greater than the poisoning effect produced by a 20-min exposure to mercury vapor between runs 17 and 18.

Similar reactivation was observed when access of mercury was again interrupted after run 27. After run 33, the catalyst had become quite effectively poisoned and hydrogenation runs in the absence of further mercury produced no reactivation.

DISCUSSION

Nature of the Adsorbed State of Mercury

The results of the work on supported nickel showed evidence for two main types of mercury incorporation. Mercury taken up in the first of these processes was responsible for the displacement of hydrogen left on the nickel surface after the reduction of the catalyst. This mode of adsorption could occur at mercury relative pressures (p/p_0) of less than 0.1. The results with nickel films were broadly consistent with this, because the saturation value in Fig. 3, at $p/p_0 = 0.41$, corresponded to a mercury coverage considerably higher (4.5×10^{17} atoms mercury/mg nickel) than the amount which was known to be necessary to displace hydrogen chemisorbed on nickel film (2.34×10^{17} atoms/mg nickel) (*4*). Because of the simple stoichiometry of this displacement, the process was considered to be chemisorption.

At higher values of p/p_0 further adsorption occurred, the extent of which was dependent on the pressure of mercury vapor over the surface. This additional uptake was ascribed to physical adsorption. The uptake of mercury increased with increase in p/p_0, but above the value 0.64, for supported nickel, an additional feature appeared—the uptake continued to increase with time without any obvious tendency to reach a steady state value. This stage of the uptake is tentatively suggested to be condensation in pores and fissures. The same general features were shown by nickel films, but the results did not make it possible to define so precisely the p/p_0 values at which the boundaries occurred between the various types of adsorption. The stage of continuing incorporation was observed with nickel films at $p/p_0 = 0.85$.

We think it unlikely that part of the mercury uptake on the pumice-supported nickel is associated with the support alone, either by adsorption on the surface or within pores. The ratio chemisorbed mercury: total mercury adsorbed at $p/p_0 = 0.41$ was 0.52 for films. For pumice-supported nickel under similar conditions ($p/p_0 = 0.44$) the ratio was 0.51. The similarity of these ratios leads us to believe that the physical adsorption takes place on a layer of chemisorbed mercury on the metal surface, in both forms of nickel.

The Mobility of Adsorbed Mercury

Figure 4 shows that access of mercury vapor to the catalyst is sufficiently good for hydrogen displacement to be completed at an early stage in the mercury uptake processes. It is evident, therefore, that the chemisorption of mercury is not greatly inhibited by diffusion effects arising as a consequence of the finely divided nature of the catalyst. In the phase of the mercury uptake which we have ascribed to physical adsorption there is evidence to show that the adsorbed mercury on the whole of the catalyst is not in equilibrium with the vapor. Thus, we interpret the results depicted in Fig. 5 as follows. The mercury uptake during the first 13 hr was part of the chemisorption stage. When access of mercury vapor was interrupted for the next 9 hr, the optical density fell rapidly as the mercury vapor in the catalyst vessel became adsorbed. A final p/p_0 value of 0.05 was indicated. The count rate from the adsorbed mercury remained constant during this period.

The chemisorption fraction of the mercury uptake had been completed before access of vapor was again interrupted. Once again, continuing adsorption caused a fall in the optical density of the vapor, but not to such a low value as before ($p/p_0 = 0.12$). On this occasion the mercury count rate decreased with time, and this is interpreted as the diffusion of mercury into the catalyst bed, *away* from the counter (see Fig. 1). The effect of this is a redistribution of physically adsorbed mercury from regions of high coverage at the macrosurface to regions of lower coverage within the catalyst bed. This migration may occur *via* the gas phase.

Thermal desorption studies (*6*) on a platinum-asbestos catalyst have shown evidence for two types of mercury adsorption of differing strengths in this system also.

Mercury as a Catalyst Poison

The behavior of mercury as a poison for the hydrogenation of cyclopropane over nickel has been satisfactorily explained (*2*) in terms of its ability to block sites for the adsorption of hydrogen. Accordingly, it was concluded that the mercury responsible for the poisoning effect was chemisorbed by the metal, and that significant physical adsorption only commenced when high chemisorption coverages had been achieved. When this condition was reached, the catalyst was in a highly poisoned state. The features of that aspect of the poisoning which was studied in the present work are (a) partial reactivation when cyclopropane hydrogenation was carried out on a partially poisoned catalyst, and (b) an increase in the count rate of the mercury on the catalyst simultaneous with its reactivation. It should be emphasized that both of these features were observed without any change being made in the amount of mercury present. Bond and Wells (*3*) have observed similar reactivation phenomena in the hydrogenation of acetylene on a partially mercury-poisoned palladium-alumina catalyst, and have interpreted their results in terms of the "crowding" of adsorbed mercury atoms into a compact group. Our results with palladium on pumice are consistent with this interpretation, but show that this migration of mercury under the influence of the hydrogenation reaction is not merely localized to small distances from the original site of adsorption of the mercury, as is shown in the following way. The palladium on 120-mesh pumice was sufficiently finely divided for the diffusion of reactant gases into the catalyst bed to have an important effect in determining the reaction rate. The turnover of reacting molecules would be expected to be greater for sites near the top of the bed. If migration of chemisorbed mercury occurred as a consequence of the hydrogenation reaction it would be expected gradually to result in a net transfer of mercury to sites further into the catalyst bed, in which position it will be relatively less disturbed by the occurrence of the reaction. This process will have two consequences. Firstly, the reaction rate will increase, because extra sites are being created in that region of the catalyst where reaction rate is least diffusion-dependent. Secondly, mercury in the adsorbed state will move down the catalyst bed, *nearer* to the counter (Fig 2), and hence will produce an increase in count rate. Both of these effects were observed in practice. Furthermore, the reactivation only occurred as a result of the reaction: it was not observed when the catalyst was allowed to stand under vacuum for periods of time comparable with those required to perform several reaction runs.

Evidence for the profound disturbance of the metal atoms constituting the surface sites is given by the work of Jech (*7*). In this study, radioactive krypton or xenon introduced into a platinum surface by ion bombardment remained there under vacuum conditions but was released when hydrogen and oxygen were allowed to interact on the platinum. In the light of this work it seems reasonable also to postulate the movement of surface-adsorbed species, even though firmly held, during the course of surface chemical reactions.

Our inference from the present work is that mobility of mercury by diffusion is prominent in the physically adsorbed fraction, but the chemisorbed layers are essentially immobile except when a chemical reaction is taking place on the catalyst. We conclude that in using mercury as a catalyst poison caution is necessary in assigning mercury adsorption entirely to the sites of catalytic activity.

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