JOURNAL OF CATALYSIS 36, 291-304 (1975)

Weak Chemisorption of Hydrogen by Platinum Black

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Received July 2, 1974

Following the titration of an oxygenated platinum black surface with hydrogen, chemisorption isotherms have been determined in the range of hydrogen pressures from 0.001 to 50 mm Hg from 77.4 to 303 K. These data are shown to be reversible over most of the pressure range and isosteric heats for chemisorption have been derived from the Clausius-Clapyron equation. These heats decline with coverage from 69 to 23 kJ/mole H_2. BET surface area measurements of the sample (Kr: 77.4 K) are compared with the area derived from the titration of the oxygenated surface. The maximum error which can be introduced into surface area measurements (by the titration technique) due to the presence of weak, reversible chemisorption is estimated to be 12%.

INTRODUCTION

The current emphasis on the use of single crystals for chemisorption studies at very low pressures has led to a neglect of chemisorption which takes place in higher pressure ranges, i.e., Type C chemisorption (*1*). If conventional pressure-composition-temperature (p-c-t) methods are employed, this weak chemisorption must be studied using samples of very high surface area. Generally, high surface area samples, which cannot be outgassed at elevated temperatures because of the possibility of sintering, do not have the degree of surface cleanliness which can be obtained for the small surface area samples. The latter type of sample can be subjected to rigorous pretreatment in ultrahigh vacuum. To a limited degree platinum black is an exception because it can be prepared in an oxygen-free condition by titration of the chemisorbed oxygen with hydrogen (*2*). Many papers have been concerned with the titration with hydrogen of the oxygen chemisorbed on platinum for the purpose of determining the surface area of either pure platinum or the platinum in supported catalysts (*2–9*). Wilson and Hall (*7*) have recently pointed out that the variable surface oxygen stoichiometry can complicate the titration method; however, they estimated that this should not lead to an error in the surface area of more than 16.7%.

A further complication can be introduced by the occurrence of weak chemisorption after the completion of the strongly held monolayer of hydrogen. The endpoint of the titration would be obscured by the presence of weak chemisorption. There is ample evidence that weakly chemisorbed (Type C) hydrogen exists on platinum at relatively high pressures. Pliskin and Eischens (*10*) attributed the two infrared bands which they observed when hydrogen was chemisorbed on supported platinum to hydrogen chemisorbed on top of platinum atoms (weakly) and between platinum atoms (strongly). Toya (*11*) has discussed these two possibilities from the theoretical viewpoint. Tsuchiya, Amenomiya and Cvetanovic (*12*) have found evidence for weak and strong chemisorption of hydrogen by platinum from their temperature programmed desorption studies. At high pressures they found a H:Pt (surface) ratio of 1.8 showing that further chemisorption occurs on platinum black after the completion of a first monolayer. Vannice, Benson and Boudart (*4*) also found evidence of H : Pt > 1 at high pressures of hydrogen, > 50 mm Hg.

Recently Basset *et al.* (*8*) have made a calorimetric investigation of the O/H titration on supported platinum. Coverages in excess of a monolayer (H:Pt > 1) were found following the titration. The heat of chemisorption of hydrogen for $\theta > 1$ was approximately 42 kJ/mole H_2. Data were not detailed enough to discern a trend in the heats of chemisorption (weak) with coverage but the irreversible chemisorption which occurs below 10^{-1} mm Hg (313 K) was found to have heats of chemisorption which declined with coverage from 117 kJ/mole H_2 ($\theta = 0$) to 54.4 kJ/mole H_2 at $\theta = 1$. Reversible chemisorption took place at $P > 10^{-1}$ mm Hg (room temperature).

Primet, Basset and Mathiru (*9*) investigated weak chemisorption of hydrogen on dispersed platinum using infrared absorption. A band which is attributed to the weakly chemisorbed hydrogen appears at 2120 cm^{-1}. Chemisorption isotherms were determined by measurements of the intensity of this band at various pressures. These results generally confirmed those of their calorimetric study. A dissociative Langmuir isotherm was found to fit the data from 10^{-1} to 700 mm Hg from 300 to 368 K. The heat of chemisorption was 50 kJ/mole H_2 in good agreement with their previous results.

There is therefore ample evidence in the literature to suggest that weak chemisorption of hydrogen on platinum takes place and some evidence has been offered that this occurs after completion of a strongly chemisorbed monolayer of hydrogen. On the other hand, workers employing samples of small surface area, which have been cleaned under UHV conditions, have found that below room temperature the first monolayer is incomplete at pressures of approximately 10^{-4} mm Hg (*13*). Procop and Völter (*13*) have determined heats of chemisorption for the first monolayer and these values decline from 67 kJ/mole ($\theta = 0$) to approximately 21 kJ/mole at $\theta = 0.5$. Norton and Richards (*14*) observed a sharp decline in the isosteric heats of chemisorption in the vicinity of $\theta = 0.45$ from approximately 75 kJ/mole ($\theta = 0.38$) to 46 kJ/mole at $\theta = 0.46$. From LEED studies Lang, Joyner and Somorjai (*15*) found that certain planes did not chemisorb hydrogen at all (298 K). Lewis and Gomer (*16*) have investigated the adsorption of hydrogen by platinum using field emission. They conclude that a strongly bound atomic state occurs at $\theta < 0.5$ with $q = 67$ kJ/mole H_2 and a molecular state forms at higher coverages with heats decreasing from about 63 kJ/mole H_2 to values characteristic of physisorption. Both states were desorbed by evacuation at 320 K. These results on small samples can be reconciled with the data obtained using large area samples, if the monolayer is complete when the pressure increases to the millimeters of Hg range (298 K). Weak chemisorption would then consist mainly of completion of the first monolayer. One motive of this research was to determine if the amount of additional hydrogen chemisorption which occurs when the pressure and temperature change from ~ 10^{-4} (136 K) to 50 mm Hg (298 K) is large enough to link the data obtained under these different conditions.

There have been no recent systematic studies by direct p-c-t techniques under mercury- and grease-free conditions of the reversible chemisorption which occurs in the high pressure range; e.g., 10^{-3} to 100 mm Hg. The main goal of this research was to obtain isotherms for this weak chemisorption for this range of pressures over a considerable temperature range. A large surface area platinum black sample was employed for this purpose and the study was made with a grease- and mercury-free apparatus.

EXPERIMENTAL METHODS

The research was carried out in a metal-glass ultrahigh vacuum system using Granville Phillips type C valves and a series of Barocel diaphragm pressure transducers with an effective operating range of 10^{-3} to 10^{3} mm Hg. Although the vacuum system was not used to its full capability; i.e., to obtain UHV conditions, its grease- and mercury-free characteristics are believed to be important. Two platinum black samples, both from Engelhard Industries Inc. lot No. 20762, were used; the first sample weighed 5.5 g and a second sample weighed 1.7 g.

The appropriate sample was sealed in a reaction chamber having a volume of approximately 40 cm^3 without any pretreatment and was then evacuated for 24 hr at 298 K until the pressure was approximately 10^{-6} mm Hg. Research grade hydrogen was first admitted to a dosing chamber (volume, ~200 cm^3) where its pressure was measured. A valve separating the dosing and reaction chambers was then opened and the pressure in the combined volumes was monitored on a chart recorder until equilibrium was reached. The quantity of gas adsorbed by the sample was determined using the perfect gas law. For subsequent doses, the valve between the dosing and reaction chambers was closed, the dosing chamber repressurized and the valve opened again.

Sample 1 was titrated with 152 doses while sample 2 required only 20. Following the titration, the sample was evacuated at 298 K for a standardized interval (14 hr) resulting in a pressure of 2 to 5×10^{-6} mm Hg in the reaction chamber. Every subsequent isotherm run was initiated when the pressure reached the low 10^{-6} mm Hg range. This condition was assumed to correspond to the complete removal of the weakly chemisorbed hydrogen leaving a monolayer of strongly chemisorbed hydrogen on the surface. This assumption is discussed further in Results.

Surface areas of the samples were determined using the BET method with krypton at liquid nitrogen temperature using the dosing method described above. The usual BET plot was made and this closely intersected the origin. No correction was needed for thermal transpiration (*17*) because of the large diameter (~ 1.5 cm) of the reaction tube at the top of the liquid nitrogen bath.

RESULTS

Titration

Sample 1 was titrated at 273 K and appeared to have been slightly sintered following its titration; the upper section of the sample had a greyish appearance. The sintering was confirmed by subsequent surface area measurements. Sintering reduced the surface area by approximately 20%. Sample 2 was titrated at 195 K and there was no appearance of any sintering. Vannice, Benson and Boudart (*4*) have pointed out that titrating at 273 K leads to sintering, whereas titration at 195 K does not. However, besides the temperature factor, another crucial factor is the rate of the titration and it is believed that titration can be successfully performed at 273 K if the rate is very slow. Sample 1 sintered only after an initial large dose of hydrogen was added but did not sinter further when small increments of hydrogen were added. The pressure build-up during the titration is shown in Fig. 1 (the water formed was removed by freezing in a trap at 195 K).

Chemisorption (Weak) Isotherms

After titration and subsequent evacuation at 298 K for a standardized time period (14 hr), a vacuum of 2 to 5×10^{-6}

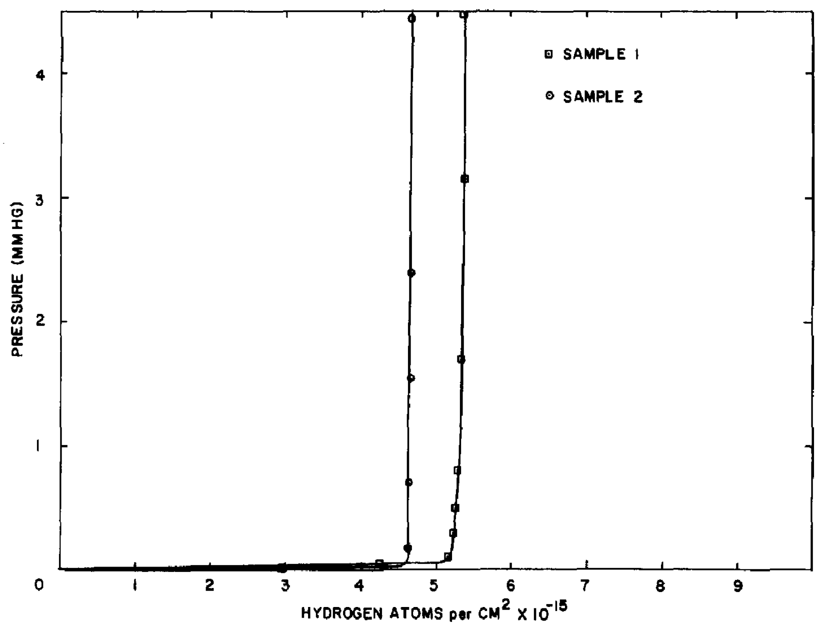

FIG. 1. Titrations of oxygenated-platinum black with hydrogen. Sample 1 (5.51 g) titrated at 273 K; sample 2 (1.66 g) titrated at 195 K.

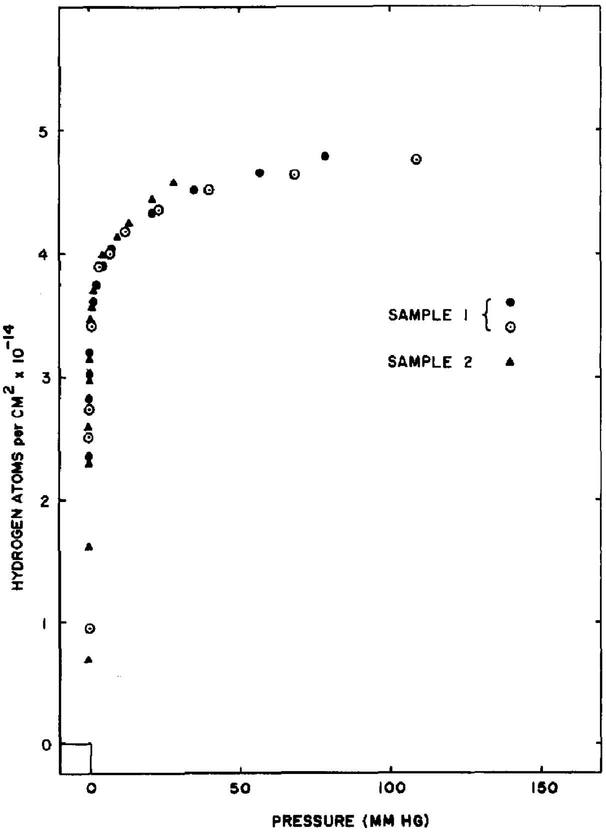

FIG. 2. Typical chemisorption isotherms for samples 1 and 2 (273 K) after titration and standard evacuation period.

mm Hg was obtained. Chemisorption isotherms were then determined with samples 1 and 2 at 273 K (Fig. 2). The samples were then reevacuated for the standard period and the isotherms were repeated. Adsorption is expressed in terms of atoms per square centimeter using the areas determined from BET measurements. The results were fairly reproducible indicating that the same amount of hydrogen was removed during each cycle of evacuation. It is clear that weak, reversible chemisorption occurs following evacuation. This chemisorption is reversible in the sense that it can be removed by room temperature evacuation; whereas, the bulk of the hydrogen from the titration or immediately following the titration remains on the surface during this period of evacuation.

The data from this and several other temperatures are replotted in Fig. 3 according to the Temkin isotherm (*18*); i.e.,

$$\frac{RT}{q_0}\ln p + \frac{RT}{q_0}\ln A_0 = \theta' = b\Sigma n_w, \quad (1)$$

where θ' is the coverage based only upon the chemisorption which occurs following evacuation and reexposure to hydrogen and is proportional to Σn_w, where Σn_w represents the atoms of additionally chemisorbed hydrogen per square centimeter. In Eq. (1) $q = q_0\ (1-\theta') = q_0\ (1-b\Sigma n_w)$, where q is the heat of chemisorption per mole of hydrogen and $A_0 = a_0 e^{-q_0/RT}$ (*18*). This isotherm is valid only over an inter-

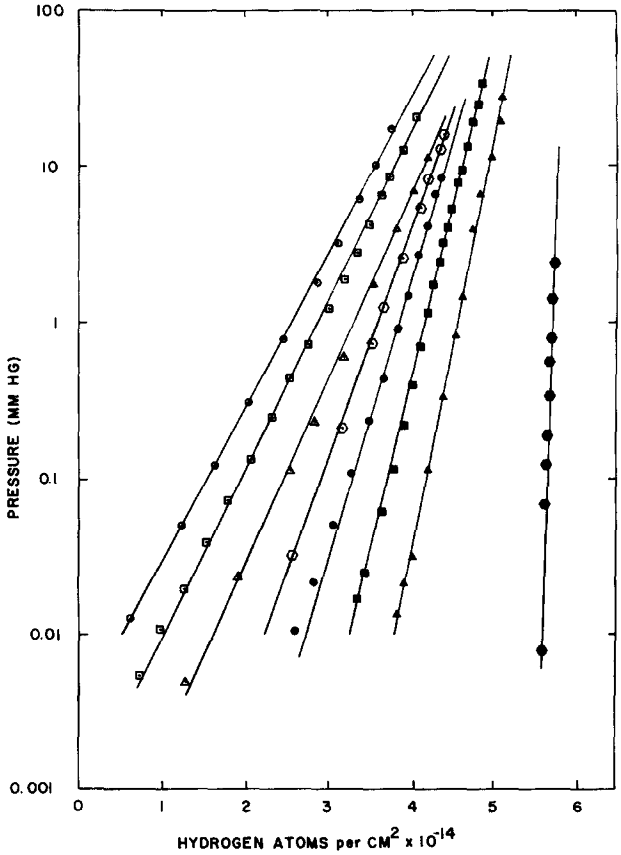

FIG. 3. Chemisorption data for sample 1 plotted via the Temkin isotherm. (○) 303K; (□) 291 K; (△) 273 K; (○) 258 K; (●) 243 K; (■) 223 K; (▲) 195 K; (●) 77 K.

mediate range of coverages, i.e., 0.9 > θ > 0.1 (*19*). As shown in Fig. 3, there is a remarkable adherence to this isotherm over a very wide pressure range; i.e., 0.01 to 10 mm Hg at 273 K. The Temkin isotherm plots for sample 2 were measured with more emphasis upon the lower pressure range and were found to be linear from ≃0.001 to 10 mm Hg. Since fewer temperatures were measured for this sample, data are shown instead for sample 1 (Fig. 3) but the range of adherence to the Temkin isotherm can be considered to be 0.001 to 10 mm Hg (273 K).

The time required to establish equilibrium varied considerably in the course of an isotherm determination. The kinetics of chemisorption at 273 K is briefly discussed to illustrate this. At equilibrium pressures less than ≃0.05 mm Hg, equilibrium was rapidly obtained. When an initial dose of 7.08 mm Hg was added to the sample after the usual evacuation period, 99.6% of the hydrogen was chemisorbed in less than 2 min. The equilibrium pressure of 0.008 mm Hg was attained in ≃0.5 hr. It should be emphasized that the method of following the attainment of equilibrium is very sensitive. The pressure was monitored by a recording tracing such that the full-scale deflection of the chart corresponded to the smallest possible pressure range; e.g., the full-scale deflection was 0.010 mm Hg when a final equilibrium pressure of 0.008 mm Hg was recorded.

Subsequent uptakes are plotted in Fig. 4 during the same isotherm determination and it can be seen that equilibrium is rapidly established up to approximately 0.1 mm Hg and even at these equilibrium pressures the deviations from the final equilibrium pressure were quite small after the first 0.5 hr. At pressures >0.1 but <3 mm Hg equilibrium was slowly established but again the deviation from the final equilibrium pressure was rather small after about 0.5 hr. For equilibrium pressures greater than about 3 mm Hg the establishment of equilibrium was again rapid. Tsuchiya, Amenomiya and Cvetanovic (*12*) also ob-

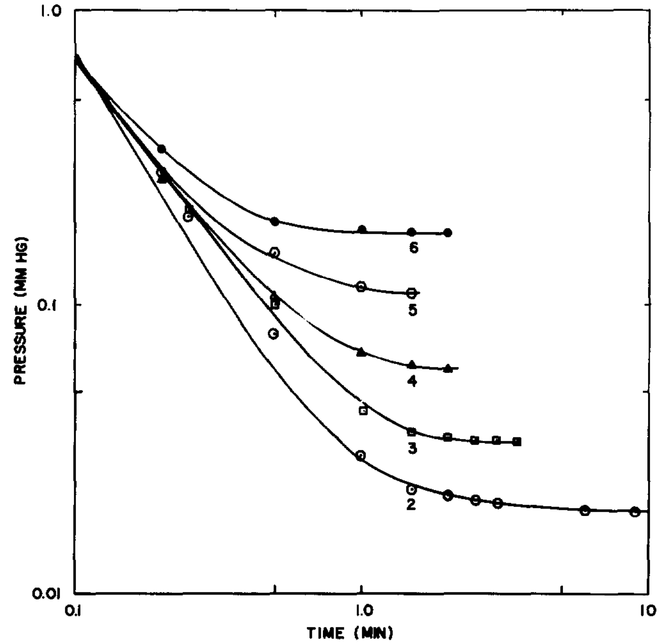

FIG. 4. Several pressure–time relationships for hydrogen chemisorption on sample 2 at 273 K, beginning with second dose after standard evacuation period.

served slow adsorption of hydrogen by platinum black with energies of activation, ≤ 8.4 kJ/mole H_2. Different activation energies were assigned to various types of adsorbed states. It is our view that only one type of adsorption occurs here (Fig. 3) and the sluggish uptake in certain pressure ranges is due to a physical effect.

In addition to sluggish equilibria over certain pressure ranges, a peculiar type of hysteresis was observed. Typical data are shown in Fig. 5. The "hysteresis" is present only if the equilibrium pressure is rather large and it appeared to occur only once; i.e., after arriving on the "desorption" loop the data appear to remain there even for subsequent adsorption points. There was only a very small "hysteresis" if the equilibrium pressure was $\simeq 5$ mm Hg. Significant hysteresis appears only when the final equilibrium pressure is in the pressure-coverage range where deviations from the Temkin isotherms appear. At lower temperatures hysteresis is found at smaller equilibrium pressures (deviations from the Temkin plot appear at lower pressures at temperatures below 273 K). The hysteresis does not appear to be an artifact resulting from sluggish equilibria because data for both adsorption and desorption fall on the lower "branch" after the hysteresis has occurred and this would not be the case if sluggish equilibria were responsible. This hysteresis may be associated with the porous nature of the platinum black. It is of interest that with samples of palladium black of comparable surface area this phenomenon was not ob-

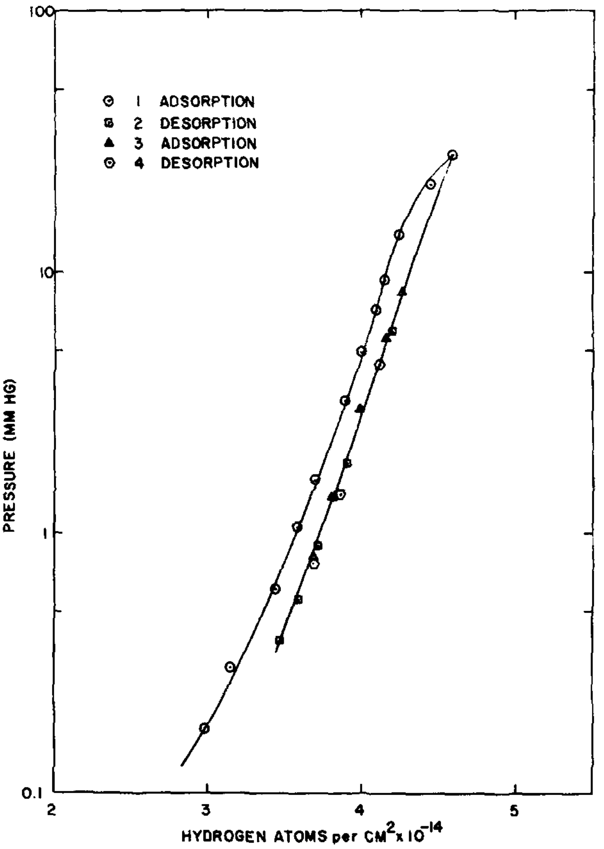

FIG. 5. "Hysteresis" behavior for sample 2 (273 K). First chemisorption point (lower left) represents 11th dose after standard evacuation period.

served (*20*). In palladium the equilibration of hydrogen on the surface of pores can occur via a process of transport through the bulk and readsorption onto the walls of any pores. Such mechanism is not available to platinum. The physical adsorption of krypton was rather slow in certain pressure ranges, again indicating difficulties of transport through pores.

Some chemisorption runs were performed at 77.4 K. Equilibrium was only slowly established at this temperature except at equilibrium pressures greater than 1 mm Hg. For example, to reach a final equilibrium pressure of 0.03 mm Hg, 5 hr was needed. If, however, the sample was warmed to 298 K and then quenched to 77.4 K equilibrium was rapidly established.

In the pressure range < 5 mm Hg at 273 K there was no "hysteresis" and the application of the Clausius-Clapeyron equation is fully justified; i.e., chemisorption is thermodynamically reversible. Fortunately, this covers most of the range of interest because at a hydrogen coverage corresponding to 5 mm Hg at 273 K, the equilibrium pressures at lower temperatures occur in a range where hysteresis does not occur. Therefore up to a value of $\Sigma n_w = 3.8 \times 10^{14}$ H atoms/cm^2 (sample 1) the isosteric heats can be evaluated without ambiguity. Above this coverage isosteric heats have also been evaluated using the

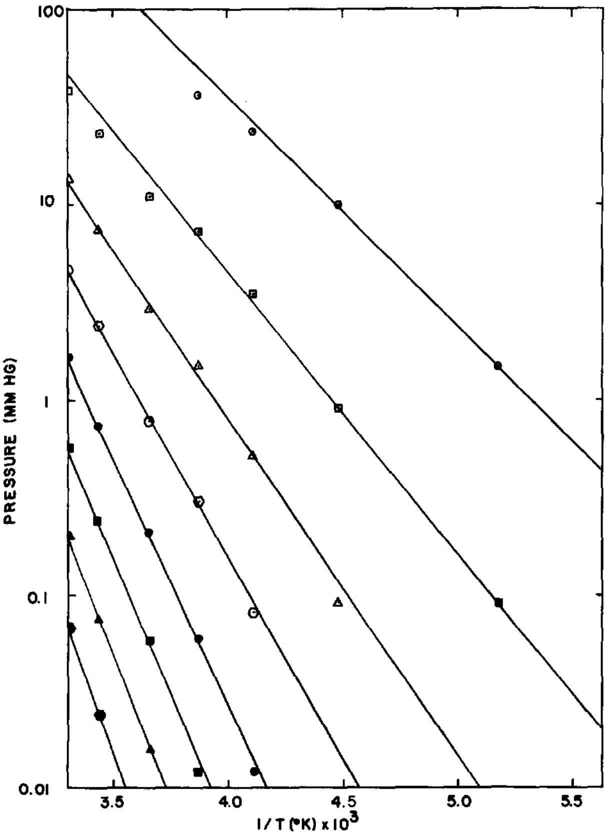

FIG. 6. Typical plots of log P_{H_2} against $1/T$ for sample 1 using data from Fig. 3. (●) 1.38×10^{14} H atoms/cm^2; (▲) 1.84×10^{14} H atoms/cm^2; (■) 2.3×10^{14} H atoms/cm^2; (●) 2.76×10^{14} H atoms/cm^2; (○) 3.22×10^{14} H atoms/cm^2; (△) 3.69×10^{14} H atoms/cm^2; (□) 4.15×10^{14} H atoms/cm^2; (○) 4.61×10^{14} H atoms/cm^2, where the coverages represent excess chemisorbed hydrogen after the standard period of evacuation at 298 K.

Clausius-Clapeyron equation but these values must be regarded as questionable. The isosteric heats determined for a few coverages using data on the desorption branches of several isotherms were found to give heats of chemisorption comparable to the reversible range.

Isosteric heats are shown in Figs. 6 and 7 for the large sample; results for the small sample were very close to these if they were compared at the same values of Σn_w. The almost linear decline in the isosteric heats with coverage is compatible with the Temkin isotherm. They are in the range from 62 to 23 kJ/mole H_2.

The slopes of the Temkin isotherms as they have been plotted in Fig. 3 should increase with $1/T$ [Eq. (1)]. This appears to be the case and such a correlation is shown in Fig. 8 which includes data from both samples including a determination of the slope at 77.4 K. It is of interest that the data at 77.4 K line up quite well with the higher temperature data indicating that the same type of chemisorption occurs at 77.4 K as at room temperature. The value of $bq_0\alpha$ can be evaluated from the slope of Fig. 8 as 1.88×10^{-13} kJ –cm^2/mole H_2. An alternate way of deriving $bq_0\alpha$ is from the plot of q against Σn_w (Fig. 7). If this is extrapolated to $\Sigma n_w = 0$, $q_0 = 84$ kJ/mole H_2 and from the slope $bq_0\alpha$ can be evaluated as 1.34×10^{-13} kJ – cm^2/mole H_2, which is in fair agreement with the other method and demonstrates the self-consistency of the Temkin analysis of the data.

There appears to be inconsistencies in the literature concerning whether hydrogen titration of an oxygenated platinum surface occurs by the reaction,

$$H_2 + Pt\text{-}0 \rightarrow Pt + H_2O, \quad (2)$$

followed by

$$\tfrac{1}{2}H_2 + Pt \rightarrow Pt\text{-}H, \quad (3)$$

or as a one-step process

$$\tfrac{3}{2}H_2 + Pt\text{-}0 \rightarrow Pt\text{-}H + H_2O. \quad (4)$$

The present results are unaffected by which process occurs but the ambiguity does relate to the previously measured heats of chemisorption of hydrogen during

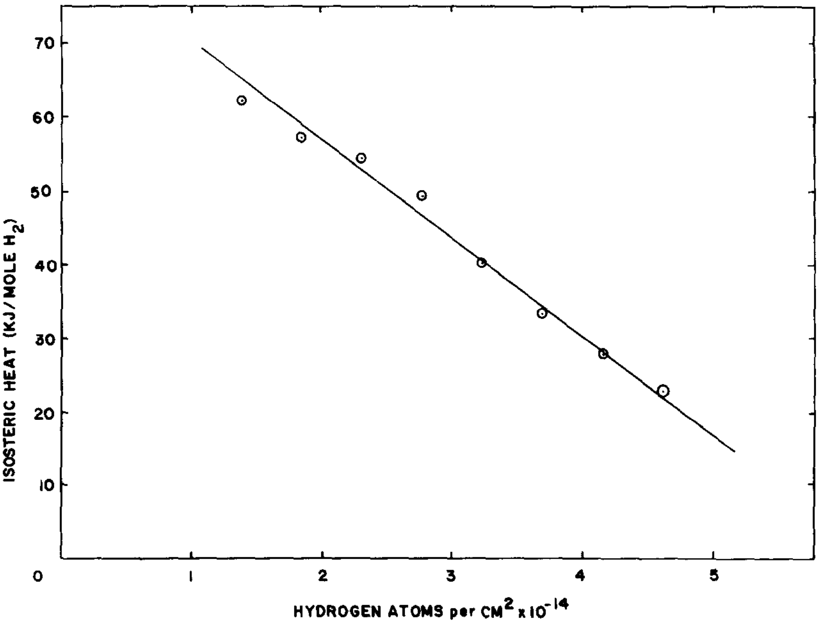

FIG. 7. Isosteric heats plotted against coverage (excess chemisorbed hydrogen after the standard period of evacuation) using data from Fig. 6.

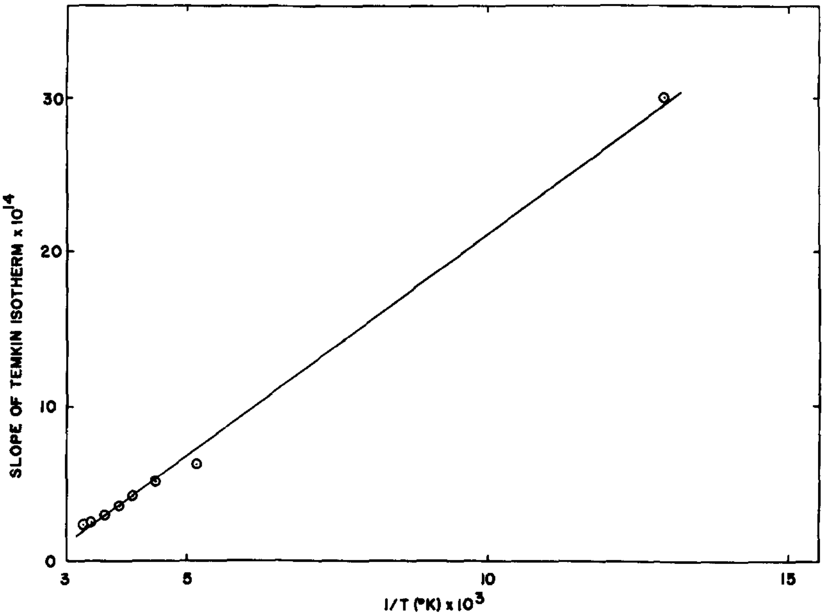

FIG. 8. Slopes of the Temkin isotherms ($\Delta \log p/\Delta\Sigma n_w$) plotted against $1/T$.

and after titration. Benson and Boudart (*3*) stated that in the titration two hydrogen atoms react with each surface oxygen and a hydrogen atom is simultaneously left on each surface platinum atom. Vannice, Benson and Boudart (*4*) did not state explicitly which process occurs but the sequential process is implied because they stated that as water leaves the surface following a titration at 194 K it is not replaced by hydrogen. Chon, Fisher and Aston (*2*) clearly said that the titration proceeds by steps (2) and (3); however, after an initial sharp fall from 32.5 ($\theta = 0$) to 71 kJ/mole H_2 ($\theta = 0.17$), their heats of chemisorption are rather small. In fact, Bond (*1*) has cited these heats as evidence for Type C (weak) chemisorption. Basset *et al.* (*8*) also state that Aston's heats (64–21 kJ/mole H_2 after the sharp decline) reflect reversible chemisorption which occurs after completion of the monolayer. Basset *et al* regard the titration to take place in one step (reaction 4) and the heats subsequently measured are characteristic of weak chemisorption. The situation is ambiguous because the surface area of Chong, Fisher and Aston's sample apparently leads to the conclusion that the titration takes place sequentially; however, their sample may have sintered during titration (4).

Differential Entropies of Chemisorption

The differential entropies of chemisorption (weak) can be calculated from the isosteric heats and the equilibrium hydrogen pressures at any coverage and temperature. Typical data are shown in Fig. 9 at 273 K. The differential entropy increases with coverage. This is the opposite trend found for weakly chemisorbed hydrogen on palladium (*20*). This suggests that the thermal contribution to the entropy is more important than the configurational term as the coverage increases. In the region of coverages encompassed by the isotherms (Fig. 3) the configurational term would not be expected to alter significantly; indeed, a term like this is omitted in the derivation of the Temkin isotherm.

Surface Coverage

One of the basic questions posed in this research can be answered negatively. If

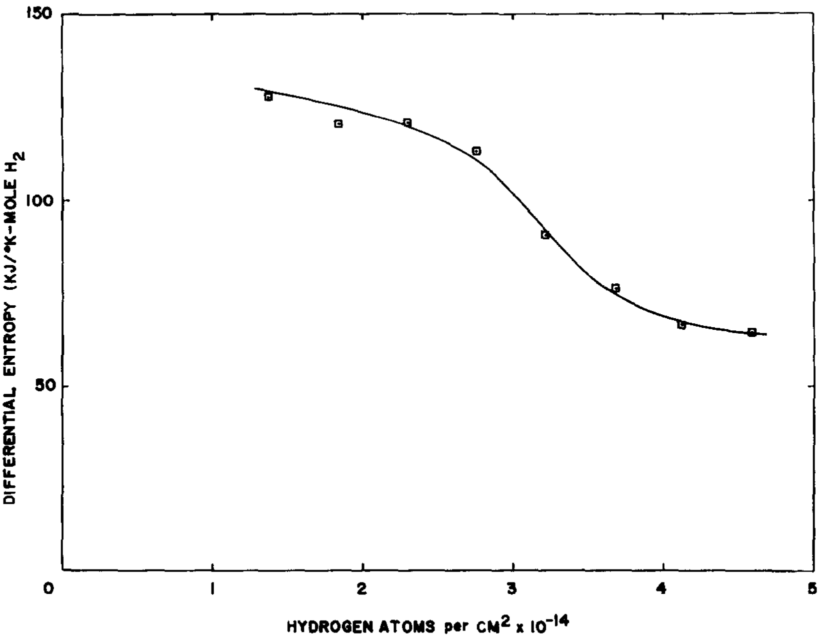

FIG. 9. Differential entropy of chemisorption plotted against excess hydrogen chemisorbed after standard period of evacuation (273 K).

Fig. 3 is examined, it can be estimated that very little change in surface coverage should occur by increasing the pressure from 5 × 10^{-4} mm Hg to either 0.1 or 50 mm Hg if the temperature is simultaneously increased from 136 to 298 K. Thus the observation of a coverage of 0.5 at 5.8 × 10^{-4} mm Hg at 136 K on a small sample (platinum sheet) (*13*) is incompatible with a coverage of 1 in the mm Hg pressure range at 298 K (*4*) because the change in coverage in passing from one set of conditions to the other (Fig. 3) is too small to account for the difference.

During titration of sample 2 at 195 K, 3.65 × 10^{-3} g-atoms of H were removed from the gas phase. Assuming a stoichiometry of one oxygen atom per surface platinum atom, 1.87 × 10^{-3} g-atoms H formed water; this value is based on the BET area of the sample (47 m^2, total surface area) and the value of 1.2 × 10^{15} platinum surface atoms/cm^2, which is the average of the three most prevalent crystallographic planes (*4*). The remainder of the hydrogen, 1.78 × 10^{-3} g-atoms, is retained by the surface. Following evacuation under the standard conditions and reexposure to hydrogen at the same temperature and pressure 0.39 × 10^{-3} g-atoms H are adsorbed. This approximate argument shows that the major fraction, 0.78, of the hydrogen remains on the surface after evacuation at 298 K under a vacuum of 4 × 10^{-6} mm Hg. It is difficult to reconcile this with the data for the small foil sample of Procop and Völter (*13*) where coverages of only 0.5 were found at lower temperatures at a vacuum of 5.8 × 10^{-4} mm Hg. Admittedly the vacuum quoted here, 4 × 10^{-6} mm Hg, is measured under dynamic pumping conditions but after closing off the pumps, the vacuum remained better than 5.8 × 10^{-4} mm Hg.

It is of interest to pursue in a more detailed manner the question of the surface coverage which obtains during the reversible chemisorption measured here. Sample 2 was titrated at 195 K and did not sinter. With reference to Fig. 3 the question arises: At which pressure does the monolayer form during the titration? The slope of a Temkin plot of the pressure versus amount of chemisorbed hydrogen after completion of the titration is the same as for data determined at the same temperature in the usual manner (Fig. 3). This suggests that after removal of the oxygen from the surface, reversible chemisorption takes place which is the same as that which occurs after evacuation and reexposure to hydrogen. The temperature at which the titration is performed determines the extent of the weak chemisorption; e.g., titration at 195 K involves a greater degree of weak chemisorption than one at 298 K.

Vannice, Benson and Boudart (*4*) report that a H:Pt ratio of 1 is found at 50 mm Hg and 298 K. If this condition is taken, the shift in the value of Σn_w from 195 to 298 K can be estimated from the isotherms (Fig. 3). A value of 1.53×10^{15} H/cm^2 is obtained for the monolayer using the BET area of the sample. On the other hand, Primet, Basset and Mathiru (*9*) suggested that 0.1 mm Hg at 298 K is the transition pressure between the first layer and further chemisorption (weak). If this value is used, the shift can be estimated from the isotherms and a value of 1.48×10^{15} H/cm^2 is obtained for the monolayer.

An alternative procedure and one which is employed here is to assume that all of the additionally chemisorbed hydrogen following the prolonged evacuation represents hydrogen chemisorbed in excess of the monolayer. By subtracting the value of Σn_w for the isotherm at 195 K where it intersects the pressure axis at 10^{-3} mm Hg (where the pressure measurements commence) from the total amount of hydrogen removed from the gas phase during titration and dividing the result by a factor of 3, a value of 1.43×10^{15} H atoms/cm^2 is obtained.

The value of 1.43×10^{15} H/cm^2 is 16% greater than the value of 1.2×10^{15} platinum atoms/cm^2 computed using the average of the three prominent crystallographic planes; on the other hand, Procop and Völter (*13*) suggest that a value of 1.5×10^{15} platinum atoms/cm^2 is more reasonable since this considers the reconstruction of the (100) planes. Our preferred value, 1.43×10^{15} H/cm^2, in fact all three of our derived values, agree very well with 1.5×10^{15} Pt/cm^2.

It may be concluded by reference to Fig. 3 (195 K) that the maximum uncertainty which can be introduced into the titration by the presence of weak chemisorption, which obscures the end point, is approximately 12%—the additional chemisorption that takes place at 195 K after evacuation at 298 K. The larger uncertainty appears in the number of platinum atoms per square centimeter—Vannice, Benson and Boudart (*4*) also concluded that this introduces the largest uncertainty into the titration. The possibility of surface reconstruction during reduction of the surface may also be a factor (*7*).

While the titration and calculated surface area are not affected greatly by the presence of weak chemisorption (12% maximum) because of the magnification by a factor of 3, reactions (2), (3) or (4), there is no doubt that a large amount of reversible chemisorption occurs. It is tentatively assumed that the additional chemisorption which occurs following evacuation represents Type C (weak) chemisorption following completion of the monolayer. The remarkable adherence to the Temkin isotherm supports the view that the chemisorption observed here is all of the same type; i.e., it does not represent the overlap of the completion of the first monolayer and the initiation of a new type of chemisorption on different types of sites at H:Pt > 1. Second, there is ample evidence in the literature that coverages in excess of 1 do occur (*4,12*). Thirdly, evidence found here using the titration and the BET surface area suggests that the monolayer is formed during the titration.

At 300 K, Primet, Basset and Mathiru (*9*) estimated $\theta' = 0.5$ when the pressure of hydrogen was 43 mm Hg, where θ' is based only on the H : Pt ratio for the hydrogen in excess of the monolayer. This value was derived from their Fig. 1 together with their quoted value of D_M, where D_M is the maximum optical density obtained from dissociative Langmuir plots. Under these same conditions the coverage estimated here, using the BET surface area and the assumption that all additionally chemisorbed hydrogen is in excess of the monolayer, is 0.30. This agreement is not bad considering the circuitous routes used for the evaluations of θ'. Our estimated values of θ' are such that the bulk of the isothermal data fall in the range 0.1 to 0.4 (Fig. 3) justifying to some extent the estimated values of θ' because the Temkin isotherm does apply in this range of coverages.

Values found here for the heat of chemisorption are certainly within the range expected for Type C (weak) chemisorption of hydrogen on platinum (*1*). Basset *et al.* reported heats of 38 and 50 kJ/mole H_2 by direct calorimetry on supported platinum (*8*) and isosteric values from 50 to 40 kJ/mole H_2 by their infrared technique (*9*). These are within the range of our values. Comparisons with the literature are dependent upon the discrepancy between data for small samples and large samples and on the question of whether the titration takes place consecutively or simultaneously. Thus Chon, Fisher and Aston (*2*) have determined values following titration of an oxygenated surface of about 134 kJ/mole H_2 ($\theta = 0$) which declines rapidly to about 71 kJ/mole H_2 ($\theta = 0.1$) and then slowly falls to about 25 kJ/mole H_2 ($\theta = 0.8$). Basset *et al.* (*8*) cite these values as for weak chemisorption which occurs following completion of the monolayer, but Chon, Fisher and Aston regard these as first layer values. These values from Chon, Fisher and Aston correspond approximately with first layer coverage reported by Procop and Völter (*13*) using a flash filament technique. These workers found values of 67.2 kJ/mole H_2 which declined to about 20 kJ/mole H_2 at $\theta = 0.5$. Over a very narrow range of coverages, Norton and Richards (*14*) found isosteric heats which decline from 76 kJ/mole H_2 at $\theta = 0.38$ to 46 kJ/mole H_2 at $\theta = 0.46$. The detailed agreement between these two sets of data on small samples is only fair but they do agree in order of magnitude. Earlier data in the literature give values the range of which is 74.6 kJ/mole H_2 (*21,22*) to 129 kJ/mole H_2 (*23*) without any clear cut trends with surface coverage.

It is not known whether the weak chemisorption examined here is dissociative. From the adherence of their data to the dissociative Langmuir isotherm, Primet, Basset and Mathiru (*9*) argued that weak chemisorption is dissociative. Similar weak chemisorption of hydrogen on palladium black is probably dissociative because it is in rapid, dynamic equilibrium with absorbed hydrogen which is in the dissociated form (*20*). Infrared work by Pliskin and Eischens (*10*) also supports the view that weakly chemisorbed hydrogen on platinum is dissociatively adsorbed. On the other hand, Lewis and Gomer (*16*) argued the opposite. The adjective weak with reference to chemisorption is, of course, a relative term and refers to the experimental conditions employed in this study, i.e., this is weak chemisorption in the temperature range employed, 195 to 303 K.

CONCLUSIONS

Reproducible adsorption isotherms have been determined over a wide pressure and temperature range for weak chemisorption of hydrogen on platinum black. The data were obtained in a system capable of obtaining ultrahigh vacuum, although ultrahigh vacuum conditions were not in fact realized; the mercury- and grease-free aspects of the system were undoubtedly a factor in obtaining reproducible data. The surface is believed to be free from oxygen contamination because the initially oxygenated surface was titrated with hydrogen. The data exhibit a remarkable adherence to the Temkin isotherm. The chemisorption is tentatively assigned to additional (Type C) weak chemisorption which occurs following the completion of a strongly held monolayer. This interpretation is consistent with the BET surface area and the titration data. An uncertainty arises in the value to be assigned to the number of platinum atoms per unit surface. An unresolved discrepancy is discussed between chemisorption data obtained with large surface area platinum black samples and with the relatively smooth, small surfaces of bulk samples. It may be that a detailed comparison of chemisorption data obtained on the very imperfect surfaces of platinum black with the relatively perfect surfaces of bulk platinum is not justified.

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