JOURNAL OF CATALYSIS 38, 245–256 (1975)

The Calorimetric Heats of Adsorption of Hydrogen on Platinum Films

S. ČERNÝ, M. SMUTEK AND F. BUZEK

The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Máchova 7, Prague 2, Czechoslovakia

Received January 28, 1974; revised September 15, 1974

Four platinum films have been prepared at a pressure of 10^{-9} Torr, and heats of adsorption of hydrogen have been measured calorimetrically up to the coverage which prevails at an equilibrium pressure of 10^{-4} Torr. The experimental data have been treated in two ways: (i) the standard methods of processing of the data by correlation have been applied to the plot of the quotients $\Delta Q/\Delta n$ vs n, instead of the customary drawing of a smooth curve through this plot by hand; (ii) the said traditional plotting has been abandoned and replaced by producing an integral plot fitted by a correlation curve which was subsequently differentiated. Applicability and reliability of the two approaches in adsorption calorimetry have been analyzed.

In all the four experiments, a linear decrease of the heat in the mentioned range of coverage is likely. The initial heats have been estimated as 22.0, 22.6, 21.2 and 19.2 kcal mole^{-1}, respectively; whereas the integral heats have been found to have approximately the same value of about 17 kcal mole^{-1} on the four films in the investigated range of coverage. As reasons for the lower initial heat and milder heat decrease obtained with one of the films, a lower extent of surface contamination and a possible lesser heterogeneity have been tentatively suggested.

INTRODUCTION

Although platinum has an outstanding importance in heterogeneous catalytic processes involving transfer of hydrogen, there exists uncertainty about the heat of adsorption of hydrogen on platinum surfaces and its dependence on the adsorbed amount (Table 1). Since little information is usually published about the experimental details and method of treatment of the experimental data, an independent assessment of the reliability of the reported results is often difficult. Apart from the gas phase experiments, electrochemical methods have brought interesting results (*29–32*), revealing far-reaching similarities between the heat-coverage curves for the platinum–hydrogen system in electrolytic solutions and in the gas phase.

A need for reliable values of the heat of adsorption of hydrogen on platinum has been felt both by theoreticians and experimentalists, e.g. (*33–37*). In connection with our investigation of the hydrocarbon–platinum system (*38*), it has been desirable to have a heat-coverage curve for hydrogen on platinum films. Because no such data have been available, we have undertaken the present exploratory study, although we have been aware that the films used are not quite representative for extremely clean surfaces, and that their crystalline state is not defined.

EXPERIMENTAL METHODS

The adsorption apparatus used was a glass bakeable volumetric device without any greased parts in its vacuum section, equipped with mercury float valves (*39*). By a mercury diffusion pump, a pressure

Copyright © 1975 by Academic Press, Inc.
All rights of reproduction in any form reserved.

TABLE 1
Experimental Heats of Adsorption of Gaseous Hydrogen on Platinum Surfaces[a]

Ref.	Form of platinum	Method of the heat determination	Value of the heat (kcal mole^{-1})	Note
(*1*)	(110) plane of a tip	Desorption rate in a field emission microscope	26	
(*2*)	(111) plane	Not given	18	Assumed molecular state
			18	Assumed atomic state
(*3*)	Tip	Desorption rate in a field emission microscope	16	Electronegative species (atomic)
			Up to 15	Electropositive species (molecular)
(*4*)	Filament	Thermal desorption	23	
(*5*)	Filament	Calorimetry	24.7	273 K; sharp fall when reversibility of adsorption attained
			21.2	77 K; monotonic decrease
			23	77 K; thermal pre-equilibration of the adsorbed layer before each dose
(*6*)	Ribbon	Thermal desorption	17 ± 3	
			(10 ± 3)	
(*7*)	Foil	Isosteric heat from isobars obtained by quasi-equilibrium thermal desorption	16.3	Decreasing
(*8*)	Film	Equilibrium data treated by statistical thermodynamics	15	
(*9*)	Pt black	Calorimetry	19; 28.5; 33	Decreasing
(*10*)	Pt black	Calorimetry	59.6	
(*11*)	Pt black	Calorimetry	16	Constant from $\theta = 0.05$ to $\theta = 0.25$
(*12*)	Pt black	Calorimetry	17–18	
(*13*, *14*)	Pt black cleaned by titration with hydrogen	Calorimetry	32	273 K; sharp fall to $\theta = 0.15$
			10	120 K; $\theta > 0.30$; constant up to $\theta = 0.55$, then decreasing
			12	60 K; $\theta = 0.25$; decreasing up to $\theta = 0.45$

(15, 16)	Pt black cleaned by titration with hydrogen	Calorimetry	27	280 K; sharp fall to $\theta = 0.15$
			10	150 K; slow fall up to $\theta = 0.6$, then a sharp decrease
(17)	Pt black cleaned by titration with hydrogen	Calorimetry	17.5 ± 0.2	280 K; almost constant up to $\theta = 0.2$
(18, 19)	Pt black	Isosteric heat	18 ± 0.5	570 K; constant up to $\theta = 0.3$
(20)	Pt black	Isosteric heat	14	273–313 K; $\theta = 0.55$; sharp fall to $\theta = 0.95$
(21)	Pt black	Thermal desorption	10; up to 23	Two types of adsorption
(22)	Pt black	Thermal desorption	12	Four forms of adsorption
(10)	Asbestos-supported Pt black	Calorimetry	31; 33.6	
(23)	Silica-supported Pt black	Isosteric heat	16.9	383 K; mildly decreasing
			17.8	403 K; mildly decreasing
			19.7	423 K; mildly decreasing
(24)	Silica-supported Pt catalyst	Equilibrium data substituted into a formula of statistical thermodynamics	27	Decreasing
(25)	Pumice-supported Pt catalyst	Application of the van't Hoff isochore to the adsorption coefficients	3–7; 13 ± 3	288–473 K
(26)	Alumina-supported Pt catalyst	From the temperature dependence of the retention volumes in the elution chromatography	10–7	333–793 K; $\theta = 0.1–0.3$
(27)	Alumina-supported Pt catalyst	Calorimetry	28	313 K; decreasing; two types of adsorption
(15, 16)	Carbon-supported Pt	Calorimetry	26	150 K; sharply falling
			32	280 K; decreasing
(28)	Pt atomically dispersed on a carbon film	Isosteric heat	36	Below 303 K; falling
			27	Above 303 K; falling

[a] Since adsorption is little or not activated in the Pt–H_2 system, the activation energy for desorption is nearly equal to the heat of adsorption.

of the order 10^{-9} Torr (1 Torr = 1.33×10^2 N m^{-2}) was attained before and during the film evaporation. The pressure was measured by a Bayard-Alpert gauge located close to the calorimeter and operated at 10 mA grid current. The value of 10 taken for the conversion factor between the ion current and the pressure in the apparatus was confirmed by calibration with nitrogen in the range of 10^{-3} and 10^{-4} Torr. The amounts of gas dosed to the calorimeter were determined by the procedure described earlier (*40*), using a McLeod manometer. The standard deviation of the dose reading was estimated as 8×10^{-9} moles. The pressure of gas remaining above the film after adsorption was measured by a Pirani gauge. The calorimeter, ion gauge and Pirani gauge were separated from the other parts of the apparatus by two traps cooled with liquid nitrogen.

The calorimeter, similar to that described earlier (*40*), was attached to the apparatus by sealing. It was made from a specially drawn cylindrical eggshell glass of a very uniform wall thickness of 0.27 mm, and with a diameter of 36 mm. Over a length of 13 cm of this thin-walled cylinder, a platinum thermometer wire 0.1 mm in diameter (Safina Vestec, Czechoslovakia) previously aged by annealing, was wound under tensioning by a constant force (*41*) and with a pitch of 2 mm, using a lathe. In the middle of this pitch, a constantan wire 0.07 mm thick was interwound, serving as a heater for the calorimeter calibration. The coils were affixed to the eggshell glass by a thin layer of transparent silicon varnish, baked at 250°C. The length of the thermometer coil exceeded the heating coil both at the upper and lower ends by two turns, to avoid a dependence of the determined value for the calorimeter heat capacity on the amount of the Joule heat supplied. Behavior of the calorimeter was analyzed by analogue simulation (*42,43*). The films were confined to about 9 cm of the eggshell glass length, thus covering some 100 cm^2 of its inner wall.

The calorimeter formed one arm of a Wheatstone bridge fed with an alternating voltage of 380 Hz. The neighboring arm of the bridge was formed by a second, nearly identical calorimeter which, however, was not connected to the adsorption apparatus. The output voltage from the bridge was amplified and displayed on a recorder by means of a circuit described elsewhere (*44*).

Both calorimeters were placed during the measurement in a thermostat consisting of a massive aluminum block shielded by two envelopes and equipped with two wells into which the calorimeters fitted closely. The temperature difference of the two calorimeters and thus the constancy of the zero line of the recorder were of the order of 10^{-5} degree or better. In the present experiments, the thermostat was kept at room temperature.

The heat capacity of the calorimeter was calibrated by the Joule heat evolved in the heating coil on the outer side of the thin-walled cylinder. In total, 40 determinations were made: 20 by the equilibrium method (*41*) with the heating power between 0.94×10^{-5} and 15.30×10^{-5} cal s^{-1}, and 20 by the pulse method (*41*) with pulses between 60 and 150 s and with the total heat evolved varying between 0.71×10^{-3} and 9.18×10^{-3} cal. The average of the 40 measurements was 1.70 cal deg^{-1}, the standard deviation of this average being $\pm 8.9 \times 10^{-3}$ cal deg^{-1}, i.e., ±0.51%, the standard deviation of the individual measurement being $\pm 5.5 \times 10^{-2}$ cal deg^{-1}, i.e., ± 3.22%.

The calorimeter sensitivity used in the present experiments was 9.64×10^4 mm cal^{-1}.

The heat liberated by a gas dose was estimated on the basis of essentially a logarithmic extrapolation of the temperature–time record to zero time (41,45). The standard deviation of the temperature rise was estimated to 0.01 ΔT. Considering the uncertainty in the calorimeter heat capacity value, the standard deviation of the evolved heat ΔQ was about 0.033 ΔQ.

The films were prepared from outgassed wires by direct evaporation and deposition on the calorimeter wall which was cooled to about 285 K by water flowing through the jacket. The total amount of impurities in the platinum wire used (Safina Vestec, Czechoslovakia) was estimated by mass spectrometry to 0.24%, the main components being tantalum (0.11%) and gold (0.09%). Hydrogen prepared by electrolysis was purified by diffusion through a hot palladium thimble.

Method of Treatment of The Experimental Data

In the calorimetric determination of heats of adsorption of gases on solids, verification of the reliability and objectivity of the results presented is often lacking. Traditionally, each point for construction of the required differential heat-coverage curve is obtained by dividing the liberated heat ΔQ by the number of moles Δn adsorbed from the admitted dose. The resulting point in the $\Delta Q/\Delta n$ vs n plot is located in the center of the corresponding increment Δn. A smooth curve is then drawn through the points, often with considerable arbitrariness. Due to limited reproducibility, more or less differing curves result from the individual experiments in the same system. Usually, an average curve is drawn through all the experimental points, again in a more or less arbitrary way (*5,40,46–49*). Sometimes, the plot of the quotients $\Delta Q/\Delta n$ vs n is presented without fitting it at all (*27,45,50,51*).

To introduce more objectivity and accuracy into the treatment of the experimental calorimetric data, we have examined two approaches:

a. to apply standard methods of processing of the data by correlation, instead of the customary drawing of a smooth curve through the plot of the quotients $\Delta Q/\Delta n$ vs n by hand;

b. to abolish altogether the said traditional plotting and replace it by producing a plot of the liberated heat $\Sigma\Delta Q_i = Q$ vs the adsorbed amount $\Sigma\Delta n_i = n$, and to fit this integral curve by a correlation which is then differentiated.

The common principle of both the approaches is to fit the raw experimental data with an analytical function $f(n)$ of the adsorbed amount, and to estimate quantitatively the reliability of this correlation. Only in exceptional cases is a theoretically based function $f(n)$ available for the plots of $\Delta Q/\Delta n$ vs n or of $\Sigma\Delta Q_i$ vs $\Sigma\Delta n_i$. Mostly we have to find an empirical correlation approximating sufficiently the true relationship throughout the experimental range. The correlation should be suitable from both the standpoints of a satisfactory fit and of a convenient way of treatment when estimating its reliability. Besides a good fit the first requirement implies also narrow confidence intervals for the adjustable parameters in the correlating function, which amounts to the choice of a function with the least number of estimated coefficients. The second requirement calls for a form of the function which allows one to estimate the optimal parameters from a system of ordinary linear equations.

Our present calorimetric data could be well fitted by the power series

$$f(x) = \sum_{i=0}^{m} a_i x^i$$

and therefore here we shall restrict ourselves to it, having either

$$\Delta Q/\Delta n = \sum_{i=0}^{k_a} a_i n^i \qquad (1)$$

(in the case of the quotients plot),

or

$$Q(n) = \sum_{i=0}^{k_b} b_i n^i \tag{2}$$

(in the case of the integral curve).

In Eq. (2), the theory requires $b_0 = 0$, because $Q_{n=0} = 0$. However, it is with advantage to retain the b_0 term to see whether the correlation is consistent with the said theoretical requirement even in the experimentally uncovered range of low coverages. If the reliability tests show b_0 significantly nonzero, the correlation breaks down at some low coverage. This signals either that the adsorptive properties change in the uncovered range, or that some parasitic effects impair the first calorimetric data due either to the adsorption outside the studied sample or to an interaction of the admitted gas with some residual impurity (*52,53*). In our experiments with hydrocarbons (*38*), a correction accounting for the independently measured amount of gas trapped in the cold traps brought the nonzero value of b_0 to zero.

The quotients $\Delta Q/\Delta n$ in Eq. (1) are unbiased estimates, but subject to large errors. In the present case, the standard deviation s_n for Δn has been about 8×10^{-9} mole, the standard deviation s_Q for ΔQ has been 0.033 ΔQ, and the average dose 10^{-7} mole. This gives the average standard deviation s of $\Delta Q/\Delta n$ about 0.086 $(\Delta Q/\Delta n)$, due almost entirely to s_n and increasing nearly linearly with decreasing Δn. Strictly, $\Delta Q/\Delta n$ is an unbiased estimate of the sought differential heat dQ/dn in the middle of the interval Δn for a linear dependence of dQ/dn on n only, but the scatter in the quotient value makes this source of error significant only exceptionally.

On the other hand, the quantities $Q(n)$ in Eq. (2) consist of the sums $\Sigma\Delta Q_i$, so that the standard deviation s of $Q(n)$ increases approximately with the square root of the number k of terms in the sum,

$$s = 0.033 \left(\sum^{k} (\Delta Q_i)^2\right)^{1/2}.$$

Moreover, differentiation of Eq. (2) introduces an additional uncertainty.

The right sides of both Eqs. (1) and (2) contain quantities subject not only to considerable errors in Δn, but again to the effect of summation. (In our present case, the summation effect in Δn is less pronounced than in $Q(n)$, because on average three doses were taken from the same store.) Thus the correlation both of $\Delta Q/\Delta n$ and of $Q(n)$ to an exact value of n is uncertain. This uncertainty is somewhat larger for $Q(n)$, because random and independent errors in ΔQ and Δn can accumulate in the same directions and shift $Q(n)$ with respect to n.

It follows from the outline given that the applicability of standard methods for estimates of the reliability of the fit, based on the assumed gaussian distribution of differences between the introduced data and their estimates from the correlation, is not quite obvious due to the high value of s_n, the inconstancy of the error in Q, n and $\Delta Q/\Delta n$, and finally due to a possible dependence between two neighboring errors, which may arise by the summation. These factors may cause the confidence intervals for the overall fit and for the estimates of the parameters to be appreciably larger than would be indicated by the estimate of the standard deviation of the fit. To elucidate this problem, model computations were performed, with numerical values tailored to the present experimental data. To the starting quadratic relationship between Q and n, with a nonzero b_0, random gaussian errors were assigned, forming thus 9 independent sets, each with 10 pairs of entries. Processing of the data by the correlations (1) and (2) gave the following major results:

a. The Quotient Correlation (1)

The linear correlation was throughout satisfactory, the quadratic one giving no significant improvement. The differences between the entries and the best-fit value were random and consistent with the hypothesis of a constant variance of the fit over the whole range of n. If b_0 is not very high and the experimental points not too few, or if a corrected entry for the first quotient is used, the standard deviation of the fit is only insignificantly higher than that predicted without accounting for the summation error in n, so that standard processing can be performed safely.

b. The Integral Correlation (2)

Due to appreciable interactions between the summed quantities $\Sigma\Delta Q_i$ and $\Sigma\Delta n_i$ a higher reliability of the fit is simulated than is actually the case. Therefore, the criterion for the simplest satisfactory correlation should be the standard deviations of the parameters, not the variance of the overall fit. For rejection of such a correlation, a wider margin is necessary than follows from standard methods of estimation. The scatter of the deviations was consistent with the hypothesis of the randomness. The differences between the quantities dQ/dn calculated from the quadratic fits and the true values had a scatter about twice as large as indicated the standard deviations of the best parameters b_i, and a little larger than with the correlation (1). Though statistically insignificant, this effect is probably realistic and due to the synchronized errors in the summed Q and n values.

In summary, Eq. (2) represents a substantially better correlation than could be obtained by integration of Eq. (1). Moreover, it gives an estimate of the integration constant b_0, which besides its usefulness mentioned above can serve to correct the first quotient $\Delta Q/\Delta n$ and thus to improve the fit [Eq. (1)]. Further, the correlation (2) indicates whether a pronounced departure occurs in some region from the course of dQ/dn vs n, thus enabling one to correct the quotients according to $(dQ/dn)_{n_k} = \Delta Q_k/\Delta n_k - b_3(\Delta n_k/2)^2 - \ldots$. By comparing the standard deviations for a_i and ib_i, the actual reliability of the correlation (2) can be estimated.

RESULTS

Four platinum films were prepared for the present study (Table 2). The heat liberated by successive doses was measured until a coverage was attained at which the residual pressure of $1 - 2 \times 10^{-4}$ Torr was measured in the gas phase by the Pirani gauge. The corresponding adsorbed amount is denoted as n^*. Further admission of hydrogen resulted in a continuing

TABLE 2

CHARACTERISTICS OF THE PLATINUM FILMS AND OF THE ADSORPTION OF HYDROGEN

Film No.:	1	2	3	4
Wt (mg)	65.5	55.0	47.5	42.5
Time of evaporation (min)	437	290	540	120
Mean rate of condensation $\times 10^{-15}$ (atom min^{-1} cm^{-2})	4.6	5.9	2.7	11.0
Thermal treatment (K)	335	335	335	—
(min)	35	60	5	
Vacuum during evaporation (Torr)	1×10^{-9}	$2\text{–}4 \times 10^{-9}$	$2\text{–}4 \times 10^{-9}$	$2\text{–}4 \times 10^{-9}$
Vacuum during thermal treatment and preparation of the first dose (Torr)	1×10^{-9}	2×10^{-9}	4×10^{-9}	1×10^{-9}
Time from the end of evaporation				
to the first dose (min)	297	298	290	190
to the last dose (min)	518	533	580	598
Number of doses up to n^*	14	11	10	14
n^* per 100 mg of the film (μmoles)	2.10	2.06	2.08	2.14
Integral heat of adsorption between $n = 0$ and $n = n^*$ (kcal mole^{-1})	16.4	17.3	17.2	17.3

uptake by the film with liberation of heat. Determination of the heat, however, became difficult because the increasing equilibrium pressure led to an appreciable transport of heat between the calorimeter and the cold traps via the gas phase.

Regressional Analysis of the Integral Curve

The integral curves resulting from all four experiments can be well fitted by the quadratic equations. The best parameters b_i, their standard deviations s_i, and the overall standard deviation s of the quadratic fit are given in Table 3. Also included are the number of moles n_0 corresponding to the nonzero value of b_0, and the number of moles n^*_{corr} obtained by correcting the experimental value of n^* for the amount n_0.

With all four films, cubic correlations give but insignificantly lower standard deviations along the fitted curves, and the coefficient b_3 is significantly nonzero with film 1 only. With all four films the standard deviations of b_1 and b_2 are lower for the quadratic fit than for the cubic one. These facts, along with the differences in the values and even in the signs of the coefficients b_2 for the particular experiments if cubic correlations are applied, indicate that the quadratic fit should be preferred in all four experiments. Thus linear dependences of the differential heat of adsorption on the adsorbed amount are obtained, with the initial heats of 22.0, 22.6, 21.2 and 19.2 kcal mole^{-1} in Expts 1-4, respectively. The differential curves obtained by differentiation of the equations fitted to the corresponding integral curves, are presented in Fig. 1. For comparison, points obtained by the traditional method of plotting the quotients $\Delta Q/\Delta n$ vs n are shown in Fig. 2.

As shown in Table 3, the first three experiments give fairly similar results;

TABLE 3

RESULTS OF THE REGRESSIONAL ANALYSIS OF THE INTEGRAL CURVES

Film No.:	1	2	3	4
b_0	−0.2336	−0.2950	−0.3032	+0.1255
s_{b_0}	0.0478	0.0904	0.0391	0.0323
b_1	21.9948	22.6063	21.2198	19.2345
s_{b_1}	0.1502	0.2947	0.1668	0.1489
b_2	−3.9795	−4.4136	−3.7125	−2.2932
s_{b_2}	0.1019	0.2158	0.1505	0.1495
n_0 (μmoles)	0.0106	0.0131	0.0143	−0.0065
n^*_{corr} (μmoles)	1.3656	1.1190	0.9724	0.9170

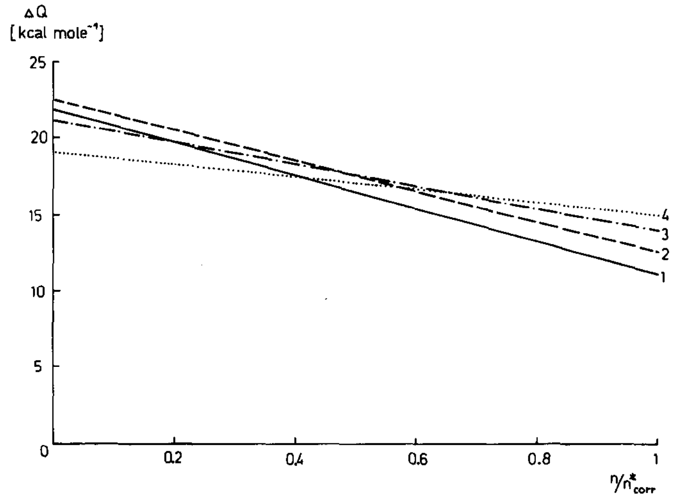

FIG. 1. Differential heat-coverage curves obtained by differentiation of the fitted integral curves for films 1, 2, 3 and 4.

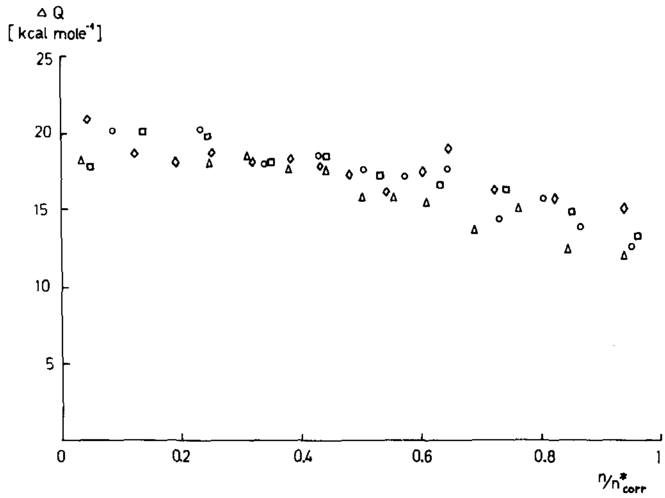

FIG. 2. Plot of the quotients $\Delta Q/\Delta n$ vs n. Film: (△) 1; (○) 2; (□) 3; (◇) 4.

whereas Expt 4 differs significantly. The coefficient b_0 is negative in Expts 1, 2 and 3, indicating an initial uptake of 1.0–1.5 × 10^{-8} moles of hydrogen outside the film. With film 4, however, b_0 is positive.

Regressional Analysis of the Curve Fitted to the Quotient Plot

As discussed in the outline of principles of the data processing, the standard deviations s_i of the integral correlation simulate a lower variability than the true one. To obtain better estimates, linear regression of the quotients was performed. The first quotient in each experiment was corrected for the value of n_0 obtained from the estimate of b_0 in the corresponding integral curve fit. The results are summarized in Table 4. As required, the correlations of the quotient curves and of the integral curves give fairly coinciding values for a_1 and b_1, and for a_2 and $2b_2$ in the particular experiments. The variances indicated by the standard deviations are, however, clearly higher with the regression of the quotient curve than of the integral curve. In both cases, the overall deviations along the fitted curves do not differ significantly for the individual experiments, as shown by the F test. Hence, the accuracy in establishing the individual points is about the same with all the four films and the joint standard deviation equals 0.1047 with the integral curve fit, and 0.7308 with the quotient curve fit.

TABLE 4
RESULTS OF THE REGRESSIONAL ANALYSIS OF THE QUOTIENT CURVES

Film No.:	1	2	3	4	Av
a_1	21.5115	21.9879	21.1948	19.2670	
s_{a_1}	0.3708	0.5656	0.2977	0.4408	
a_2	−7.4067	−7.6398	−7.7547	−4.3823	
s_{a_2}	0.4984	0.7802	0.5431	0.9054	
s	0.7136	0.8619	0.4873	0.7917	
$a_2 n^*_{corr}$	−10.1146	−8.5489	−7.5407	−3.9900	
s_{a_1}/s_{b_1}	2.4687	1.9192	1.7848	2.9604	2.2833
s_{a_2}/s_{b_2}	2.4455	1.8077	1.8043	3.0281	2.2714
Av	2.4571	1.8634	1.7945	2.9942	2.2773

The F test reveals that the differences in a_1 are not significant among films 1, 2 and 3, whereas a_1 for film 4 differs significantly. Thus the initial heat of adsorption is probably much the same with films 1, 2 and 3, viz, 21.5 ± 0.5 kcal mole^{-1}; whereas with film 4 it is significantly lower, viz, 19.3 ± 0.9 kcal mole^{-1}. Even more interesting is that also the values of a_2, i.e., the slopes of the linear decrease in the heat, represent estimates of the same true value with films 1, 2 and 3; whereas with film 4, a_2 is clearly lower.

Further Analysis of the Variance in the Integral Curves

To gain further evidence on whether the initial heats and the slopes of their linear decrease with coverage are the same in Expts 1, 2 and 3, three models were examined.

Model I. Values obtained for b_0, b_1 and b_2 in Expts 1, 2 and 3 represent estimates of the same true values.

Model II. Values obtained for b_0 and for b_1 (the initial heat) in the three experiments represent estimates of the same true values, whereas the coefficients b_2 (the slopes of the heat decrease) differ in the individual experiments.

Model III. Values obtained for b_0 and for b_2 in the three experiments represent estimates of the same true values, whereas the parameters b_1 (the initial heats) differ.

Analysis of deviations in the particular models showed that models I and II gave appreciably higher deviations along the correlation curve than did model III. Thus the main contribution to the variability in the three experiments results from the variance in b_1. This was further confirmed by a detailed analysis of variance.

Finally, analysis of the integral curves in pairs was performed, i.e., deviations along the fitted integral curves for the doublets of experiments (1 and 2; 1 and 3; 2 and 3) were compared. A high coincidence was obtained for films 1 and 2, whereas the results with film 3 were somewhat different.

DISCUSSION

Two factors should be considered when seeking an interpretation of the results obtained: the extent of possible contamination of the films, and their surface structure.

The shortest time of evaporation, no thermal treatment, and the shortest interval between the end of evaporation and admission of the first dose, suggest that the danger of contamination of film 4 is less than with the other three films. This seems to be corroborated by the positive value of b_0 found for film 4, which could result from the occurrence of some especially active sites on the surface. Thus higher cleanliness of the surface might provide an explanation for the lower initial heat on film 4. A similar observation was reported for the heats of adsorption of hydrogen on very thin films of titanium (*54*) and of nickel (*55*). Our recent calorimetric measurements with the molybdenum–hydrogen system also have brought lower heats on cleaner films (*56*).

On the other hand, a preliminary experiment with a film in a vacuum of about 4×10^{-8} Torr gave results coinciding well with the heats obtained in the 10^{-9} Torr region. This appears to weaken the hypothesis that the differences in the heats found with the particular films are due to different degrees of surface contamination, but it is probably not an argument sufficient to rule out the suggested explanation.

Since no data on the surface area and other structure characteristics of the studied films are available, a discussion of the possible effect of the structure on the measured heats of adsorption can only be speculative. Thermal treatment of the film, its thickness (weight), and the rate of its condensation have been considered as the factors which could influence its structure and thereby the heat obtained. As expected, no effect of the applied thermal treatment has been found. The apparent relation between the film weight and the slope of the heat decrease (the thicker the film, the more pronounced is the heat fall and the lower is the heat at n^*) does not seem to be convincing in view of rather small differences in the weight of the individual films and markedly different rates of condensation. The relation between the rate of film condensation and the heat of adsorption might be more meaningful. An explanation for the lowest heat being observed with film 4 which was condensed at the highest rate could be that this film has the lowest number of high-index planes exposed to the gas phase. Because high-index crystal surfaces of platinum were shown to consist of low-index terraces linked by steps (*57*), and the interaction of chemisorbed gases with stepped surfaces is much stronger than with low-index planes (*58*), film 4 should have the lowest initial heat of adsorption, as actually found. In view of the mobility of hydrogen on platinum at room temperature (*3*), the fall of the heat when the coverage increases can be understood at least partially in terms of mobile adsorption on a heterogeneous surface [some considerations referring to this have been published recently (*5*)]. Therefore, the slower fall of the heat obtained with film 4 could suggest a lesser surface heterogeneity of this film. However, this tentative interpretation should be tested by the study of the actual surface structure of the investigated films.

It should be also noted that the integral heat in the studied range of the surface coverage, and the value of n^* referred to unit weight of the film, do not differ with the four films. Again, a positive value of b_0 was found with film 4, which could result either from some unknown parasitic reaction of the hydrogen or from the existence of some particularly active sites on this surface. The latter alternative would evidently contradict the suggested hypothesis of the lesser heterogeneity of film 4.

Further work is required to clarify the effect of surface contamination and of the surface structure on the heat of hydrogen adsorption. Along with the different reliability of the various methods used to acquire the heat values, these two factors undoubtedly cause the diversity in the heat of adsorption of hydrogen obtained hitherto on various forms of platinum.

ACKNOWLEDGMENTS

The authors express thanks to Dr. Z. Knor for his interest and critical comments on the draft of this paper, and to Dr. M. Cukr for the mass-spectrometric analysis of the platinum wire.

REFERENCES

1. Rootsaert, W. J. M., Van Reijen, L. L., and Sachtler, W. M. H., *J. Catal.* **1,** 416 (1962).

2. Weinberg, W. H., and Merrill, R. P., *Surface Sci.* **33,** 493 (1972).

3. Lewis, R., and Gomer, R., *Surface Sci.* **17,** 333 (1969).

4. Wiesendanger, H. U. D., *J. Catal.* **2,** 538 (1963).

5. Norton, P. R., and Richards, P. J., *Surface Sci.* **44,** 129 (1974).

6. Nishiyama, Y., and Wise, H., *J. Catal.* **32,** 50 (1974).

7. Procop, M., and Völter, J., *Surface Sci.* **33,** 69 (1972).

8. Mignolet, J. C. P., *J. Chim. Phys.* **54,** 19 (1957).

9. Taylor, G. B., Kistiakowsky, G. B., and Perry, J. H., *J. Phys. Chem.* **34,** 799 (1930).

10. Flosdorf, E. W., and Kistiakowsky, G. B., *J. Phys. Chem.* **34,** 1907 (1930).

11. Maxted, E. B., and Hassid, N. J., *J. Chem. Soc.* **1931,** 3313.

12. Maxted, E. B., and Moon, C. H., *Trans. Faraday Soc.* **32,** 1375 (1936).

13. Chon, H., Fisher, R. A., and Aston, J. G., *J. Amer. Chem. Soc.* **82,** 1055 (1960).

14. Chon, H., Fisher, R. A., Tomezsko, E., and Aston, J. G., *Actes Congr. Int. Catal., 2nd, 1960* **1,** 217 (1961).

15. Aston, J. G., *J. Phys. Chem.* **67,** 2042 (1963).

16. Aston, J. G., Tomezsko, E. S. J., and Fisher, R. A., Jr., *J. Amer. Chem. Soc.* **86,** 2097 (1964).

17. Tomezsko, E. S. J., and Furukawa, G. T., *J. Catal.* **8,** 386 (1967).

18. Kwan, T., *J. Res. Inst. Catal. Hokkaido Univ.* **1,** 81 (1949).

19. Kwan, T., *in* "Advances in Catalysis" (W. G. Frankenburg, V. I. Komarewsky and E. K. Rideal, Eds.), Vol. 6, p. 67. Academic Press, New York, 1954.

20. Lapluye, M., *Actes Congr. Int. Catal., 2nd,* 1960 **1,** 225 (1961).

21. Kubokawa, Y., Takashima, S., and Toyama, O., *J. Phys. Chem.* **68,** 1244 (1964).

22. Tsuchiya, S., Amenomiya, Y., and Cvetanović, R. J., *J. Catal.* **19,** 245 (1970).

23. Maidanowskaja, L., and Bruns, B., *Acta Physicochim. URSS* **9,** 927 (1938).

24. Schuit, G. C. A., and Van Reijen, L. L., *in* "Advances in Catalysis" (D. D. Eley, W. G. Frankenburg, V. I. Komarewsky and P. B. Weisz, Eds.), Vol. 10, p. 242. Academic Press, New York, 1958.

25. Bond, G. C., and Newham, J., *Trans. Faraday Soc.* **56,** 1501 (1960).
26. Gruber, H. L., and Hausen, A., *Kolloid-Z. Z. Polym.* **214,** 66 (1966).
27. Basset, J. M., Theolier, A., Primet, M., and Prettre, M., *Actes Congr. Int. Catal., 5th, 1972,* Pap. No. 65.
28. Gentsch, H., Guillen, N., and Köpp, M., *Z. Phys. Chem. Neue Folge* **82,** 49 (1972).
29. Breiter, M. W., *Trans. Faraday Soc.* **60,** 1445 (1964).
30. Podvyazkin, J. A., *Zh. Fiz. Khim.* **46,** 452 (1972).
31. Grishina, T. M., Logacheva, L. I., and Vovchenko, G. D., *Zh. Fiz. Khim.* **48,** 2716 (1974).
32. Kinoshita, K., Lundquist, J., and Stonehart, P., *J. Catal.* **31,** 325 (1973).
33. Sinfelt, J. H., Yates, D. J. C., and Taylor, W. F., *J. Phys. Chem.* **69,** 1877 (1965).
34. Weinberg, W. H., Deans, H. A., and Merrill, R. P., *Surface Sci.* **41,** 312 (1974).
35. Byrne, M., and Kuhn, A. T., *J. Chem. Soc. Faraday I* **1972,** 1898.
36. Trasatti, S., *J. Chem. Soc. Faraday I* **1972,** 229.
37. Schrieffer, J. R., *J. Vac. Sci. Technol.* **9,** 561 (1972).
38. Černý, S., Buzek, F., and Cuřínová, A., unpublished data.
39. Knor, Z., *Catal. Rev.* **1,** 257 (1967).
40. Černý, S., Ponec, V., and Hládek, L., *J. Catal.* **5,** 27 (1966).
41. Černý, S., and Ponec, V., *Catal. Rev.* **2,** 249 (1968).
42. Černý, S., Ponec, V., and Hládek, L., *J. Chem. Thermodyn.* **2,** 391 (1970).
43. Hládek, L., Černý, S., and Cettl, L., *Collect. Czech. Chem. Commun.* **36,** 1709 (1971).
44. Hládek, L., *J. Sci. Instrum.* **42,** 198 (1965).
45. Klemperer, D. F., and Stone, F. S., *Proc. Roy. Soc., Ser. A* **243,** 375 (1957).
46. Brennan, D., and Hayes, F. H., *Phil. Trans. Roy. Soc. London A* **258,** 347 (1965).
47. Bröcker, F. J., and Wedler, G., *Discuss. Faraday Soc.* **41,** 87 (1966).
48. Wedler, G., and Bröcker, F. J., *Surface Sci.* **26,** 454 (1971).
49. Wedler, G., and Schroll, G., *Z. Phys. Chem. Neue Folge* **85,** 216 (1973).
50. Gravelle, P. C., and Teichner, S. J., *in* "Advances in Catalysis" (D. D. Eley, H. Pines and P. B. Weisz, Eds.), Vol. 20, p. 167. Academic Press, New York, 1969.
51. Breysse, M., Guenin, M., Claudel, B., and Veron, J., *J. Catal.* **28,** 54 (1973).
52. Černý, S., *Discuss. Faraday Soc.* **4,** 111 (1966).
53. Brennan, D., *Discuss. Faraday Soc.* **41,** 56 (1966).
54. Wedler, G., and Strothenk, H., *Ber. Bunsenges. Phys. Chem.* **70,** 214 (1966).
55. Wedler, G., *Discuss. Faraday Soc.* **41,** 104 (1966).
56. Černý, S., *Surface Sci.,* in press.
57. Lang, B., Joyner, R. W., and Somorjai, G. A., *Surface Sci.* **30,** 440 (1972).
58. Lang, B., Joyner, R. W., and Somorjai, G. A., *Surface Sci.* **30,** 454 (1972).