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Calorimetric Heats of Adsorption of Hydrogen on Molybdenum Films

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An improved technique of calorimetric measurements on evaporated metal films is described and results of measurements of heats of hydrogen sorption on molybdenum films at 20°C are presented. The initial heat of hydrogen adsorption on molybdenum is 40 kcal mole^{-1}, and integral heat of adsorption (for surface coverage up to $\theta = 0.9$) is 31 kcal mole^{-1}. Molybdenum ranks between tungsten and iron as regards the value of the heat of hydrogen adsorption and the dependence of the heat on surface coverage. A partial coverage of the molybdenum surface by oxygen leads to a very slight increase of the heat of the following hydrogen sorption (by several per cent). A dependence of this increase on the extent of oxygen preadsorption was not found. No signs of a reaction of preadsorbed oxygen with hydrogen were detected calorimetrically.

I. INTRODUCTION

Chemisorption and mutual reactions of hydrogen and oxygen on transition metals are studied in our laboratory in the first place by measuring changes, called forth by sorption, of the electric conductivity and of the work function of evaporated films of these metals (*1–4*). As a further method we have introduced calorimetry on evaporated metal films. The data concerning the heat effect of adsorption and the possible mutual reaction of oxygen and hydrogen on clean metal surfaces are of considerable importance, yet they are, so far, rather incomplete. Of the metals with which the behavior of hydrogen and oxygen has been of greatest interest to us up to now (Ni, Pd, Rh, Mo, Fe, and others), molybdenum seems to have been very little studied calorimetrically. The respective calorimetric data on molybdenum were desirable not only in order to complete studies of this metal by other methods (*3*), but also in a wider connection with endeavors to find a correlation of catalytic activity of metals in oxidation–reduction reactions with other properties of metals (*5*). Up to this time only the heat-coverage curve of the adsorption of oxygen by molybdenum film has been published (*6*). Some authors cited a value of 40 kcal mole^{-1} for the initial heat of adsorption of hydrogen by molybdenum, but so far it has been substantiated only by a private communication of Beeck's collaborator Dr. A. W. Ritchie (*7*). A heat-coverage curve for hydrogen was not known at all, nor was the heat of sorption of hydrogen by molybdenum with preadsorbed oxygen. The scantiness of calorimetric data measured on films is due to the relatively great difficulty encountered in such experiments. This paper therefore deals with the description of several improvements in the technique of measuring heats of sorption on films and, also, gives and discusses the results of measurements of heats liberated by hydrogen at 20°C on clean molybdenum films and on films partially covered by oxygen.

II. EXPERIMENTAL

a. Adsorption Apparatus

The volumetric adsorption apparatus used here was made of tubing with an

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internal diameter of 11 mm. It contained no greased cocks or ground joints, but only mercury float valves (*8, 9*). The calorimeter was sealed to the apparatus. A one-stage mercury diffusion pump of Becker construction (*10*), backed by active charcoal cooled with liquid nitrogen, exhausted the apparatus up to a pressure order of 10^{-8} to 10^{-9} mm Hg. In the course of evacuation the whole apparatus was heated by heating tapes to 250–300°C. The vacuum in the apparatus was measured by an ionization gauge in the Bayard-Alpert modification. Both the ionization gauge and the calorimeter were protected against mercury vapors by traps cooled with liquid nitrogen. The amount of sorbed gas was determined by measuring the pressure with a McLeod gauge in the modification described in ref. 8, the constants of which were 1.11×10^{-6} mm^{-1} and 1.49×10^{-3} mm^{-1}. Hydrogen was obtained by electrolysis and purified by diffusion through the hot palladium thimble. Oxygen was obtained by thermal decomposition of $KMnO_4$.

b. *Calorimeter*

So far all authors (*6, 11–18*) working with the Beeck type of calorimeter (*11*), have used ordinary commercial glass tubes etched or drawn in order to obtain the egg-shell glass necessary for making the calorimetric vessel. However, the procedures mentioned tend to increase the nonuniformity of the wall thickness of the glass tubing, which circumstance can impair the value of measured results as pointed out by Hayward (*16*); Brennan, Hayward, and Trapnell (*6*); and Brennan and Jackson (*19*). These difficulties cannot be fully removed even by the spherelike calorimetric vessel suggested by Wedler (*20*). This is the reason why for the construction of calorimeters used in this report we had especially made thin-walled tubes, drawn directly in the glass-works with the required diameter (30 mm) and about 35 m long. From their middle sections, which show the best uniformity, we cut the required lengths (of about 25 cm) of the egg-shell glass for making the calorimetric vessels. Thus vessels of satisfactory quality were obtained. For example, in calorimeter A, with which the majority of measurements presented in this report was made, the vessel was made from a section of egg-shell glass with a wall thickness of 0.26 mm, whose variations round its circumference did not exceed ±3.5%, variations along its length being even considerably less. Thus the uniformity of the wall thickness in our calorimetric vessels exceeded by far vessels made by hand-drawing or etching ordinary tubes (*6*).

The heats of sorption presented in this report were measured with two calorimeters marked A and B. Calorimeter A was constructed of a Kovar glass tube of 30-mm diameter, its wall thickness being 0.26 mm and the length 22 cm. About 11.5 cm of the length was provided with the winding of a resistance thermometer, starting 2.5 cm from the lower rounding-off of the tube. The thermometer consisted of a platinum wire (diameter 0.05 mm) annealed, before winding, by electric current to red glow for an hour. The wire was wound on the calorimetric tube on a lathe under tensioning by a constant force. The pitch between turns was 2.5 mm, the total wire resistance amounted to 298.5 Ω at 20°C. A calibration coil was interwound in the same way centrally between the thermometer turns as suggested by Klemperer (*14*) and Klemperer and Stone (*15*). This interwinding, serving to calibrate the calorimeter or to determine its heat capacity, respectively, was made of constantan wire of 0.1-mm diameter and with a total resistance of about 290 Ω. The last uppermost and lowest turns were formed by the thermometric wire. This is of importance for ensuring the independence of the determined heat capacity of the calorimeter on the intensity of the calibration current. The wires were firmly affixed to the egg-shell glass by a thin transparent layer of diluted silicon varnish baked after coating in a tube oven at 250°C. The ends of both the thermometric and calibration winding were spot-welded to nickel foil which was in turn spot-welded to thick molybdenum leads (diameter 1 mm) reaching upwards through the calorimeter jacket (diameter 55 mm)

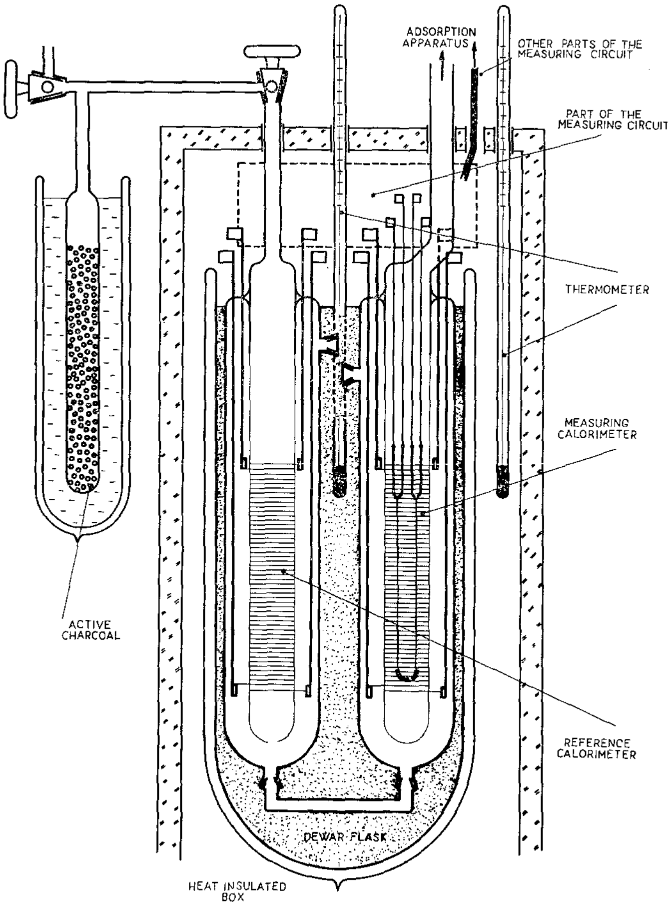

FIG. 1. Sketch of the calorimeter assembly.

(Fig. 1). After leaving the jacket through molybdenum-in-glass seals these leads were provided with spot-welded gilded platinum foils to which the respective connections of the measuring circuit were soldered.

Calorimeter B differed from the A type in two main features. Firstly, the thermometric winding, again formed by a platinum wire of 0.05-mm diameter, had a pitch of 4 mm between turns and its total resistance was at 20°C only 155.9 Ω. Secondly, the two calorimeters differed in the geometry of the gas inlet. In the case of calorimeter A no hindrances were made for the incoming gas (Fig. 1), while in calorimeter B the socket bearing the evaporating filament was analogous to that shown, e.g., in ref. 3, so that gas entered through an annulus on the calorimeter circumference. Other differences between the two calorimeters were of minor importance.

c. *Measuring Circuit*

The increase of temperature in the calorimeter, caused by liberated heat of sorption, was measured and automatically recorded by an electrical circuit described in detail in ref. 21.

The main feature of the circuit is its symmetry, electric as well as thermal. To this end two as far as possible equal calorimeters have been used, the measuring and the reference one. The latter, however, is not connected to the adsorption apparatus and does not contain a film. The temperature of the outer jackets of both calorimeters is equalized by means of a removable copper foil of 0.1-mm thickness

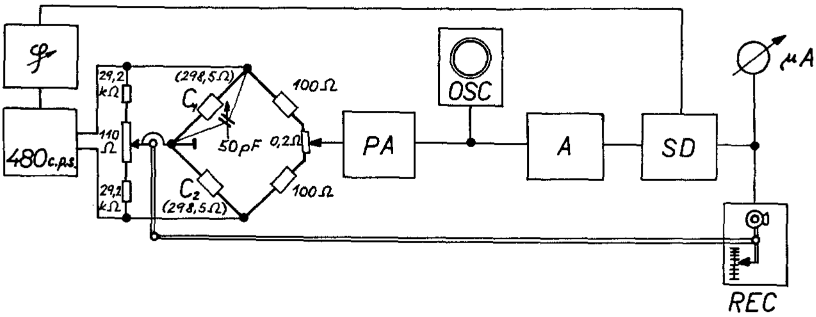

FIG. 2. Block scheme of the measuring circuit.

which has been wound round each calorimeter and then round both. The two calorimeters forming thus one unit are immersed into a Dewar flask containing about 5 liters of water of 20°C (Fig. 1). The jackets of both calorimeters, after finishing the evaporation and the eventual following thermal stabilization of the film, are interconnected and jointly exhausted by a rotatory pump and then by outgassed active charcoal cooled by liquid nitrogen to a vacuum of 10^{-5} to 10^{-6} mm Hg. The Wheatstone bridge formed by the calorimeters' thermometers, two manganin resistors (each 100 Ω) and balancing potentiometers (Fig. 2), is fed by alternating voltage of 480 cps. The bridge output is amplified and then synchronously detected. The resulting DC output actuates the amplifier of a 5-mV f.s.d. servomechanical recorder with two slidewires, the measuring and the retransmitting one. The thermometer bridge is continuously balanced by the retransmitting slidewire (110 Ω) which is a part of the bridge. Thus the deflection of the recorder pen is proportional to the temperature difference between the measuring and the reference calorimeter.

This arrangement of the bridge and the method of measuring the temperature of the measuring calorimeter are somewhat more complicated than the procedures hitherto used in working with the Beeck-type calorimeter (*6*, *11–18*, *20*), but they offer a number of advantages. In the first place the insensitivity of the symmetric bridge to the variation of surrounding temperature is such as to render it practically unnecessary to thermostat water in the Dewar flask in which both calorimeters are placed. The stability of the temperature sensitivity of the bridge is, thanks to its independence from the feeding voltage, so good that the results of the heat capacity calibration repeated after 7 months do not differ within the compass of the exactness of the measuring. A further valuable advantage is the automatic and continuous recording of the course of temperature of the measuring calorimeter on a strip chart (width 25 cm) with a precision unattainable in periodical visual reading of the galvanometer deflections or in manual operation of the bridge with a galvanometer as a zero indicator. For the sake of illustration a tracing of the heat of adsorption evolved by a dose of hydrogen on molybdenum film in calorimeter A is reproduced in Fig. 3.

The sensitivity of the measuring circuit can be altered in a wide range. In this work while measuring with calorimeter A, an over-all circuit sensitivity corresponding to the recorder deflection of 8.51×10^3 mm/deg was used, while in measuring with calorimeter B the sensitivity was 8.25×10^3 mm/deg.

d. Calibration of Heat Capacity of the Calorimeter

The heat capacity of the calorimeter can be determined either from the weight and value of the specific heat of individual parts composing the calorimeter, or on the basis of the warming up of the calorimeter by a known amount of heat. The first method mentioned was used by Beeck and his associates (*11*, *22*, *23*). A comparison with the new results based on a careful heat capacity measurement (*18*) showed that Beeck was able to estimate the heat capacity of his calorimeter correctly. Nevertheless the heat capacity determined on the basis of the liberation of the measured amount of Joule heat is, of course, considerably more reliable; the said heat can be supplied either on the inner or the outer side of the calorimetric vessel. In the first case the calibration current passes directly through the evaporated film (*6*, *13*, *20*), in the second alternative it passes either through the thermometric coil (*12*) or, a better method, through a separate calibration coil (*14*, *15*). The former method offers the advantage of imitating more nearly the conditions of the real liberation of the heat of adsorption, as well as the possibility of measuring the heat capacity of individual sections of the calorimeter (*16*). The main problems of this method are connected with suitable construction and placing of the contacts. As it is not possible to place them on the very ends of the film, which tend to be somewhat diffuse, there arise the questions of whether heating of the whole film can be ensured and whether or not dependence of determined heat capacity on the intensity of the calibration current will appear. No data have been published in the literature on the examination of this dependence. Certain problems could also arise in respect to the homogeneity of the heating up of the film (owing to its varying thickness in different parts of the calorimeter) and as regards the ensuring of a satisfactory contact of lead-ins with the film.

The heating of the calorimetric vessel by a current passing through the calibration winding on the outer side of its wall is simpler and ensures uniform heating of the whole length of the calorimeter. From the calculation of the rate of heat transfer from the respective calibration winding (*24*) it

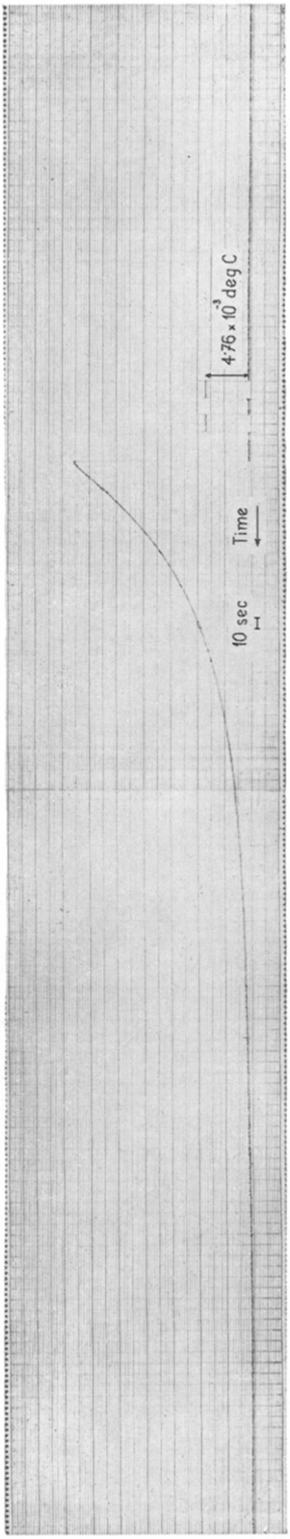

FIG. 3. Reproduction of trace of the liberation of heat of adsorption on admission of hydrogen dose (0.836 μmole) to molybdenum film in calorimeter A. There evolved 2.735 × 10^{-2} cal which corresponds with 32.7 kcal mole^{-1}. This figure also shows control marks of the circuit sensitivity by switching-in the parallel resistance.

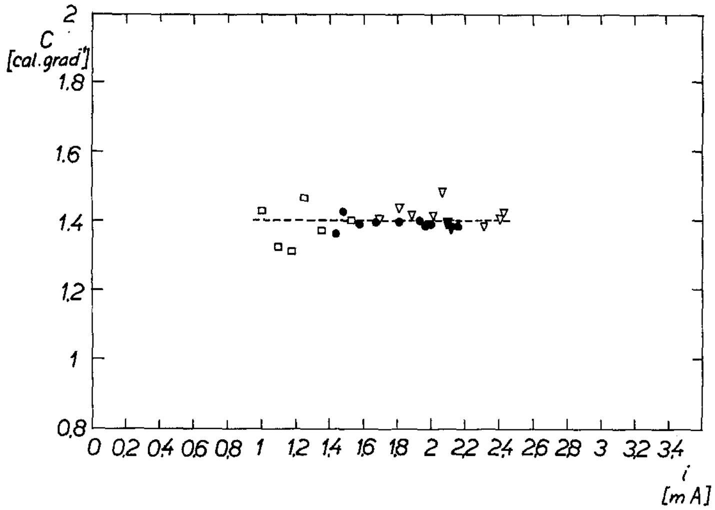

FIG. 4. Results of determining the heat capacity of calorimeter A: ○, sensitivity 1 (deflection of 12.60 m/deg); △, sensitivity 2 (deflection of 8.51 m/deg), used for measurements; □, sensitivity 3 (deflection of 7.35 m/deg). Filled marks pertain to calorimeter with evaporated film, open marks to that without film.

seems that the conditions of this process probably do not substantially differ from conditions of the evolution of heat on the inner side of the calorimetric vessel. This is the reason why this procedure was used in the calibration of heat capacity of calorimeters A and B. The respective evaluation was made by following the equilibrium method of Wahba and Kemball (*12*). Cooling curves after switching off the calibration current were, after transformation into semilogarithmic coordinates, strictly linear from the very beginning of the cooling period and no signs were noticed of a local overheating in the neighborhood of the heating winding, etc.

Results of the heat capacity measurements of calorimeter A are given in Fig. 4. The average of 25 measurements is 1.40 cal deg^{-1}, the mean error of this average being $\pm 7.83 \times 10^{-3}$ cal deg^{-1}, i.e., ±0.56% and the mean error of the individual measurement being $\pm 3.91 \times 10^{-2}$ cal deg^{-1}, i.e., ±2.8%. The heat capacity of calorimeter B, established from 25 measurements, is 1.76 ± 0.016 cal deg^{-1}. As an additional check on the correctness of the determination of the heat capacity, the heat of adsorption of hydrogen on nickel was measured in calorimeter A. The resulting heat-coverage curve is in agreement with results obtained by previous authors (*18*).

e. Film Preparation, Method of Measurement, and Evaluation of Records

The films were evaporated from a wire braided from two filaments of spectroscopically pure molybdenum, the diameter being 0.2 mm (Radium E.G., Wipperfürth). The evaporation wire, the total length of which was 22 cm, was bent to a U shape. Round its bend was wound, to the length of about 15 mm, a piece of the same wire in order to prevent the evaporation of metal into the lower rounded-off end of the calorimeter. Then the wire was spot-welded to nickel leadings (*25*) and the calorimeter was sealed to the adsorption apparatus, whereupon the molybdenum wire was heated for about 60 to 70 hours to red glow ($i \sim 4.2$ amp) with evacuation by a diffusion pump and heating of the whole apparatus, together with the calorimeter, by heating tapes, to about 300°C. The films were evaporated at a pressure of 10^{-8} mm Hg (see Table 1). The current intensity in the beginning of the evaporation was about

7.1 amp. During the evaporation cooling water (~15°C) flowed through the calorimeter jacket. The resistance thermometer extended both above and below the evaporated film by several turns. After evaporation the film was left for a few hours at room temperature. On the basis of the analysis (*26*) made for a similar type of apparatus it can be deduced that the contamination of the film in the present calorimeter even in the course of many hours after the evaporation did not exceed 1% of its surface. The film weight was determined as a difference in the weight of the filament before and after evaporation.

A rapid transport of gas to the film is of considerable importance with this type of calorimetry. This is the reason why the admission of individual doses to the film was effected in the following way: Hydrogen at a pressure of about 3 to 4 $\times 10^{-2}$ mm Hg was prepared in the apparatus. By opening the valve to the calorimeter for 1 sec or so, about one-quarter to one-third of the prepared gas penetrated to the film, i.e., 0.4 to 0.9 μmole. The exact amount of the gas admitted was obtained from differences of pressures in the apparatus before and after the valve was opened. This procedure ensured that, up to the values of θ around 0.9, when the adsorption slowed down and residual pressure appeared over the film, the liberation of all heat corresponding to the given hydrogen dose was finished in a few seconds (Fig. 3). Then it was possible, in order to get the required recorder deflection corresponding to the total evolved heat, to use quite simply and with sufficient accuracy an extrapolation of the cooling curve transformed to semilogarithmic coordinates, to zero time as suggested by Klemperer and Stone (*15*). In the best cases the adsorption was finished so rapidly that it was possible to extrapolate the deflection directly from the trace. It is necessary to point out that the extrapolation method mentioned is based on the assumption that it is possible to neglect the time during which the heat evolves, in comparison with the time of the cooling of the calorimeter alone. If this condition is not fulfilled, e.g., due to the slow diffusion of gas to the film, a greater deflection value is obtained by extrapolation than that which in fact belongs to the liberated amount of heat. With regard to the logarithmic scale on the axis of ordinates this error grows rapidly with the lengthening of the time of heat liberation. In such a case it is necessary to obtain the required deflection value by constructing the adiabatic curve of the course of the calorimeter temperature (*6, 16*), which is rather laborious. The possibility of heat transfer between the calorimeter and its surroundings through the gas phase constitutes a further danger of the slow transport of gas to the film.

The total adsorbed amount of hydrogen, which did not change any more with time at a pressure of the order of 10^{-3} mm Hg, was considered as $\theta = 1$ for the hydrogen sorption on clean films as well as on films partially covered by the preadsorption of oxygen. Individual points on heat-coverage curves always correspond with the center of each gas increment. Calculation of the evolved heat of adsorption ΔQ was made by application of the usual relation

$$\Delta Q = \frac{1}{\Delta n} \mathrm{C} \frac{x_0}{\alpha R S},$$

where Δn stands for the number of moles of gas adsorbed, C is the heat capacity of the calorimeter, x_0 is the deflection corresponding to the whole heat evolved, α is the temperature coefficient of resistance of the platinum thermometer, R is the resistance of the thermometer, and S is the sensitivity of the measuring circuit.

III. RESULTS AND DISCUSSION

Important data concerning the individual experiments with molybdenum films are summarized in Table 1. The measured heats of sorption are given in Fig. 5 and/or Fig. 6. The following conclusions can be drawn from these experiments.

a. Method of Measurement

Measured heats of hydrogen sorption on molybdenum do not depend on the con-

TABLE 1

Experiment	I	II	III	IV	V	VI	VII
Vacuum at the beginning of evaporation (mm Hg)	2×10^{-8}	1.5×10^{-8}	2×10^{-7}	7×10^{-8}	2×10^{-8}	8×10^{-8}	2×10^{-7}
Time of evaporation (min)	59	53	119	51	22	47	38
Weight of film (mg)	31	18.5	46	33	17	24	21.5
Time from end of evaporation to the beginning of experiment (hours)	17	14	7	16	13	18	7
Total adsorption of: oxygen (μM)	—	—	—	—	2.09	2.79	4.95
hydrogen (μM)	13.24	8.45	10.62	10.45	7.12	8.86	6.09
Relation $(H_2)_{ads}:(O_2)_{ads}$	—	—	—	—	3.4	3.2	1.2

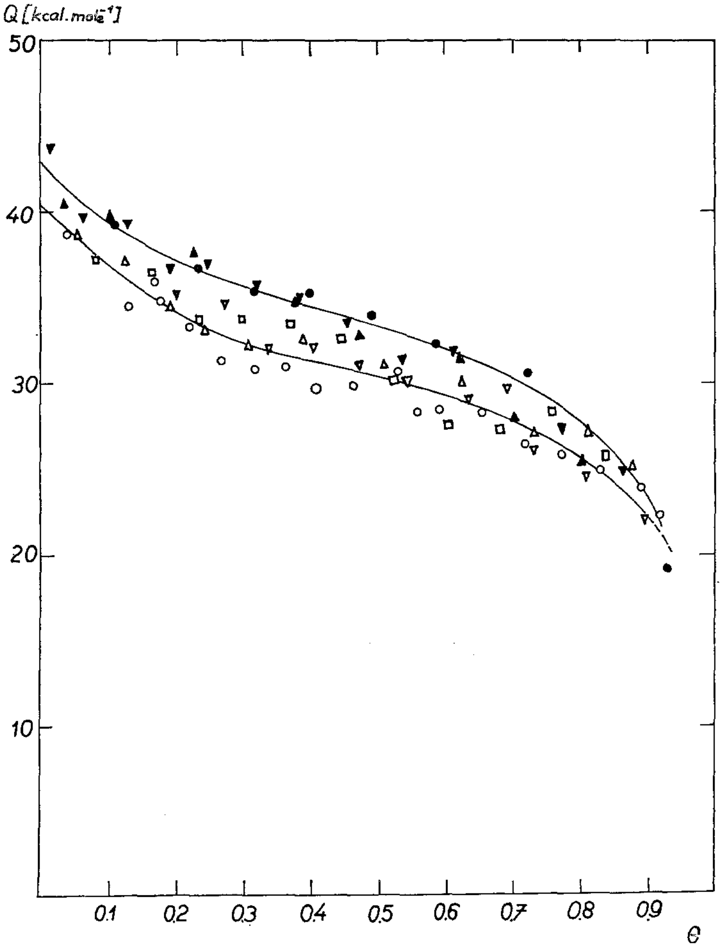

FIG. 5. Heats of sorption of hydrogen on molybdenum films. Open points: clean molybdenum films; ○, Experiment I; □, Experiment II; △, Experiment III; ▽, Experiment IV. Filled points: molybdenum films with preadsorbed oxygen; ▲, Experiment V; ▼, Experiment VI; ●, Experiment VII.

struction of the calorimeters used by us. Although the pitch of turns of the thermometric winding was 2.5 mm in calorimeter A and 4 mm in calorimeter B and the two calorimeters differed in the geometry of the inlet part, the results obtained are the

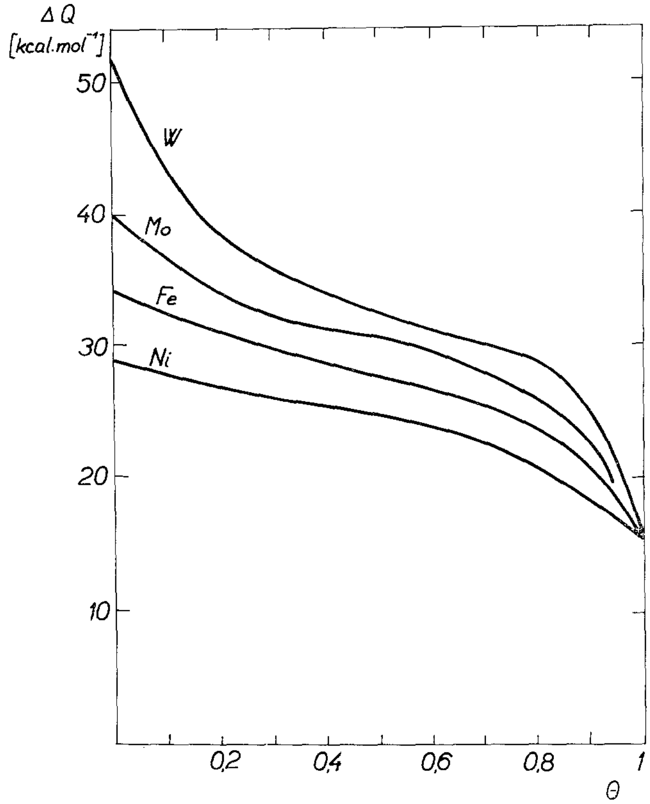

FIG. 6. Comparison of heat of adsorption of hydrogen on films of some transition metals: Mo, measured in this work; Ni, W, Fe, measured in ref. 12.

same within the compass of experimental errors.

Curves which could be drawn through points measured in individual experiments on clean molybdenum films differ by several per cent. With regard to the level of the experimental technique used, in the first place the explanation should probably be looked for in the properties of the films themselves. For example, it is known (*27*) that heats of adsorption on individual crystallographic planes of the same metal can differ more than the total heats of adsorption on various metals. Due to the difficult reproducibility of placing the wire in the calorimetric vessel and with regard to the distribution of heat along the glowing wire, it is probable that individual films will differ in the extent of areas more or less sintered or ordered (i.e., of areas with a certain mutual relation of individual crystallographic planes). For the same reasons it is necessary to expect also certain nonreproducibility of the distribution of the film thickness in the calorimeter and, for example, the paper of Wedler and Fouad (*28*) on the CO–Ni system shows that also the mechanism of adsorption can depend to some extent on the film thickness. These circumstances can lead to the mentioned shift of heat-coverage curves in different experiments, amounting to several per cent. To a certain degree they could explain even the scattering of individual points on the same curve, especially so if the respective doses of gas are small and thus the heat does not represent an average value for a larger surface area. However, the main cause of this spread of points is, above all, by our experience, an error in determining the adsorbed amount. This point is the weakest spot of the whole measuring procedure, because the precision of measurements with the McLeod pressure gauge never exceeds 1–2% and the manner used for determining the adsorbed amount from the difference of the initial and final pressure makes possible a cumulation of these errors of measurement.

b. Heats of Hydrogen Adsorption on Clean Molybdenum Surface

On a clean surface of molybdenum hydrogen is instantly adsorbed at 20°C up to about 90% of the extent of its total adsorption. Adsorption of the remaining part is slower and above the film there appears a residual pressure. This residual gas mediates the heat exchange between the calorimeter and its surroundings whereby a calorimetric measuring is rendered impossible with these high coverage values in the arrangement used. The integral heat of adsorption of hydrogen on molybdenum between $\theta = 0$ and $\theta = 0.9$ is 31 kcal mole^{-1}. The initial heat of adsorption of hydrogen on molybdenum is 40 kcal mole^{-1}, which agrees with Dr. Ritchie's private communication (*7*). Thus molybdenum fits well between tungsten and iron (Fig. 6). This is in agreement with expectations, because the heat of adsorption of oxygen on molybdenum (*6, 24*) lies also between the heat on tungsten and iron and, in accordance with the rule of Tanaka and Tamaru (*29*), the order of metals according to the value of the heat of adsorption does not depend on the adsorbed gas.

The decrease of the heat of adsorption with the coverage can be understood as a symptom of the mobility of the adsorbed hydrogen on a heterogeneous film surface (*18, 23*), and thus the measured heat-coverage curve can be held to be very near to the curve of the real differential heat. This decrease of the heat of adsorption is smaller with molybdenum than with tungsten, but sharper than with iron, nickel, rhodium, etc. (Fig. 6). An explanation can be sought on the basis of the difference in the crystallographic structure of metals as suggested by Takaishi (*30*). In the case of metals with face-centered cubic (or hexagonal close-packed) lattices, as, for example, nickel or rhodium, electrons in *d* orbitals clearly contribute to the metallic binding in a lesser degree (*31*) and the energy levels of *d* orbitals of surface atoms, which perhaps preferentially enter into chemisorption binding, are thus less affected by the surface geometry. On the other hand in metals with a body-centered-cubic lattice, such as W, Mo, and Fe, the *d* electrons participate strongly in the metallic binding. Their energy levels, mainly in surface atoms, are therefore seriously affected by the surface geometry and this reveals itself by a more significant heterogeneity of the surface in the process of adsorption than with fcc metals. The measured heat-coverage curve of molybdenum, given together with Wahba and Kemball's (*12*) data for W, Fe, and Ni in Fig. 6, is in agreement with this hypothesis [the curves of Beeck (*22*), involving moreover Rh, as well as those of Brennan and Hayes (*18*) for W and Ni, give the same general picture, in spite of some discrepancy in numerical values]. At the same time this is at variance with the attempt of Kavtaradze (*32*) to describe the heat-coverage curves of hydrogen on all metals with a unique equation. Also, the measured value of the heat of hydrogen adsorption on molybdenum at $\theta = 0.5$ ($\sim$30.5 kcal mole^{-1}) differs from the value of 36–37 kcal mole^{-1} predicted by Kavtaradze (*33*) and shows that his attempt at a simple correlation of heats of adsorption of hydrogen with the position of the metal in the Periodic System of elements is not correct.

c. Heats of Sorption of Hydrogen on Molybdenum Partially Covered with Oxygen

The heats of sorption of hydrogen on molybdenum partially covered with oxygen are, up to high values of θ_H, slightly, but nevertheless clearly higher than on a clean surface (Fig. 5).* In our paper (*3*) it was

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* In principle, two methods are possible for presenting data for surfaces partially precovered by oxygen. It is possible to calculate θ_H as (1) a fraction of the complete hydrogen adsorption, or (2) as surface coverage of the whole surface. The unique curve for different extents of oxygen preadsorption and the absence of signs of mutual hydrogen–oxygen interaction in our case, justifies the plot according to (1).

stated that the behavior of hydrogen on a clean and partially covered molybdenum film is analogous and that neither the extent of adsorption nor the electric conductivity in the course of the sorption process offer any signs of a reaction between hydrogen and preadsorbed oxygen. However, it would be, for example, possible that this reaction proceeds in the surface layer which does not contribute with its electrons to the current through the film (*34*) and therefore it is not detectable by measuring the film resistance. The calorimetric behavior of this system can be considered as an additional support of the conclusion that a reaction of hydrogen with preadsorbed oxygen on molybdenum probably does not take place at all. For instance, no decrease in the rate of the heat liberation was noticed. The calorimetric method applied is highly sensitive in this respect and the lower rate of the heat liberation would suggest that not an adsorption, but a slower reaction in the adsorbed state is involved. Also, the whole course of the hydrogen sorption on a partially covered surface was, irrespective of the extent of oxygen preadsorption, entirely analogous, in point of calorimetry, with the adsorption on a clean surface.

There remains a question, of course, of how to explain the several per cent increase of the heat of hydrogen sorption on a partially covered surface. In the sense of considerations by Sachtler and van Reijen (*35*) it could be conceived, for example, that the oxygen preadsorption leads to a decrease of free valences on the metal surface so that the following adsorption of hydrogen will take place with a lower heat of adsorption. This, however, is at variance with our experimental results. A reverse hypothesis could be made, namely that the adsorption of oxygen leads to a disturbing of the film surface and a formation of new free valences so that thereupon hydrogen adsorption proceeds on a thus "prepared" surface with a higher heat of adsorption. If oxygen admitted in doses covers the film in successive bands beginning from the top of the calorimeter (*19*), the free metal valences produced by the oxygen adsorption would exist only on the borderline between the covered and uncovered part of the film, so that their number and therefore also the increase of the heat of the following hydrogen adsorption would not depend on the extent of the oxygen preadsorption. This hypothesis, of course, needs further experimental evidence. Thus, for the time being, there is no definitive answer to this problem.

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