Reports of the Academy of Sciences of the USSR

N. N. KAVTARADZE

1957

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1957. Volume 114, No. 4

PHYSICAL CHEMISTRY

N. N. KAVTARADZE

ADSORPTION OF HYDROGEN ON NICKEL LAYERS CONDENSED IN HIGH VACUUM

(Presented by Academician A. N. Frumkin, 27 XI 1956)

The nature of the adsorption of hydrogen on metals is still unclear. To study this phenomenon we used layers obtained by evaporation of metals of high purity. As a result, two groups of metals were identified, sharply differing in the character of adsorption of H_2 ($^{1-3}$). Data on the adsorption of H_2 on nickel make it possible to describe the features of metals of one of these groups. The layers were obtained in a round-bottom flask with an internal surface of 200 cm^2, sealed to a vacuum apparatus. A vacuum of $\leq 1–1.5 \times 10^{-7}$ mm Hg was attained by diffusion pumps operating on octoil S, and by cooling two traps with liquid nitrogen. The adsorption of H_2 (and Kr, when measuring the surface of the layers) was determined at temperatures from −195 to 100° and pressures from 10^{-6} to $2–4 \cdot 10^{-2}$ mm Hg by admitting a portion of gas and by the method of gas flow through a capillary (^{4,5}). The pressure was measured with a Pirani manometer. The influence of thermal effusion was taken into account by the method we published (^{6}). Ni layers were obtained by heating with electric current a spiral made of Ni wire (Ni 99.97%, Fe 0.018%, C 0.010%, Si 0.010%). The electrolytic H_2 used in the study was finally purified by diffusion through a Pd capillary.

The experiment consisted of: degassing the evaporator in an auxiliary vacuum apparatus; heating the reactor with the evaporator at 450° for 5 hr in a vacuum of $\sim 2 \cdot 10^{-7}$ mm Hg; determining calibration curves (flow into an empty reactor) at 0° and at the temperatures of the experiments; heating the reactor to 450° in a vacuum of $\sim 1–2.5 \cdot 10^{-7}$ mm Hg; evaporating Ni at 0° or −78°; heating the reactor with the Ni layer (if necessary) in a vacuum of $1–1.5 \cdot 10^{-7}$ mm Hg; cooling the reactor to the experimental temperature and measuring the adsorption.

At −195°, H_2 is adsorbed on Ni extremely rapidly: after admission of a portion of gas, 91% of the amount of H_2 adsorbed in the experiment is taken up in the first minute, and after 10 min, 98.4%. After 20 min from the beginning of the experiment, adsorption ceases and the pressure in the reactor remains

Fig. 1. Adsorption of H_2 at −195° on a Ni layer (thickness 440 Å): 1—admission of H_2 into an empty reactor; 2—first admission and 3—second admission of H_2 into a reactor with a Ni layer

Figure 1: Fig. 1. Adsorption of H_2 at −195° on a Ni layer (thickness 440 Å): 1—admission of H_2 into an empty reactor; 2—first admission and 3—second admission of H_2 into a reactor with a Ni layer

constant. Measurements of adsorption by the flow method (Fig. 1) showed that the pressure, equal before the experiment to $\sim 2 \cdot 10^{-7}$ mm Hg, during the initial period of H_2 flow (from 6 to 50 min, depending on the area of the layer) remains $\leq 2 \cdot 10^{-6}$ mm Hg, i.e., hydrogen is adsorbed practically instantaneously. The pressure rises sharply only after adsorption of $\sim 88\%$ of the total amount of gas taken up in the experiment. If the flow of H_2 is stopped at the very beginning of the pressure rise, it rapidly falls to a value $< 10^{-7}$ mm Hg. This fact indicates that in the concluding stage adsorption does not occur instantaneously. Stopping the flow 20-30 min after the beginning of the pressure rise does not lead to a change in it, i.e., adsorption has already been completed.

After the first flow of H_2 and evacuation of the reactor to $4 \cdot 10^{-7}$ mm Hg, a second flow was carried out. During evacuation, less strongly bound hydrogen was removed from the surface of the layer and part of the surf-

of Ni. Repeated adsorption during the second admission characterizes this part. The curve of the second admission did not coincide with the first. The second adsorption amounts to $\leqslant 3\%$ of the total absorption during the first admission;

Fig. 1. Adsorption of H_2 at −195° on a Ni layer (thickness 440 Å): 1—admission of H_2 into an empty reactor; 2—first admission and 3—second admission of H_2 into the reactor with a Ni layer

its curve rapidly reaches saturation and, at $P > 5 \cdot 10^{-3}$ mm Hg, changes noticeably no further. By stopping the admission of H_2 at any stage of this adsorption, its kinetics cannot be detected. The curve of the third admission, measured after a new evacuation of H_2, completely coincides with the preceding one. It follows from this that adsorption of H_2 during the second and third admissions may be regarded as completely reversible and practically instantaneous, and therefore it is permissible to consider it as a function of pressure. The isotherm of reversible adsorption is presented in Fig. 2; to a first approximation it follows the Langmuir equation. After evacuation of the reactor to $4 \cdot 10^{-7}$ mm Hg, the vacuum in it remains unchanged; when the temperature of the reactor is raised to −78°, a sharp rise in pressure is observed owing to desorption of hydrogen irreversibly adsorbed at −195°. Evacuating the reactor and raising its temperature from 0 to 200°, we found that at 150° and above desorption of H_2 was practically complete, and almost the entire surface of the layer was free.

Fig. 2. Isotherm of reversible adsorption of H_2 at −195° on a Ni layer (thickness 440 Å)

Fig. 2. Isotherm of reversible adsorption of H_2 at −195° on a Ni layer (thickness 440 Å)

Figure 2: Fig. 2. Isotherm of reversible adsorption of H_2 at −195° on a Ni layer (thickness 440 Å)

Fig. 3. Adsorption of H_2 on a Ni layer

Figure 3: Fig. 3. Adsorption of H_2 on a Ni layer

The facts described show that the total adsorption of H_2 (N_Σ) already at −195° consists of two parts: irreversible, rapid (N_n) and reversible, instantaneous (N_ob), and that H_2 irreversibly adsorbed at −195° is desorbed upon raising the temperature, and at 150° the Ni surface proves to be practically free of it. It was established that the maximum value of reversible adsorption ($N_\text{ob. max}$) at −195°, calculated by the Langmuir equation, exceeds its value at $P = 2 \cdot 10^{-2}$ mm Hg (see Fig. 2) by 1%, i.e., this equation is suitable for calculating $N_\text{ob. max}$. It was also shown that the fractions of both types of adsorption of H_2 on Ni do not depend on the thickness and surface of the layers.

Adsorption of H_2 on Ni at −78° retains the same qualitative features as at −195°; the difference consists only in an increase in the fraction of reversible adsorption to 18% of the total adsorption and in a more rapid completion of the latter. The rate of adsorption of H_2 on Ni at 0° is also high; when a portion of gas is admitted into the reactor with a Ni layer condensed at 0°,

in the first minute 95% of the total amount of gas absorbed in the experiment was sorbed. Absorption of the remaining 5%, however, continued for 60–80 min. Fearing that such prolonged absorption of this 5% of gas was associated with its dissolution in the layer and in the evaporator (a nickel coil weighing ∼ 500 mg), we measured adsorption at 0, 50, and 100° on nickel layers previously heated at 200° in an H_2 atmosphere ($P = 2 \cdot 10^{-2}$ mm Hg), and then pumped at this temperature down to $2 \cdot 10^{-7}$ mm Hg.

Table 1

Surface area of Ni layers per 1 hydrogen atom adsorbed at −195°*

No.	T_ads, °C	Gas	σ_g, Å^2	σ_H, Å^2	Source
1	−195	Kr	18.5; 14.6	7.55; 5.98	Our data
2	−195	Kr	18.5; 14.6	7.78; 6.11	Our data
3	−195	Kr	18.5; 14.6	7.53; 5.94	Our data
4	−195	Kr	14.6	6.18	Beek' s data (9)
5	−78	n-C_4H_{10}	24.5	6.18	Beek' s data (9)

* T_ads is the adsorption temperature of the gas selected for measuring the surface; σ_g is the adopted value of its landing area; σ_H is the area per 1 hydrogen atom.

Fig. 3. Adsorption of H_2 on a Ni layer (thickness 1662 Å, heated at 200°) at temperatures: a —at −195°; b —at 0°; v —at 50°; g —at 100°; 1 —inflow of H_2

into an empty reactor, number of molecules in the reactor; 2 —total adsorption, and 3 —reversible part of H_2 adsorption.

In this case adsorption ended rapidly. The data obtained (Fig. 3) show that the qualitative features of adsorption determined at −195 and −78° are retained also at elevated temperatures; only the ratio between its irreversible and reversible fractions changes, the amount of adsorption increases, and at the same time the reversible part increases while the amount of irreversible adsorption decreases. It should also be noted that the initial portion of the isotherm of reversible H_2 adsorption on Ni at −78, 0, 50, and 100° deviates somewhat from the Langmuir equation, but, as calculations showed, is well described by the logarithmic dependence on pressure established by A. N. Frumkin and A. N. Shlygin ([7,8]). The qualitative features of H_2 adsorption on Ni are also characteristic of H_2 adsorption on Fe, Cr, and Pt.

To calculate the filling of the surface of the layers with hydrogen adsorbed at −195°, the surface of the same layers was determined from Kr adsorption at −195°. Our data agree well with Beek' s measurements ([9]) for layers condensed in vacuum (see Table 1): if one assumes that H,

adsorbed at −195° is in the atomic state, then it may be considered that at this temperature and $P = 2 \cdot 10^{-2}$ mm Hg the surface is almost completely covered with atomic hydrogen, i.e., with a surface hydride.

The study of the influence of the order of temperature variation on the total uptake showed that, when adsorption is measured starting from the highest temperatures (100°) down to low temperatures (−195°) and then back to high temperatures, its values are reproduced and there is no hysteresis of absorption, i.e., the sorption curve is an equilibrium one; between 0 and −78° it has a maximum. On the contrary, if adsorption is measured starting from −195° to 100°, and then to −195° (Fig. 4), hysteresis of absorption is revealed, but the maximum between 0 and 78° is again confirmed for the curve going from 100 to −195° (curve 1′). After heating the layer in H_2 at 150° and pumping out the reactor to $2 \cdot 10^{-7}$ mm Hg, the experiment was repeated in the same order (curve 2); it confirmed hysteresis, but again also confirmed the adsorption maximum (see curve 2′). Measurements of H_2 adsorption on iron layers confirmed the presence of sorption hysteresis and its maximum in this system as well, but at the same time showed a more sharply expressed decrease in hydrogen uptake when the temperature was lowered from −78 to −195° or from 0 to −78 and −195°.

Fig. 4. Sorption of H_2 (with a constant amount of it in the system) by a Ni layer (thickness 1674 Å): 1 and 1′—sorption of H_2 on a Ni layer heated at 150° in vacuum; 2 and 2′—sorption of H_2 on the same layer, but heated in H_2 ($P \sim 2 \cdot 10^{-2}$ mm Hg) at 150° and then pumped down to $2 \cdot 10^{-7}$ mm Hg.

The data presented show that adsorption of H_2 on Ni, and also on Fe, Cr, and Pt, is a complex process: it is composed of reversible and irreversible parts, the first of which depends sharply on pressure and temperature, while the second depends mainly on temperature; no influence of pressure on the magnitude of adsorption is observed in the pressure range studied.

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
22 XI 1956

CITED LITERATURE

1. N. N. Kavtaradze, *Heterogeneous Catalysis in the Chemical Industry*, Materials of the All-Union Conference, 1953, Moscow, 1955, p. 150.
2. N. N. Kavtaradze, *Electronic Phenomena in Catalysis and Adsorption*, Publishing House of the Academy of Sciences of the USSR, 1956, p. 235.
3. N. N. Kavtaradze, Abstracts of Papers, Conference on Catalytic Hydrogenation and Oxidation, Alma-Ata, 1954, p. 24.
4. C. Zickermann, *Zs. Phys.*, **88**, 43 (1934).
5. S. Yu. Elovich, F. F. Kharakhorin, *Problems of Kinetics and Catalysis*, **3**, 225 (1937).
6. N. N. Kavtaradze, *ZhFKh*, **27**, 1083 (1954).
7. A. N. Frumkin, A. N. Shlygin, *DAN*, **2**, 176 (1934).
8. A. N. Frumkin, A. N. Schlygin, *Acta Physicochim.*, **3**, 791 (1935).
9. O. Beeck, A. W. Ritche, *Disc. Farad. Soc.*, No. 8, 159 (1950).

Note: Figure translations are in progress. See original paper for figures.