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Sorption and Reactions of Atomized Hydrogen on Metals

V. PONEC, Z. KNOR, AND S. ČERNÝ

From the Institute of Physical Chemistry, Czechoslovak Academy of Sciences, Prague

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The sorption of atomized hydrogen on films of transition metals and of copper and its reaction with oxygen have been studied by volumetric measurements of the extent of sorption and by following the changes in the electric resistance of the films. The extent of hydrogen atom sorption indicates the dependence on the metal–metal bond strength; the reactivity of adsorbed gases is in some way correlated with the heat of adsorption. An attempt has been made to locate the activation energy barrier in the hydrogen–oxygen interaction.

Sorption of hydrogen atoms on metals is of particular interest since sources of atomic hydrogen are often incorporated near to metal surfaces, which may be either clean or partially covered with adsorbate, in many vacuum systems, e.g., ionization gauges, etc. This fact, combined with the possibility of gaining a deeper understanding of adsorption and catalytic oxidation of hydrogen on metals, which a study of the interaction of atomic hydrogen offers, was an incentive for the present work.

On transition metals molecular hydrogen is readily adsorbed even at low temperatures (78°K) (*1*). This ready sorption of "molecular" hydrogen by transition metals (even without atomization in the gas phase) is evidently the reason why scant attention has hitherto been accorded in the literature to interactions of atomized hydrogen with the surfaces of transition metals (*2*). Judging from a note (*3*), the problem is at present being studied by Herley. It is highly probable that hydrogen adsorbed on the surface of transition metals is in a great part dissociated. With some of the transition metals hydrogen even forms relatively stable hydrides, the formation of such hydrides being, e.g. exothermic for palladium and endothermic for nickel and iron. Somewhat more information is available on the interactions of atomic hydrogen with the surfaces of copper (*5–8*), mercury (*8–9*), glass (*8–11*), silver (*5–7*), gold (*5–7*), carbon (*12*), and germanium (*13*): On all such surfaces sorption takes place to a considerable extent at 78°K, but from the metallic elements hydrogen desorbs when heated to 273°K.

EXPERIMENTAL WORK

Apparatus and Technique Used

The apparatus, the measuring procedure, the preparation of films, and the evaluation of experimental data have been previously described (*14*). Hydrogen was atomized on a hot tungsten filament 0.05–0.15 mm diam, 50–60 mm long placed in a spherical vessel 60 mm diam, with platinum contacts stuck to glass on the sides of the vessel (*15*). Metallic films of nickel, molybdenum, and rhodium were condensed at 78°K by direct evaporation of the respective wires 0.2–0.4 mm diam, copper and manganese were evaporated from a tungsten or molybdenum coil electrolytically coated with a layer of the respective metal (*16*). The vacuum during the evaporation of metals was of the order of 10^{-8} Torr except for manganese, when the pressure was one or two orders of magnitude higher.

The temperatures specified in the sections to follow as temperatures of adsorption or interaction are those of the thermostatic baths; the temperature of the film was not measured. The analysis of the composition of hydrogen–oxygen mixtures was carried out using Pirani and McLeod gauges.

RESULTS

Clean Surfaces of Metals, Temperature of 78°K

Hydrogen was first adsorbed on the surface of metals without atomization in the gas phase. Since the population of the individual crystallographic planes in the surface of metals is not known, it is not possible to determine the number of atoms in the metal surface from the known surface area measured with krypton or xenon (*17*). Moreover, some uncertainties also exist as regard the proper mechanism of hydrogen adsorption (*18*). It is not known, for instance, whether the adsorption is exclusively dissociative. But it may be asserted with considerable evidence that the extent of hydrogen adsorption without external atomization (i.e., the number of occupied adsorption sites) corresponds (*15*) to at least one-half of the surface atoms of the metal on nickel, rhodium, and molybdenum [and also on platinum (*19*) according to literature]. For such an estimate the value of the extent of hydrogen adsorption at 78°K attained in steady state (after about 1 hour) at pressures of the order of 10^{-2} Torr when adsorption no longer changes either with pressure or time ($\theta = 1$) was always used.

Of the remaining metals being studied, the extent of hydrogen adsorption without atomization is very low at 78°K ($\approx$20% of maximum sorption at 195°) for manganese. This agrees well with data by Greenhalgh and Trapnell (*20*), and Suhrmann *et al.* (*21*). On copper molecular hydrogen is not adsorbed [see also (*1, 5–8*)].

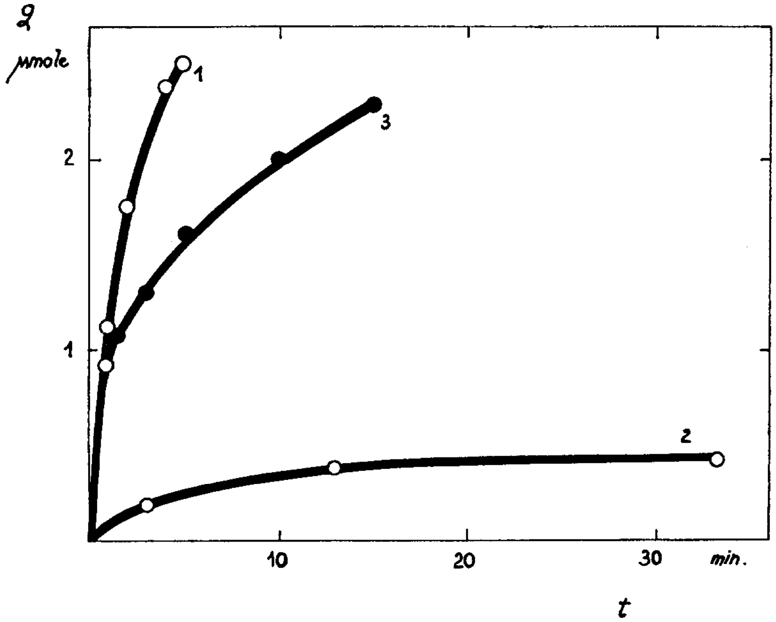

FIG. 1. Time course of sorption (in μM) of atomized hydrogen on various surfaces at 78°K: 1, molybdenum covered with preadsorbed oxygen; surface area of film prior to hydrogen sorption, 1300 cm²; 2, molybdenum covered by sorption of hydrogen without atomization; surface area of film, 2160 cm²; 3, nickel covered by sorption of hydrogen without atomization; surface area of film, 850 cm². Sorption took place from one dose, pressure during the course of slow sorption was of the order of 10^{-2} Torr.

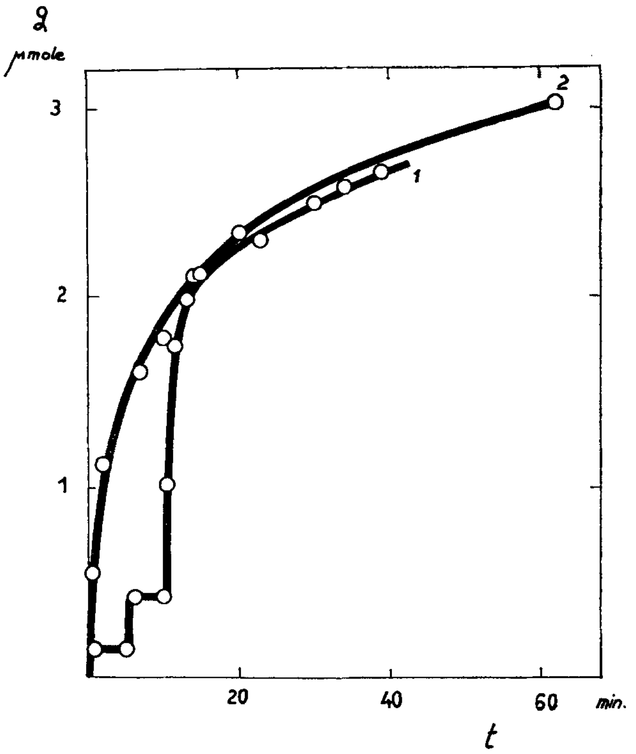

FIG. 2. Time course of sorption (in μM) of atomized hydrogen on various surfaces at 78°K: 1, rhodium covered by sorption of hydrogen without atomization; surface area of film, 985 cm^2. Sorption took place in three doses; in the first two pressure dropped to zero almost instantaneously; pressure at the end of third dose ~ 10^{-2} Torr. 2, Copper; surface area of film not measured. Surface area of copper films measured in other experiments was of the same order of magnitude as that of other metals (Rh, Ni). Sorption took place from one dose, pressure at the end of measurement ~ 10^{-2} Torr.

After attaining a steady state of sorption without atomization at 78°K, the gas phase was evacuated at this temperature [no more than 1% to 2% of previously adsorbed hydrogen desorbs at this temperature from the surface of nickel (*22*), molybdenum (*15*), and rhodium (*23*), and the heating of the atomizing filament in the adsorption vessel switched on. The resistance of the film always increased slightly (more at 273°K than at 78°K) when the heating of the filament was switched on and correspondingly decreased when switched off. The increase in resistance is apparently caused by radiative heating of the film, and the presence of gas slightly raises the temperature of the film yet further. The value of film resistance established with the hot atomizing filament in vacuum, was taken for the initial (zero) value. During the experiment doses of hydrogen were introduced into the vessel with the tungsten filament hot, and the sorption of this gas observed while simultaneously measuring the change in film resistance. Very rapid sorption of atomized hydrogen takes place on nickel and rhodium; it does not slow down until the extent of sorption corresponding to $\theta = 1$ according to the above definition is exceeded several times. The extent of atomized hydrogen sorption at 78°K is likewise large on manganese and copper (Figs. 1 and 2); it is quite comparable with that of the metals mentioned above. The sorption is accompanied by an increase in film resistance which proves that hydrogen is actually sorbed by the film and not only

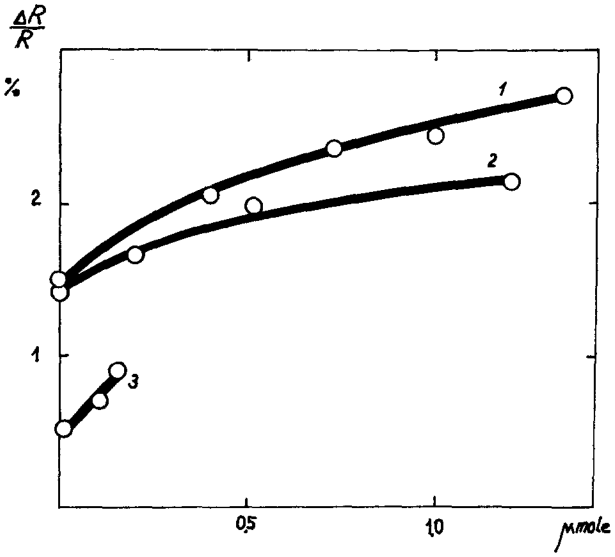

FIG. 3. Relation between relative change (%) of film electric resistance and extent of sorption of atomized hydrogen (μM); 1, nickel; 2, rhodium; 3, molybdenum. Initial value of resistance change corresponds to $\Delta R/R$ caused by adsorption of hydrogen without atomization on the same surface.

by glass, leads, etc. (Fig. 3). In all cases under investigation, hydrogen atomized in the gas phase caused an increase in resistance of films with clean surfaces during its sorption.*

The rate of formation of hydrogen atoms depends on the temperature of the tungsten filament, which varies owing to the pressure decrease during hydrogen sorption. The temperature of the filament was not determined and different filaments were used in comparative experiments; consequently the kinetics of sorption could not be examined quantitatively.

Molybdenum differs significantly in the extent of its sorption of atomized hydrogen from the metals hitherto discussed. Its sorption of atomized hydrogen already stops at 78°K on reaching $\theta \approx 1.12$ (average of three experiments).

Clean Surfaces of Metals, Temperature of 273°K

If the surfaces of nickel, molybdenum, or rhodium are covered with a complete layer of hydrogen (formed by the adsorption of molecules) at 273°K, no sorption of hydrogen atomized in the gas phase at this temperature but merely its recombination takes place. [All metals under study rather efficiently catalyze the recombination of hydrogen atoms at 273°K (*25*)]. This means that in the steady state the coverage of the surface with hydrogen is the same during the recombination as when gaseous molecular hydrogen is admitted to the film. The electric resistance of the film remains unchanged within the limits of experimental error.

The behavior of copper films at 273°K is an open question. Copper at this temperature does not adsorb molecular hydrogen. But a considerable sorption of atomized hydrogen follows the heating of the tungsten filament. In view of the character which the dependence of the film resistance variations accompanying such sorption possesses (see Fig. 8) one cannot entirely exclude the possibility that this sorption —at least partly—rests in the interaction between hydrogen and the impurities which were present on the surface of copper film, despite the fact that the preparation of

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* NOTE: As preliminary results (*24*) indicate, iron by its behavior may also be included in this group of metals (Ni, Cu, Rh).

films was accorded the utmost care. Sorption of atomized hydrogen is for the most part irreversible—after switching off the atomizing filament, only a negligible portion (less than 1% to 2% of the preceding sorption) of hydrogen desorbs.

If a certain amount of atomized hydrogen is adsorbed on the surface of copper film at 78°K, hydrogen does not desorb completely when the temperature is raised to $T = 273$°K (Fig. 4, Table 1).

The presence of impurities on the surface of manganese is even more probable.

Sorption and Interaction of Atomized Hydrogen on Surface of Metals Covered with Oxygen

In another series of experiments the surface of metals under study was covered with oxygen at 78°K or 273°K, and the sorption of atomized hydrogen at 78°K examined.

On molybdenum the subsequent sorption of atomized hydrogen at 78°K was substantially enhanced by preadsorption of oxygen as compared with that of a clean metallic surface (Fig. 1). When a molybdenum film which was covered with oxygen ($\approx$2 μM) at 273°K and then saturated at 78°K (to a state close to the steady one) with atomized hydrogen (2.6 μM) is rap-

TABLE 1

SORPTION AND DESORPTION OF HYDROGEN ON THE SURFACE OF COPPER

Extent of oxygen preadsorption, (μM)	Extent of sorption[a] of atomized hydrogen at 78°K (μM)	Extent of hydrogen desorption[b] after heating to 273°K (μM)
0.39	0.65	0.12 (18%)
0.24	1.09	0.13 (12%)
0	3.04	2.18 (72%)[b]
0	1.25	1.02 (82.5%)[b]
0	0.83	0.33 (44%)[b]

[a] Under conditions close to steady state.

[b] Data pertain to desorption following the first sorption of atomized hydrogen. In repeated cycles of sorption and desorption on the same film, desorption of newly sorbed amount is always complete (Fig. 4).

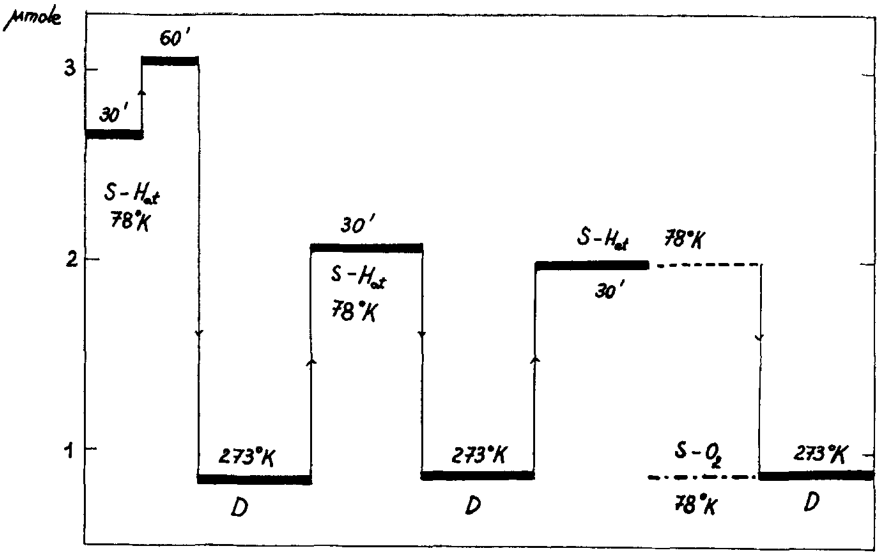

FIG. 4. Repeated sorption on copper at 78°K (extent marked $S\text{-}H_{\mathrm{at}}$) and desorption at 273°K. Total amount of irreversibly consumed hydrogen (i.e., of part of hydrogen not desorbing in the form of hydrogen gas) is denoted with D. Time of duration of sorption (in min) marked in diagram. Extent of oxygen sorption at 78°K into layer of hydrogen marked $S\text{-}O_2$. Sequence of measurements: Hydrogen sorption at 78°K, desorption of 273°K, sorption at 78°K, desorption at 273°K, sorption at 78°K. Then, oxygen sorption (.-.-) into the layer of sorbed hydrogen and hydrogen desorption at 273°K.

idly heated to 273°K, a virtually instantaneous desorption of about 40% of hydrogen occurs while another 10% escapes in the course of subsequent slow desorption at 273°K (*15, 26*) with ensuing slight decrease in film resistance.

The character of sorption of atomized hydrogen at 78°K on copper entirely covered with oxygen (at 273°K) in no way differs from that of sorption on an uncovered surface. When the film is rapidly heated at 273°K, a substantially smaller part of the hydrogen is desorbed. Table 1 and Figs. 4 and 5 may be used for the purpose of comparison.

The extent of sorption of atomic hydrogen on nickel at 78°K is large even after preadsorption of oxygen, but sorption on a surface previously completely covered by oxygen at 273°K is characterized in that at 78°K no change in film resistance (Fig. 6) occurs during the sorption of atomic hydrogen. A surface covered with 1.95 μM of oxygen, sorbed after 30 min at 78°K 0.95 μM of atomized hydrogen (no hydrogen without external atomization being sorbed by the film at all). When rapidly heated, with the atomizing filament switched off, to 273°K, 0.21 μM of hydrogen desorbed from the surface of nickel, thus covered, in 1 min; subsequently the sorbed amount remained time-invariant (Fig. 7). But after heating to 273°K the resistance of the film slowly decreased (Fig. 7). The same film rapidly heated to 273°K prior to sorption of atomized hydrogen attained in 1 to 2 min a value of resistance that varied no longer.

The initial interaction of atomic hydrogen with rhodium surfaces covered by oxygen at 78°K (the oxygen having been adsorbed at the same temperature) results in a small increase of film resistance. Subsequent doses cause a slow decrease which evidently accompanies the interaction of hydrogen with oxygen (*23*).

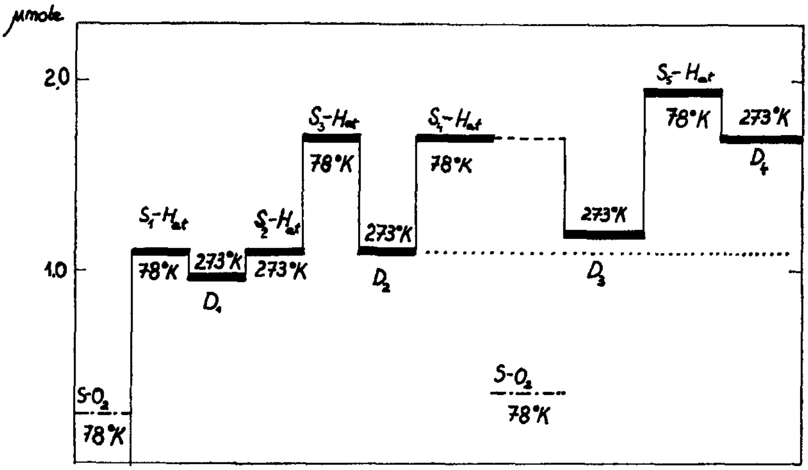

FIG. 5. Sorption of atomized hydrogen (S_1–H_{at}) at 78°K on copper covered with oxygen (.–.–). Repeated sorption at 78°K and 273°K (S_2–S_5) and desorption at 273°K. Total amount of irreversibly consumed hydrogen, i.e., of part not desorbing after heating to 273°K in the form of hydrogen gas, is denoted with D. Difference in extent of desorption of atomized hydrogen between D_2, D_3, and D_4 gives evidence of interaction with adsorbed oxygen.

At a temperature of 273°K hydrogen atomized in the gas phase reacts with preadsorbed oxygen on molybdenum (*15, 26*), nickel (*26*), and copper as well. Both rhodium (*23*) and palladium (*27*) surfaces covered with oxygen react with hydrogen at this temperature even without the aid of external atomization. The initial instantaneous sorption of atomic hydrogen on molybdenum films causes an increase in

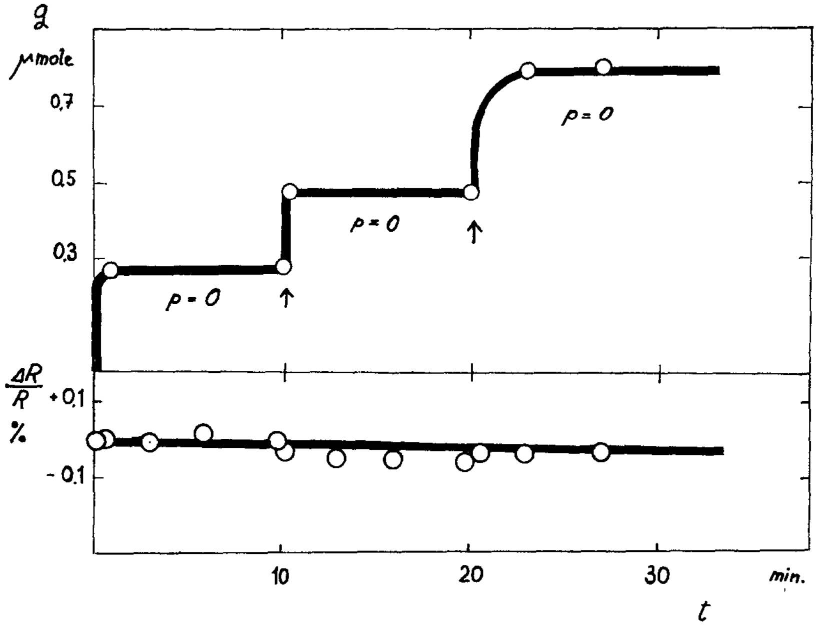

Fig. 6. Time course of sorption of atomized hydrogen (in μM) at 78°K on nickel with surface completely covered by oxygen adsorption (1.95 μM); ↑ denotes instant of dose introduction. Pressure of hydrogen was zero at the end of sorption. Lower part of diagram indicates time course of change in film electric resistance measured during sorption of atomized hydrogen.

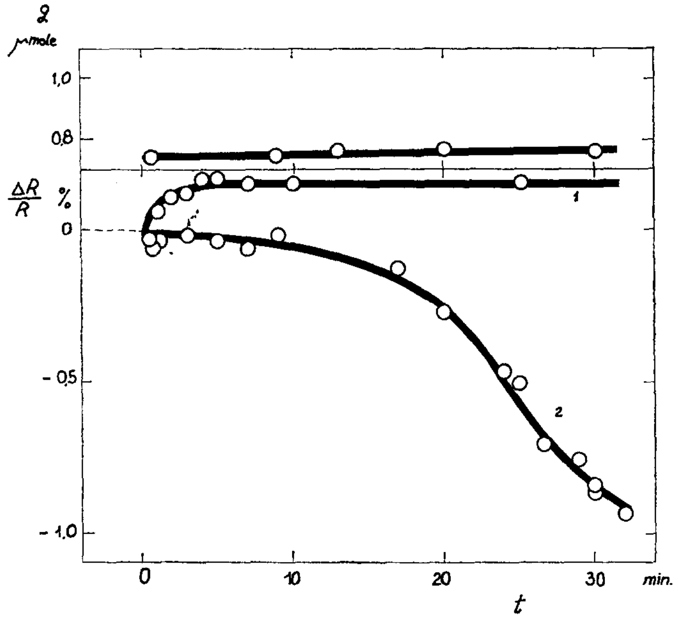

Fig. 7. Upper part: Extent of sorption of atomized hydrogen by nickel at 273°K. Nickel surface was completely covered with oxygen—1.98 μM—at 78°K. Lower part: Time course of changes (%) in electric resistance during rapid heating of film from 78°K to 273°K: 1, surface of film covered with oxygen only; 2, surface of film covered with oxygen and saturated by sorption of atomized hydrogen in given extent (0.95 μM). Pressure in gas phase at 274°K, 1.7 × 10^{-2} Torr.

resistance. Subsequently, *in vacuo*, the resistance of the film decreases as a result of a slow process that follows. In contrast, the resistance of nickel film (*26*) decreases monotonically from the very beginning of sorption when atomized hydrogen is sorbed in the layer of adsorbed oxygen at 273°K. An effect similar to that on molybdenum may be observed on copper (Fig. 8): The resistance decreases only after an initial increase. Whereas on molybdenum and nickel sorption of neither oxygen nor atomic hydrogen can be repeated at 273°K on a surface on which the interaction between preadsorbed oxygen and atomized hydrogen had already taken place (to a state close to the steady one), on copper the cycle: sorption of oxygen–sorption of atomized hydrogen–sorption of oxygen can be repeated several times. If the gas phase is evacuated, the value of resistance of copper film repeatedly decreases after each cycle.

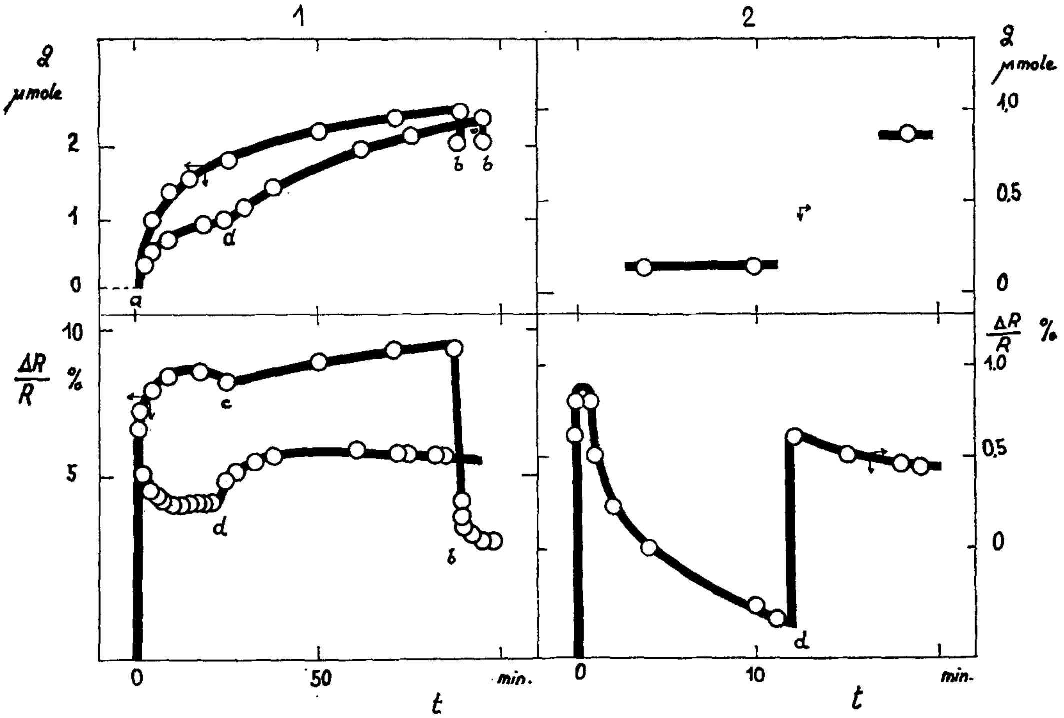

FIG. 8. Sorption of atomized hydrogen on copper at 273°K: 1, surface uncovered by oxygen preadsorption (for two different measurements); 2, surface covered by oxygen preadsorption; a, heating of atomizing filament switched on; b, atomizing filament switched off; c, increasing temperature of atomizing filament; d, new dose introduced. Lower part: Time dependence of changes (%) in film resistance. Upper part: Time dependence of adsorbed amount; desorption at switched-off filament (b) is indicated.

Sorption of Oxygen by Surfaces Covered with Hydrogen

If oxygen is introduced at 78°K on a film of molybdenum covered with a layer of hydrogen (sorption without atomization in the gas phase), the electric resistance of the film increases during the oxygen sorption and 30% to 40% of hydrogen desorbs, as stated in our previous paper (*15*).

After adsorbing "molecular" (without atomization) hydrogen on nickel films at 78°K, admitting oxygen caused the resistance to increase. Hydrogen does not desorb when the system is heated to 273°K.

If oxygen is introduced at 78°K on the surface of nickel covered with a complete layer of hydrogen (produced by supplementing the adsorbed layer of hydrogen with sorption of atomized hydrogen), oxygen sorption raises the film resistance and no hydrogen desorbs. But a substantial portion of hydrogen bonded on the film in the course of sorption with atomization desorbs during rapid heating* of the system to 273°K. Oxygen does not desorb following an increase in temperature (Table 2, Fig. 9).

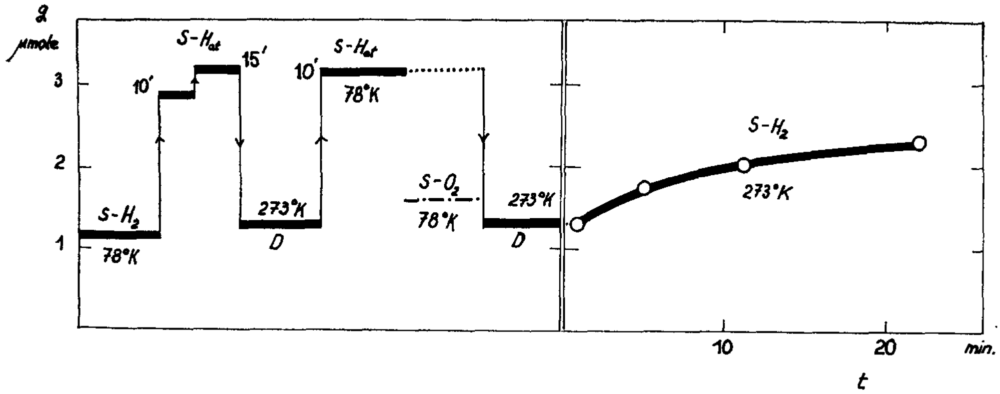

Fig. 9. Repeated sorption and desorption of hydrogen on nickel in the sequence shown on the figure. S–H_{at}, extent of sorption with atomization of hydrogen in gas phase; S–H_2, extent of sorption without atomization at given temperature; D, extent of irreversible sorption after heating of film to 273°K; S–O, extent of oxygen sorption at 78°K into hydrogen layer. Time course of slow hydrogen consumption after heating the composite adsorbed layer to 273°K is shown.

TABLE 2

Thermal Desorption of Hydrogen from Nickel—Desorption of Hydrogen from Layer Completed by Oxygen Sorption

Extent of hydrogen sorption at 78°K (μM)		Extent of subsequent oxygen sorption at 78°K (μM)	Extent of hydrogen desorption after heating to 273°K
Sorption of molecules	Sorption of molecules + atoms		
0.41	3.3	—	2.6 (79%)
0.41	3.3	0.67	2.0 (61%)
1.07	3.4	—	2.12 (62%)
1.07	3.4	1.51	2.06 (60%)

Copper behaves entirely analogously, as does nickel. On repeated sorption of atomized hydrogen at 78°K and desorption at a higher temperature, a state may be attained in which all sorption of atomized hydrogen is reversible with temperature (Fig. 5). If oxygen is admitted at 78°K into the layer (the film resistance increases) and the system rapidly heated to 273°K, hydrogen desorbs to virtually the same extent as it does from a clean surface. If the procedure is reversed and sorption of atomized hydrogen takes place at 78°K into the complex adsorbed layer of hydrogen with oxygen, hydrogen desorbs appreciably less as the temperature is increased (Table 1).

Discussion

Hydrogen atomized in the gas phase at 78°K is sorbed to a considerable extent by films of nickel, rhodium, copper, manganese, and iron. Thus, e.g. on nickel, sorption of atomized hydrogen is several times that of hydrogen without atomization (Table 2). Sorption of hydrogen takes place to such an extent that penetration of hydrogen into film structure may be assumed. On other metals specified above, the situation is qualitatively similar. But a quantitative comparison of metals as to the extent of sorption of atomized hydrogen is rather difficult. In no case is sorption that at equilibrium but merely sorption

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* No oxygen present in the gas phase during heating.

under conditions close to the steady state at 78°K; the extent of steady state sorption might be remote from equilibrium sorption to different degrees for different metals. Moreover, the amount of sorbed atomized hydrogen is not proportional to the size of the surface; consequently no comparison can be made of the individual metals or films of the same metal as to sorption per 1 cm^2 of the metal surface. Despite this difficulty, molybdenum may be clearly distinguished from the above group of metals. Sorption of atomized hydrogen (after the sorption without atomization) is of a relatively small extent on this metal. Yet one cannot rightly state that during adsorption without external atomization molybdenum is covered with hydrogen to a larger extent than, e.g. is nickel or rhodium (*15, 23*). Neither is the dissimilar behavior of molybdenum related to its crystallographic structure. Molybdenum differs in its crystal lattice (body-centered cubic, bcc) from nickel, rhodium, and copper (face-centered cubic, fcc). Iron (*24*) which behaves similarly to the latter metals has the same crystal lattice as molybdenum. It is remarkable that covering molybdenum with oxygen produces a considerable increase in sorption of hydrogen atoms at 78°K (Fig. 1). Yet a larger portion of this sorbed hydrogen does not react with oxygen as indicated by the fact that the former desorbs into the gas phase on heating to 273°K. It seems that the extent of sorption of atomized hydrogen (attained under conditions close to steady state) is to a decisive manner affected by the strength of crystal lattice. Such an assumption enables us to explain the difference that exists between molybdenum and the other metals; from this one may infer that increased sorption of hydrogen after oxygen preadsorption is related to the fact that the surface of molybdenum is disturbed by oxygen. Were such an explanation correct, the results obtained in our study would provide further corroboration for the disturbing of bonds in metals during gas adsorption. The possibility of disturbing the metal–metal bonds in the course of adsorption is discussed in theoretical papers by Dowden (*28*); Schuit, van Reijen, and Sachtler (*19*); Sachtler and van Reijen (*30*); and Manes and Molinari (*31*).

It has already been stated in the foregoing that one can judge from the extent of sorption of atomized hydrogen as to the penetration of hydrogen into the metal structure. In spite of its assumed similarity to hydrogen dissolved in the film structure after adsorption of molecular hydrogen, atomized hydrogen causes an increase in electric resistance of the film in all cases. This fact appears to be at variance with the effect ascribed to the dissolved hydrogen by Sachtler and Dorgelo (*32*). These authors attempted some time ago to explain the complex character of the relation between the changes in film resistance and adsorption of hydrogen by assuming that the drop in film resistance, appearing when the surface is covered to a certain degree, is effected by the very hydrogen dissolved in the structure. The bond between dissolved hydrogen and metal is weak; hydrogen recombines and desorbs on heating to 273°K.

Sorption of atomized hydrogen by films of copper, molybdenum, and manganese covered with oxygen causes at 78°K an increase in film resistance. On rhodium, on which interaction takes place even at that temperature, continued sorption of atomized hydrogen brings about a decrease in electric resistance (*22*). Only on nickel covered with oxygen does the film resistance remain unchanged during sorption of atomized hydrogen at 78°K. Similar behavior was previously observed on films of palladium (*27*), saturated with hydrogen, during sorption of oxygen at 78°K. Oxygen sorption on palladium film proceeded to an unaltered extent regardless of the extent of previous sorption of hydrogen at 78°K; the change in the film electric resistance resulting from adsorption of oxygen at the same temperature decreased, however, with increasing extent of previous sorption of hydrogen. When the film was saturated with hydrogen at 78°K, oxygen had no effect on electric resistance of the film during adsorption at the same temperature.

The results obtained with palladium and nickel may be explained, e.g. by the fact that a layer containing the first sorbed gas is to some extent excluded from the process of conducting electric current through the metal (*33, 34*). However, such an exclusion is not irreversible, as proved by processes taking place during heating of the film and in interactions of hydrogen and oxygen.

The reaction of hydrogen atoms trapped in the oxygen layer is far easier on nickel and copper than on molybdenum. Atomized hydrogen sorbed at 78°K on nickel and copper reacts for the most part with preadsorbed oxygen when the film is heated to 273°K. In contrast, it reacts not at all or only for a small part on molybdenum. Hydrogen atomized in the gas phase effects at 273°K an instantaneous drop in film resistance on nickel covered with oxygen when a dose of hydrogen is admitted. In the analogous cases of copper and molybdenum, first an increase and only thereafter a decrease in film resistance is observed. The dependence of differential heat of adsorption of hydrogen on temperature (*35*) together with a comparison of curves depicting the relation between changes in film resistance and the adsorbed amount of hydrogen at 78°K and 273°K, and finally the results obtained with the field-emission electron microscope (*36, 37*) indicate that at 273°K hydrogen is mobile on the surface of molybdenum as it is on the surface of nickel. Lower (compared with nickel) activity of molybdenum in reaction of atomized hydrogen with oxygen is therefore somehow associated with higher heat of adsorption of both hydrogen and oxygen on molybdenum.

The product of interaction of hydrogen atoms with preadsorbed oxygen adheres to the surface of nickel and molybdenum (*26*) and does not desorb at 273°K, whereas on copper successive alternation of sorption of oxygen and atomized hydrogen might be repeated several times; in other words, the product of interaction desorbs and makes the surface free. Similar findings on copper have also been established by other authors (*5–7, 38*). While for nickel a free surface uncovered with oxygen (*39*), or, alternatively, the existence of adsorbed hydrogen, is a sufficient condition for molecular hydrogen to react with preadsorbed oxygen at a temperature lower than 300°K, on molybdenum hydrogen adsorbed on the free part of the surface does not react with oxygen (*15*). To nickel covered with oxygen, hydrogen capable of reaction might also be "supplied" by atomization and sorption at 78°K or by adsorption (without atomization) on the surface of nickel which is evaporated on a layer of oxygen covering the original nickel film (*26*). But on molybdenum hydrogen reacts with a layer of oxygen only if it is introduced on the oxygen layer after atomization right at 273°K. On molybdenum, the transition of atomized hydrogen to the final product of interaction (probably a hydroxyl group) is evidently preceded by sorption of atomized hydrogen. Similarly on copper, hydrogen at 273°K reacts with oxygen only if atomized. Sorption of hydrogen without atomization does not even proceed on copper uncovered with oxygen.

Comparing the above results obtained in the study of reactions between hydrogen and oxygen on the surface of various metals, we arrive at the following conclusions. Adsorption of both constituents entering the reaction, i.e., hydrogen and oxygen, and low heat of adsorption of the two gases are the prerequisites for high activity of metals in catalytic reaction of hydrogen and oxygen at temperatures lower than 300°K. This rule also seems to possess general validity for other catalytic reactions (*40, 41*).

It is of particular interest to compare experiments with a mutually reversed sequence of sorption of gases, i.e. experiments in which preadsorption of oxygen was followed by sorption of atomized hydrogen and experiments, in which presorption of atomized hydrogen was followed by sorption of oxygen. If atomized hydrogen is admitted at 78°K to the layer of oxygen adsorbed on Cu or Ni, then a reaction takes place after heating the system to 273°K. However, if the procedure is reversed and oxygen is admitted at 78°K to the surface of Ni or Cu after the adsorption of molecular hydrogen supplemented by sorption of atomized hydrogen, no reaction between oxygen and presorbed atomized hydrogen occurs when the temperature is raised to 273°K (Figs. 4 and 10). Oxygen preferentially reacts with nickel or copper and does not react with sorbed hydrogen atoms. Hydrogen at higher temperatures, i.e. at temperatures in the vicinity of 273°K, might obviously react with oxygen only if trapped from the gas phase directly by a layer of oxygen and not if trapped in the metal phase before oxygen adsorption, despite the weak bond between sorbed hydrogen and metal. As Fig. 9 indicates, hydrogen trapped in nickel first desorbs after heating and then—if the surface is incompletely covered with oxygen—reacts with oxygen preadsorbed on nickel until repeated readsorption from the gas phase takes place. If the surface is entirely occupied by oxygen, i.e. if there is during the increase in temperature from 78° to 273°K enough oxygen in the gas phase to simultaneously raise the adsorbed amount of oxygen up to the "total coverage" of the surface, hydrogen desorbs during heating and no longer enters the reaction at 273°K (Fig. 10).

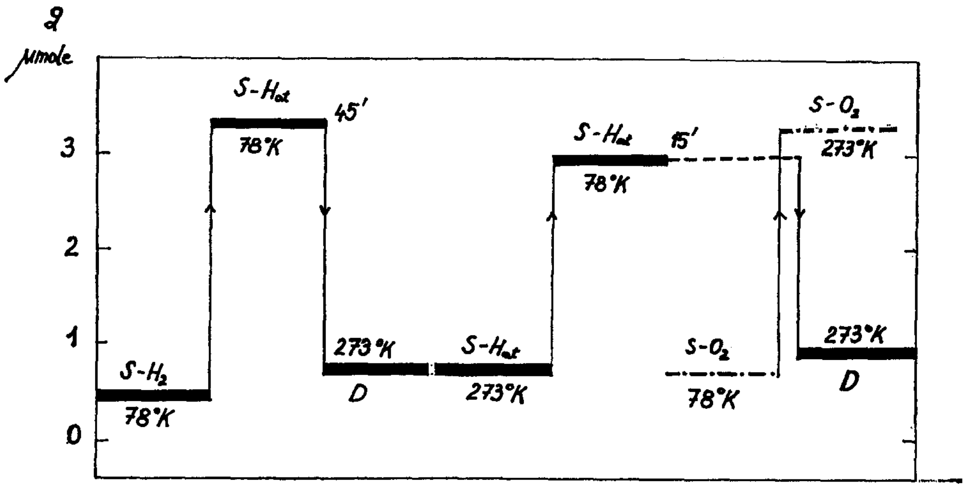

Fig. 10. Repeated sorption and desorption of hydrogen on nickel in the sequence shown on the figure. S–H_{at}, extent of sorption with atomization of hydrogen in gas phase; S–H_2, extent of sorption without atomization at given temperature; D, extent of irreversible sorption after heating of film to 273°K; S–O, sorption of oxygen into hydrogen layer at given temperature. (Oxygen in gas phase present during heating of film from 78°K to 273°K).

The results suggest that the interaction between sorbed oxygen and hydrogen atoms with the formation of the OH group proceeds through the intermediary stage of an activated complex, for the formation of which greater activation energy than the activation energy required for recombination of hydrogen atoms is necessary. There are several ways possible for the further reaction of the OH group, e.g., (i) $2\,OH_{ads} \rightarrow H_2O_{ads} + O_{ads}$; (ii) $OH_{ads} + H_{ads} \rightarrow H_2O_{ads}$, etc. Assuming that mechanism (ii) operates we can say that the difference in the products of interaction between hydrogen and oxygen on palladium, rhodium, and copper on the one side and nickel and molybdenum on the other side indicates that a sufficiently large activation energy is also associated with the reaction of the hydroxyl group with an additional atom of hydrogen on nickel and molybdenum. This is borne out by the fact that whereas hydrogen provided in the gas phase in the form of atoms is sufficient for reaction between adsorbed oxygen and hydrogen on nickel and molybdenum, the presence of atomized hydrogen in the gas phase does not suffice for further reaction between the OH group and hydrogen on these metals. On the basis of results hitherto obtained it is difficult to decide definitively whether the activation energy is merely an endothermic effect of the reaction described above (the endothermic effect represents the minimum value of activation energy) or whether a higher amount of an "intrinsic" activation energy of interaction must be provided in this case. According to the rough estimate of the heat of adsorption of the OH group it seems (*26*) that the reaction of an adsorbed OH group with an adsorbed hydrogen atom is an exothermic reaction, e.g. on nickel. So it is probable that an "intrinsic" activation energy must be connected with this reaction step. However, in general, such problems remained open.

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