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On the Forms of Nitrogen Adsorbed on Iron

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Adsorption of nitrogen on evaporated iron films has been studied in the range of temperatures 78–273°K. Films with clean surfaces and with surfaces precovered by hydrogen have been used. The adsorption of hydrogen has also been studied on clean surfaces and surfaces with preadsorbed nitrogen. On the basis of volumetric measurements of amount adsorbed, work function, and film resistance changes a conclusion has been made on the mechanism of nitrogen adsorption. Three forms of nitrogen adsorption have been detected: physical adsorption, weak, and strong chemisorption. Weak chemisorption is an unavoidable precursor for strong chemisorption.

Synthesis of ammonia, basis of the nitrogen industry, unquestionably belongs to the most important catalytic syntheses. In the years around 1940 a kinetic equation was successfully formulated which described excellently and in a wide range of pressures and temperatures, all data known at the time as well as ascertained later on concerning the said reaction (*1*, *2*). Formulation of the equation proceeded from the idea of a uniformly heterogeneous surface of iron and from the assumption that the rate of the total reaction is determined by the rate of nitrogen adsorption. The reaction of ammonia synthesis had then been for 20 years considered a favorable exception among catalytic reactions for which not only an equation describing the process, but also the physical basis of the respective mechanism were known.

However, later on it became apparent that the situation was not quite so favorable. It was found that the rate of adsorption of nitrogen depended on the extent of preadsorption of hydrogen and, further, that the ammonia synthesis showed an isotopic effect of hydrogen (*2–5*). These facts, incompatible with the original model, stimulated efforts to obtain new data on the adsorption of nitrogen and thus new impulses were given to research in the field of ammonia synthesis.

All reactants are adsorbed easily (*1*, *2*) under the conditions of the reaction except nitrogen which is adsorbed but slowly. To metals by which both ammonia and hydrogen (but not nitrogen) are adsorbed, belong in the first place the majority of Group VIII metals. However, these metals (Pt, Pd, Ni, Co) are very active for other hydrogenation reactions and and are also most active in the activation of the NH bond, as is shown by the fast exchange reaction of ammonia with deuterium (*6*). This also suggests that the reaction specificity is closely connected with the specificity of nitrogen adsorption and possibly with further reactions of adsorbed nitrogen.

Adsorption of nitrogen on clean surfaces was in the first place studied on tungsten (*7*, *8*), molybdenum (*9*, *10*), tantalum (*11a*), and rhenium (*11b*). As for iron, the majority of information has so far been obtained on powder catalysts (*12*), in most cases with promotors, but with clean surfaces of iron our knowledge is substantially more limited (*13*).

Nitrogen was the first gas with which the flash filament technique of heat desorption was used for the detection of the presence of several forms of adsorbed nitrogen on tungsten and molybdenum (*7-10*). The number of forms found varies with individual authors. However, three forms can be considered fundamental and most probable on tungsten and molybdenum: physical adsorption (denoted $\gamma^{(f)}$),* weak chemisorption ($\alpha^{(f)}$), and strong chemisorption ($\beta^{(f)}$). There are no data available for iron in this respect.

APPARATUS AND MATERIALS

Measurements were made in static volumetric apparatuses. Their description and the mode of computing adsorption data will be found in our previous paper (*14, 15*). The measuring of film resistance (DC bridge method) and of changes of film work function (shift of diode characteristics) as well as the adsorption vessels used were the same as in our previous work.

Nitrogen was prepared from sodium azide by thermal decomposition (in the presence of the forming sodium) and cleaned further only by passing through a freezing trap at liquid nitrogen temperature. Atomic hydrogen was prepared by dissociation on a hot tungsten filament.

Iron films were prepared by evaporation from degassed wire twined from two filaments of 0.2-mm diameter (Vacuumschmelze A. G., Hanau, Germany). Prior to degassing the wire was reduced by hydrogen at pressures of 20-40 torr for several hours at about 1000°K. The reduction was effected in static conditions and the period of reduction was alternated with the evacuation in such a way that products of reduction were removed. After reduction and evacuation of the apparatus for 5-6 days (with heating), a vacuum of $7\text{–}30 \times 10^{-9}$ torr was attained during evaporation. The final vacuum was limited by gases escaping from the filament itself. After evaporation the films were thermally stabilized at 293° for measurements at 78° and 200°K, or 330°K, always at least for 90 min. Adsorption of krypton was used to determine the film surface area.

RESULTS

Adsorption of Nitrogen on Clean Surface of Iron

Adsorption was observed at 78°, 200° and 273°K. Results of measuring the time changes of film resistance during adsorption are given in Fig. 1 for three different films (curves a, b, c). Film resistance changes are expressed as $\Delta R/R$ in %, where ΔR is the change caused by adsorption and R is the clean film resistance. In Fig. 2, curves a, b, and c serve to illustrate, each for one of the mentioned temperatures, changes of resistance of the same films (as on Fig. 1) as functions of the increasing adsorbed amount of nitrogen (N_a, in micromoles).

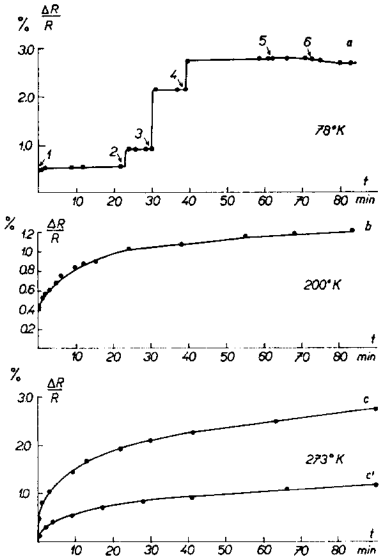

FIG. 1. Film resistance changes $\Delta R/R$ in % as a function of time (in minutes). Experiments with different films at different temperatures. Arrows mark successive doses at the curve a (78°K). Curves c and c′ correspond to films stabilized at different temperatures (see the text).

At 78°K adsorption reaches its highest extent and also the steady state is established very quickly. (Fig. 1, curve a). Values corresponding to steady states after adsorption from several smaller doses of gas are plotted in Fig. 2 (curve a). At 273°K, on the other hand, practically the whole extent of adsorption is consumed from the gas phase by a slow process and therefore, in Fig. 2 (b),

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*Note: suffix (f) is added to stress the origin of of the data—flash filament technique.

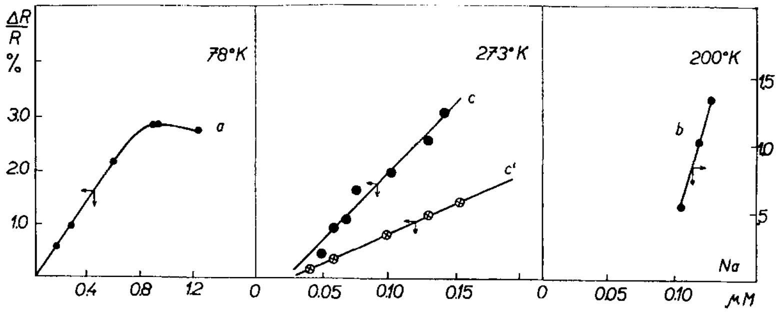

FIG. 2. Film resistance changes ($\Delta R/R$ in %) as a function of amount adsorbed (N_a in micromoles). Curves a, b, c, and c′ correspond with curves a, b, c, and c′ of Fig. 1.

values of corresponding pairs of points on curves $\Delta R/R$ versus t and N_a versus t are plotted. The time course $\Delta R/R$ versus t or N_a versus t at 273°K is described by the empirical equation

$$N_a = at^n$$

where $n = 0.3$. The linear form of the equation is illustrated in Fig. 3, where the dependence is plotted for two films, stabilized at 293°K (c) and 330° (c′).

A reduction of surface area by stabilization treatment at a higher temperature manifests itself, by change of the constant a.

Adsorption at 200°K represents an intermediate case as can be seen in Fig. 1 (curve b) and Fig. 2 (curve b). A part of the adsorption is very fast and is followed by a slow increase of the adsorbed amount as well as of the film resistance. The time course of slow sorption is again described by the same time function as at 273°K (Fig. 3, curve b). However, by this slow adsorption at 200°K, it is not possible to attain the same saturation of the surface with nitrogen as at 273°K. If after 100 min of slow adsorption at 200°K the film is rapidly heated from 200° to 273°K, and a very fast desorption takes place, followed by a slow readsorption of nitrogen (see Fig. 4).

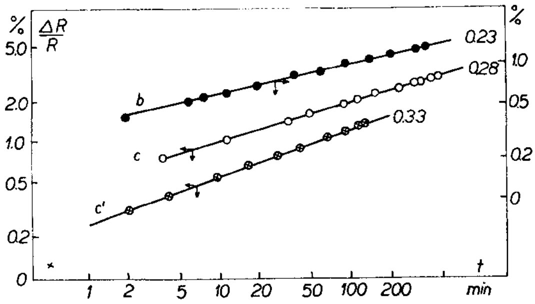

FIG. 3. Film resistance changes ($\Delta R/R$ in %) as a function of time (in logarithmic scale). Prime lines correspond with curves b, c, and c′ of Fig. 1. Value of the exponent n of the equation $\Delta R/R = a/t^n$ is shown at each line.

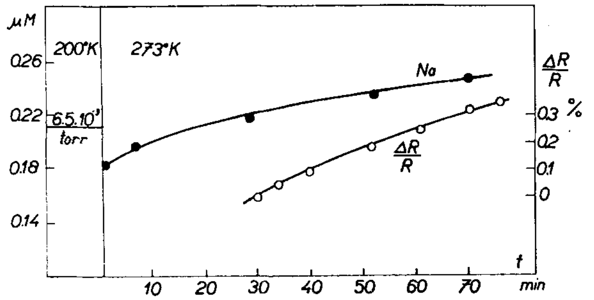

FIG. 4. Film resistance changes ($\Delta R/R$ in %) and amount adsorbed (N_a in micromoles) as a function of time for the adsorption at 273°K (pressure-6,5 × 10^{-3} torr). Before the rapid heating to 273°K the film has been saturated at 200°K by 100-min adsorption. Left column, the amount adsorbed after 100 min at 200°K.

TABLE 1
NITROGEN ADSORPTION ON THE CLEAN SURFACE AND THE SURFACE PRECOVERED BY HYDROGEN[a]

Experiment No.	Hydrogen preadsorption on clean surface T (°K)	 μmoles/cm² × 10³	 Reversible (%)	Nitrogen adsorption (μmoles/cm² × 10³) at 78°K (on hydrogen covered surfaces)[b]	Ratio: $\frac{\text{adsorption of } H_2}{\text{adsorption of Kr}}$ (on the same surface)	Change of resistance at N_2 adsorption
1	—	—	—	0.52	—	Increase
2	—	—	—	0.53	—	Increase
3	273°	0.58	26	0.166	0.71	Decrease
4	273°	0.55	28	—	0.69	—
5	78°	0.68	—	0.127	0.85	Decrease
Mean value from Roberts (*26*)	78°	—	—	—	0.8	—

[a] Adsorbed amounts for H_2 and N_2 are given for pressures 5–10 × 10^{-3} torr.

[b] For the extent of H_2 preadsorption see the left column.

It can be seen from Fig. 5 (measurements for one film) and from Tables 1 and 2 (comparison of experiments on various films—Experiments 1, 2 and 6, 7), how the "fast" adsorption is dependent on temperature and what is the share of a weak adsorption of nitrogen at low temperature. If a film is cooled down to a temperature of 78°K, after having been saturated at 273°K for a period of 100 min with nitrogen, further adsorption of nitrogen takes place, accompanied by an increase of film resistance. It is only at sufficiently high pressures of nitrogen (10^{-2} torr) that, at 78°K, a small reversible decrease of the film resistance also occurs. Thus the behavior is the same as with adsorption of nitrogen carried our directly at 78°K. Nitrogen adsorption at 273°K does not eliminate from the surface all sites with the property to bind nitrogen reversibly in a form increasing the film resistance during adsorption at 78°K (i.e., α-adsorption—see below).

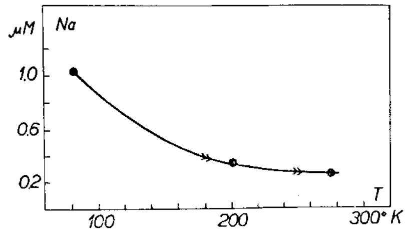

FIG. 5. Change of the amount adsorbed (N_a in micromoles) with increasing temperature T°K (film kept 10 min only at each temperature) on the same film. Pressure at 78°K, 5 × 10^{-3} torr; at 200°, 273°K, 2 × 10^{-2} torr.

Adsorption of Nitrogen on Iron Surface Covered by Preadsorbed Hydrogen

The film was covered by preadsorption of hydrogen at 273°K up to the steady state at pressures of the order of 10^{-2} torr. Hydrogen was then pumped off at the same temperature and adsorption of nitrogen followed on the surface covered with irreversibly bound hydrogen (70–75% of the original extent, see Table 1).

No more nitrogen is adsorbed at 273°K

TABLE 2
NITROGEN ADSORPTION ON THE CLEAN SURFACE AND HYDROGEN ADSORPTION ON THE SURFACE PRECOVERED BY NITROGEN

Experiment No.	Hydrogen adsorption after N_2 preadsorption T (°K)	 μmoles/cm² × 10³	 Reversible (%)	N_2 adsorption on clean surface T (°K)	 μmoles/cm² × 10³	Ratio: $\frac{\text{adsorption of } H_2}{\text{adsorption of Kr}}$	Change of resistance at N_2 adsorption	Time of N_2 adsorption (min)
6	273°	0.477	—	273°	0.081	0.60	Increase	90
7	273°	0.475	17	273°	0.11	0.60	Increase	80
8	—	—	—	200°	0.06	—	Increase	100

on a surface with hydrogen thus preadsorbed. Neither the resistance not the work function of the film (Φ) changes on admitting a dose of nitrogen to a film with preadsorbed hydrogen.

At 78° nitrogen is adsorbed even on a surface with preadsorbed hydrogen, but there are remarkable differences as compared with its behavior on a clean surface. First, less nitrogen is adsorbed on a unit surface area (see Table 1). Further, since the very beginning of its adsorption, nitrogen brings about a decrease of the film resistance. Thus it causes a quite opposite change than it would bring about on a surface free of hydrogen.

On reverting to Fig. 2 (curve a) we see that nitrogen also reduces the film resistance on a surface covered to a high degree by previous adsorption of nitrogen, and in that case gives rise to a maximum on curve a in Fig. 2.

Adsorption of Hydrogen on Iron Surface with Preadsorbed Nitrogen

At 273°K hydrogen was adsorbed on an iron surface covered with nitrogen and the adsorption proceeds with similar changes of resistance and film work function (Φ) as on a surface free of nitrogen (see below). The extent of hydrogen adsorption corresponds to the extent of nitrogen adsorption and does not indicate any specific influence in the suppression of hydrogen adsorption (see Table 2). Neither the extent of hydrogen consumption nor the curves of dependence of resistance and work function on time and/or of resistance on the extent of adsorption suggest an interaction of both gases in the adsorbed state at 273°K (Fig. 6).

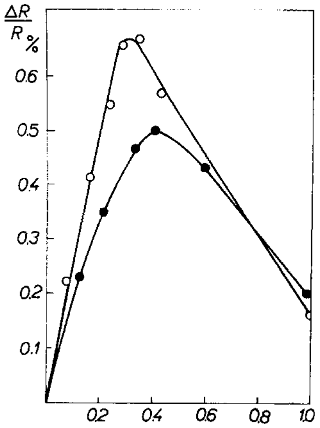

FIG. 6. Hydrogen adsorption at 273°K. Film resistance change ($\Delta R/R$ in %) as a function of the surface coverage θ. θ defined as 1 at the steady state, pressures 5–10 × 10^{-3} torr and at 273°K; ○, adsorption on the clean surface; ●, adsorption on the surface with preadsorbed nitrogen.

However, if hydrogen has been atomized in the gas phase, it behaves differently. At 273°K it causes a sharp drop of resistance of a film on which nitrogen had been preadsorbed. But in the absence of preadsorbed nitrogen neither consumption of hydrogen nor a change of film resistance takes place when atomization of hydrogen is switched on (Fig. 7). In view of the small extent of nitrogen adsorption, it is difficult to determine, the stoichiometry of interaction because the atomized hydrogen is also partly captured by the walls of the vessel. Still, the consumption of hydrogen is so

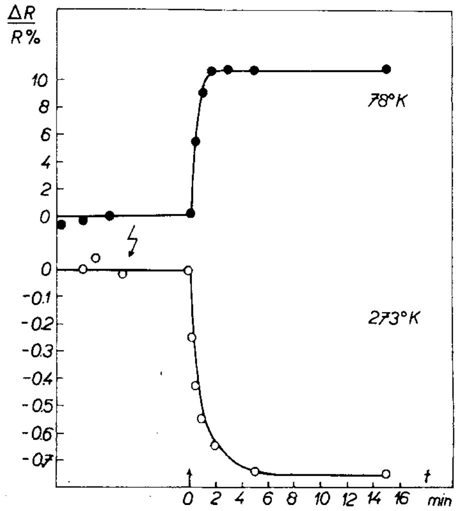

FIG. 7. Film resistance changes ($\Delta R/R$ in %) as a function of time (in minutes) in the course of the consumption of the atomized hydrogen by the surface covered by nitrogen preadsorption. Before zero time the atomization wire was switched on in vacuum and steady state was attained (arrow); at $t = 0$ hydrogen was admitted to the vessel. At 78°K an increase in resistance results as with clean film. At 273°K a decrease is found with a film covered by nitrogen. No change without nitrogen at this temperature.

large that, after all the adsorbed nitrogen had reacted, the quantity of hydrogen would also be sufficient for an eventual conversion of all nitrogen to ammonia. There is, however, no further nitrogen chemisorption after the atomization is switched off and nitrogen readmitted (after evacuation).

Work Function Changes Caused by Adsorption and Interaction of Gases

A typical example of changes in the work function ($\Delta\Phi$) is given in Fig. 8, where values are plotted of changes of work function measured after a steady state had been reached (always under conditions specified in the Figure). Since measurements are performed by the diode method, pressure in the apparatus is always lower than 10^{-4} torr when measuring the work function. Thus the values given in the Figure apply to the irreversibly bound part of the adsorption. When the influence of atomized hydrogen was not directly followed, gas was admitted at the cold cathode filament.

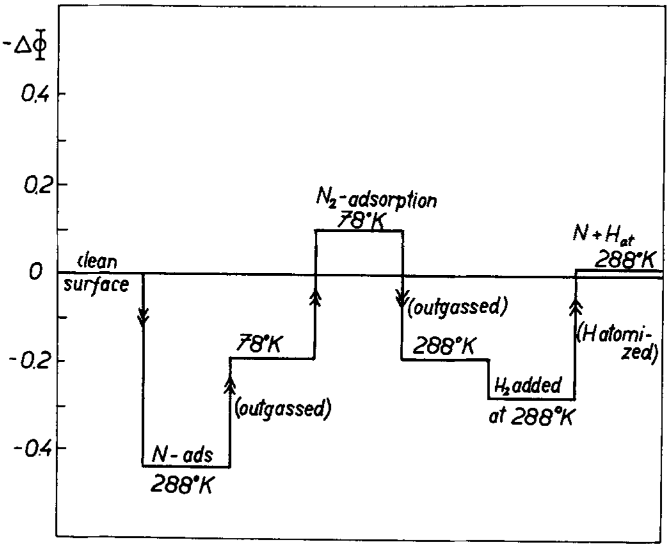

FIG. 8. Work function changes ($-\Delta\Phi$) at steady states under conditions specified in the figure.

A sign of at least two forms of nitrogen being present is the characteristic feature of the obtained results. At 288°K nitrogen causes an increase ($\Delta\Phi > 0$) and at 78°K a decrease of the work function ($\Delta\Phi < 0$).

At 288°K during adsorption without atomization hydrogen behaves in the same way both on a surface with preadsorbed nitrogen and on a surface free of nitrogen. If, however, hydrogen is atomized in the gas phase, an interaction of both gases clearly takes place, as is indicated by the consumption of hydrogen from the gas phase, by a drop of the work function, and by decrease of the film resistance after atomization has been switched on.

DISCUSSION

On summarizing the results it can be seen in the first place that several effects indicate the presence of several forms of adsorbed nitrogen: a maximum on the curve $\Delta R/R$ versus N_a at 78°K, the selective influence of hydrogen on the adsorption of nitrogen at 78°K (elimination of only one effect in changes of the film resistance), and different changes of work function during adsorption at 288° and 78°K. The presence of several forms of nitrogen follows also from further results which simultaneously indicate a mutual relation of the forms.

At 78°K adsorption of nitrogen is rapid and a part of the adsorption is reversible (40-50%). The part of the total adsorption which can be pumped out and readsorbed, shows but a small decrease with the proceeding of adsorption on a given film. At

200°K it is already easier to discern two processes. Rapid adsorption is followed by a slow process of the same character as the slow adsorption at 273°K. Although the total extent of adsorption of nitrogen at 200°K increases with time but very little, the irreversible portion which cannot be pumped off increases substantially with time. Again, film resistance change caused by adsorption is reversible for the greater part, if evacuation is carried out right in an early stage of adsorption than if it is carried out after adsorption which had been lasting some time already. The time increase of adsorption irreversibility can be clearly seen in Fig. 9. These results can be accounted for by the following model.

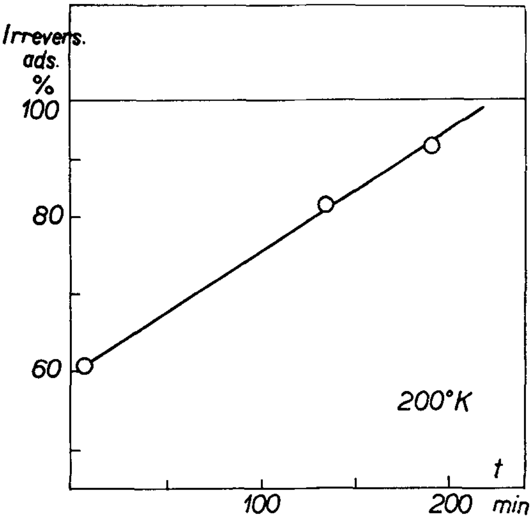

Fig. 9. Increase of the irreversibility of adsorption of nitrogen at 200°K with the time of adsorption.

At first, nitrogen is adsorbed weakly (form α) and from this form it passes in the adsorbed state to a strongly bound form (β). Both form α and form β bring about an increase of the film resistance. But form α as distinguished from form β, brings about a decrease of the work function. At 78°K the transition $\alpha \rightarrow \beta$ is hardly observable but at 200°K the transition can already be observed. During the slow resistance increase, form α changes to an irreversibly bound form β. At 273°K we can see just the rate of the transition, because form α adsorption is of but very small extent and nitrogen adsorbed in this form passes to form β more rapidly than at the lower temperature. Therefore the pumping off of the gas at 273° exerts influence neither upon the extent of adsorption nor upon film resistance change.

A weakly bound form α could be in principle either physical adsorption or weak chemisorption. Two reasons speak against the former: on the one hand—the relatively high temperature (200°K, i.e., 1.6 T_{crit}) at which the adsorption still shows itself at a relatively low pressure ($p = 10^{-2}$ torr) and, on the other hand—the influence of the preadsorption of hydrogen. It can be seen from Table 1 that preadsorbed hydrogen does not allow the formation of form β (at 273°K), and reduces the total adsorption at 78°K—this clearly by eliminating also form α. Nonspecific physical adsorption should not be dependent at 78°K on preadsorption of hydrogen. Thus the conclusion is arrived at that on the clean surface at 78°K and 200°K the overall fast adsorption is a mixture of two states: a weak specific chemisorption (form α) and a nonspecific physical adsorption (form γ).

According to the literature 70 kcal/mole (*16*) or 40 kcal/mole (*17*) are released at adsorption in the β-form. Also the fact that there is no desorption at evacuation at 273°K itself shows that even the most weakly bound portions of β-adsorption must have an adsorption heat of at least about 15 kcal/mole. Nevertheless this strong adsorption does not take place if hydrogen had been preadsorbed on the surface. Thus form β is able neither to bind itself on sites from which hydrogen has been removed by desorption (25% of the total surface), nor to displace hydrogen from the surface. We have seen from the preceding discussion that form α is the precursor for the formation of the form β and, further, that adsorption of the form β can be eliminated by adsorption of hydrogen. Thus the following interpretation offers itself.

Form α is an inevitable precursor for the formation of form β. Sites for a weak reversible adsorption of hydrogen (25% of sites) are unable to hold on the surface the form α of nitrogen, the adsorption of which is still weaker. In principle, form β could displace hydrogen thanks to the bond strength of the former but the displacement does not take place because the form β does not arise without the presence of the form α.

Hydrogen cannot be displaced from the surface by nitrogen, but its displacement can be brought about at 273°K by means of CO. Carbon monoxide, too, is adsorbed on the surface of metals in weakly or strongly bound forms. According to the results of thermal desorption (*18*) on metal wires the heat of adsorption of a weak form of CO is not much higher than that of form $\alpha^{(f)}$ of nitrogen, yet the differing effect of nitrogen and of carbon monoxide in connection with displacement could be understood so that with carbon monoxide a weak adsorption of the molecule is possible also on sites covered by hydrogen. Transition from a weak form to the strong one is then accompanied by displacement.

Hydrogen reacts at 273°K with nitrogen adsorbed in form β only if the former is atomized in the gas phase. The mere presence of hydrogen atoms formed only by adsorption without hydrogen atomization in the gas phase, will not suffice for interaction. A similar situation has already been met in the interaction of hydrogen with oxygen on molybdenum (*19*). In this system it was especially disturbing that even hydrogen atoms formed by atomization entered the reaction only after having been adsorbed and still the result differed from adsorption without atomization. Two possibilities could be offered for explanation: (1) The mobility of hydrogen atoms which has been formed by adsorption only, does not suffice to enable hydrogen atoms to reach the molybdenum–oxygen bond and to react. (2) If hydrogen atoms are to react, they must be adsorbed on a molybdenum atom which carries an oxygen atom or in the closest vicinity of the former. However, these sites are not accessible for adsorption without atomization on account of the presence of the energetic barrier or for steric reasons. Naturally the same explanations can also apply in the case of nitrogen and hydrogen on iron, where interaction with atomized hydrogen at 0°C was already found by Gundry, Haber, and Tompkins (*20*).

As already mentioned in the introduction, the existence of at least three forms of nitrogen has been proved also on other metals by the flash filament technique. These forms were marked in the order of, the growing strength of bond thus; $\gamma^{(f)}$, $\alpha^{(f)}$, $\beta^{(f)}$ (the index f having been added here for the purpose of distinction from symbols introduced in this paper). On the assumption that weak adsorption ($\gamma^{(f)}$ or $\alpha^{(f)}$) is the precursor of strong chemisorption, the authors succeeded in explaining the slight dependence of sticking coefficient on the extent of adsorption (*7–10*). Furthermore, with form $\gamma^{(f)}$ it is clear that a molecular nondissociative form is involved (*22*). Now the question offers itself whether it is possible to correlate forms α, β, γ in some way with forms $\alpha^{(f)}$, $\beta^{(f)}$, $\gamma^{(f)}$. It seems that the identity of forms β and $\beta^{(f)}$ is quite unambiguous; they obviously describe the same states on various metals. A straight corelation of the remaining forms $\alpha \leftrightarrow \alpha^{(f)}$, $\gamma \leftrightarrow \gamma^{(f)}$ cannot be made without reservations. *Inter alia* it cannot be excluded that form $\gamma^{(f)}$ in a thermal desorption peak is in fact a mixture of physical adsorption and weak molecular chemisorption, thus of the molecular forms α and γ, when using symbols according to this paper. If this is true then the forms $\alpha^{(f)}$ and $\beta^{(f)}$ both represent atomic chemisorption, of course, e.g., on various crystal planes.

The ratio of a total adsorption of nitrogen at 78°K and 10^{-2} torr (i.e., at the relative pressure of nitrogen of about 10^{-5}) to the monolayer adsorption of Kr on the same surface, is practically the same as the ratio of adsorption of krypton and hydrogen under equal conditions. This is in agreement with previous statements in the literature. Thus under the mentioned conditions about 30 Å^2 are covered by one molecule of nitrogen in the adsorbed state. This is substantially more than what would correspond with the monomolecular coverage by physical adsorption (16 Å^2). The relative pressure, to be sure, is also substantially lower here than the pressure at which the physically adsorbed monolayer is usually just completed.

It is very probable that the existence of a weak chemisorption of nitrogen does not exclude the possibility of using nitrogen for surface area determination. For monolayers of nitrogen and krypton on the surface Beeck (*17*) found a ratio equal to that found by all other authors for materials by which nitrogen is not chemisorbed. This is by no means altered by Beeck himself stating that chemisorption of nitrogen manifested itself by an increase of the extent of total adsorption. Beeck was led to the conclusion by having used 14.6 Å^2 as cross section of adsorbed krypton instead of the customary 19–21 Å^2 (*21*).

In this work it was found that adsorption of nitrogen is hindered by hydrogen. We find statements in the literature to the effect that hydrogen either exerts no influence or speeds up the adsorption of nitrogen at higher temperatures. It is clear that a different effect of temperature upon adsorption of hydrogen and nitrogen is involved. At high temperatures (exceeding 200°C) more sites by which nitrogen can be adsorbed are free of hydrogen adsorption and at an increased temperature also hydrogen is activated on the remaining surface and interaction of nitrogen with hydrogen takes place as well as the desorption of ammonia. At low temperatures the reactivity of both nitrogen and hydrogen decreases and, eventually, adsorption of nitrogen does not occur at all. From the point of view of ammonia synthesis it is also interesting that at 0°C nitrogen has the ability to react, it is found on the surface in a reactive form, but it is especially necessary to activate hydrogen in order to bring about synthesis. Adsorption of hydrogen alone is not sufficient. Clearly, hydrogenation of nitrogen atoms at low temperatures is not an easy process.

In conclusion, a few remarks about the relation of this paper to some further data from the literature. A maximum on the curve $\Delta R/R$ versus N_a for nitrogen on Fe was already found by Suhrmann, Richter, and Wedler (*23*), who explained the effect by reversible dissolving of nitrogen in iron. If we were to agree to this model, we would have to admit that preadsorption of hydrogen excludes the chemisorption of nitrogen but does not prevent the dissolving of nitrogen at 78°C, which seems improbable. Additionally, since reversible dissolving at 78°K itself does not seem to be very likely either, preference was given to the model described previously.

A very similar behavior during adsorption, i.e., the transition of weakly bound precursor into strongly bound chemisorbed particle, was found by Kuchynka and Klier (*24*) for the oxygen–NiO system. These authors drew their conclusions on the basis of similar reasoning as that used in this paper. It appears that a transition of gaseous particles to the state of strong chemisorption via the state of a precursor weak chemisorption is a quite general phenomenon (*25*).

The results of measuring hydrogen chemisorption and physical adsorption of krypton permit a comparison with Roberts' data (*26*). The agreement obtained is satisfactory and suggests that the relatively low coverage of the iron surface by hydrogen is a real one and not an artifact caused, e.g., by insufficiently clean film surface.

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