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The Interaction of Hydrogen and Nitrogen on Polycrystalline Iron Films at Low Pressures and at Low Temperatures

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The interaction of H_2 and N_2 on extremely clean iron films was investigated by mass spectrometric measurements of displacement, thermal desorption, isotopic equilibration, and by measurements of electrical resistance. The adsorption of N_2 on iron films partially covered with H_2, the adsorption of H_2 on iron films partially covered with N_2, and the alternating adsorption of N_2 and H_2 were studied.

The results were obtained in the temperature range from 77 to 400 K and at pressures up to 5×10^{-4} Torr.

Nitrogen does not displace hydrogen from the iron surface; it is physisorbed on a monolayer of chemisorbed hydrogen. Hydrogen displaces nitrogen from the iron surface. The kinetics of these reactions are discussed.

It was found that the isotopic equilibrium between $^{14}N_2$ and $^{15}N_2$ was not established even when nitrogen was adsorbed on iron in the presence of hydrogen. Thermal desorption studies produced no evidence for the formation of N–H adducts.

I. INTRODUCTION

The interaction between nitrogen and hydrogen on iron has received considerable attention in the attempt to elucidate the primary steps of the ammonia synthesis. A series of investigations has been carried out using ammonia catalysts as adsorbents (*1–10*). However, the interpretation of these results is difficult because the effects of iron and the promoters used in the promoted catalysts could not be separated. Therefore, attempts have been made to study the interaction of hydrogen and nitrogen on clean iron surfaces. Iron films are particularly well suited for these studies.

The adsorption of hydrogen and nitrogen on iron films and the interaction between these gases have been investigated by means of measurements of the kinetics (*11*), heats of adsorption (*12*), surface potential (*13, 14*) and the change in the resistivity (*14*). In the majority of these reports the authors have assumed that nitrogen is adsorbed in a dissociated state. However, it has recently been reported that nitrogen adsorbed on extremely clean iron films (evaporated under UHV conditions), is not dissociatively adsorbed at temperatures below 370 K (*15*). For these reasons a reinvestigation of the interaction between nitrogen and hydrogen seemed necessary.

The results given in this paper are restricted to the low temperature range (from 77 to 400 K) and the low pressure range ($p < 5 \times 10^{-4}$ Torr). They were obtained by an observation of the amount adsorbed

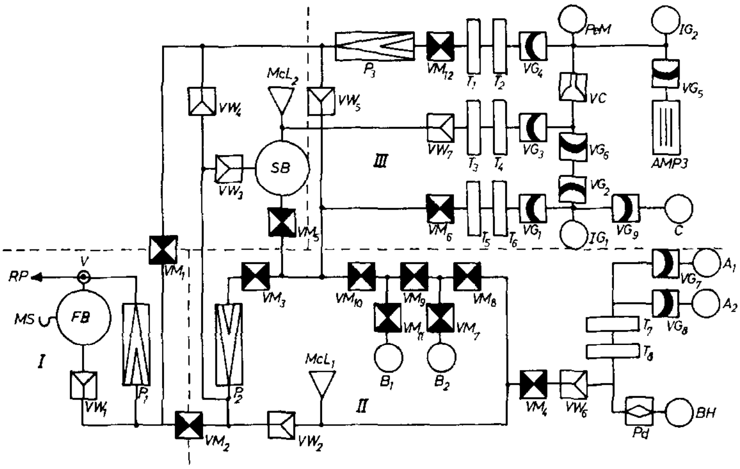

FIG. 1. Schematic diagram of the UHV apparatus: (I) Roughing pump unit; (II) unit for the preparation and dosing of the gases; (III) measuring and analyzing unit; (A) ampoules filled with sodium azide for the preparation of nitrogen; (AMP 3) Atlas quadrupole mass spectrometer; (B) Bulb containing deuterium, hydrogen, or nitrogen under known pressures; (BH) storage bulb containing deuterium or hydrogen; (C) cell; (FB) fore-vacuum bulb; (IG) ionization gauge; (McL) McLeod gauge; (MS) manometric mercury safety switch; (P) mercury diffusion pump; (Pd) electrically heated palladium tube; (PeM) Penning manometer; (RP) roughing pump; (SB) storage bulb; (T) liquid nitrogen trap; (V) 3-way stopcock; (VC) ground-in ball and socket valve with pressure reducing capillary; (VG) ground-in ball and socket valve; (VM) manometric mercury valve; (VW) water cooled mercury valve.

and displaced, the equilibrium pressure, the change in resistivity, the thermal desorption, and the isotopic exchange using iron films or iron coils as adsorbents.

II. EXPERIMENTAL METHODS

Figure 1 shows a schematic diagram of the UHV apparatus employed in this work. Details are given in the legend.

The glass UHV apparatus produced a vacuum of 2×10^{-10} Torr. The iron films were condensed at this pressure on the cooled (77 K) glass bulb C at a rate of about 10 Å/min until a thickness of about 100 Å was obtained. Sintering for 1 hr at 373 K was performed to prepare films in a more ordered state. In some experiments the iron coil from which the films had been evaporated was also used as an adsorbent.

The rest of the experimental procedure was as follows:

1. Preparation of nitrogen with a normal isotopic composition and of nitrogen enriched in ^{15}N by thermal decomposition of NaN_3 in the ampoules A_1 and A_2.
2. Admission of H_2 or D_2 into the system by diffusion through the palladium tube Pd.
3. Storage of the gases in bulbs B_1 and B_2 at a known pressure.
4. Covering of the film (usually at 77 K) in the cell C was accomplished by adding small known amounts of the gas into the system with the Hg-sealed pipettes VM_7–VM_{11}.
5. After taking a sample from the gas phase using ground-in ball and socket glass valves, the gas was analyzed with a quadrupole mass spectrometer.
6. Removal of the gas phase in the cell and the reversibly adsorbed gas by pumping: (a) without analysis, using pump P_2 and transferring the gas to storage bulb SB. (b) with continuous analysis, using pump P_3 and transferring the gas to SB.

7. Removal of the more strongly adsorbed gas by thermal desorption as in 6.
8. Analysis of the gases transferred into SB with AMP 3.

The purity of the nitrogen and the hydrogen was better than 99.9% as determined by means of mass spectrometric measurements. The iron was of specpure grade (Johnson, Matthey and Co.).

The measurements of the electrical resistance were made by means of a Wheatstone bridge, and the thermal desorption was measured in the same way as described elsewhere (*16, 17*).

III. THE SYSTEMS Fe/H_2 AND Fe/N_2

The systems Fe/H_2 and Fe/N_2 have already been described in detail. A short summary of the results is given here.

The surface area of the evaporated polycrystalline iron films depends on the annealing temperature and to a less extent on the film thickness. For the annealing temperature of 373 K and a thickness of about 100 Å which were used in this study a roughness factor (ratio of real surface area to geometric surface area) of 1.7 was found (*32*). As with evaporated nickel films (*33, 34*) it can be assumed that the surface of the iron films is preferentially composed of low index planes. Assuming that the area of the (100) planes is equal to the area of the (110) planes in the surface and assuming a roughness factor of 1.7 the number of iron atoms per square centimeter of geometric surface area is about 1.7×10^{15} Fe atoms/cm^2.

The results obtained with the system Fe/H_2 (*17–19*) are the following. The desorption spectrum is composed of three peaks, γ (90 K), β_1 (350 K) and β_2 (430 K). If the coverage is less than one half of a monolayer, then only the β_2 peak is observed. At higher coverages, up to one monolayer, an additional chemisorbed state β_1 appears. In this range of coverage the heat of adsorption decreases in a steplike manner from 23 to 18 kcal $mole^{-1}$. However, as the coverage approaches one monolayer ($H:Fe \approx 1:1$), the heat of adsorption drops rapidly to a value of less than 5 kcal $mole^{-1}$.

The work function of the Fe film increases with the adsorption of hydrogen.

The electrical resistance of the film increases until a coverage of approximately $\frac{2}{3}$ monolayer is reached. Then it decreases slightly and approaches a constant value. At 77 K it is possible to obtain coverages greater than one monolayer. This results in the observation of an additional γ peak in the desorption spectrum. This peak must be assigned to a physisorbed state. Experiments using deuterium instead of hydrogen have resulted in no noticeable differences in the two systems with respect to the changes in the electrical resistance, the work function or the desorption spectrum.

The results obtained with the system Fe/N_2 (*15, 20–22*) are the following: It is possible to distinguish between four adsorption states. A β_1 state, with a desorption maximum between 200 and 250 K, has its adsorption sites already filled at a coverage of only a few percent of a monolayer. The formation of the γ state is characterized by a simultaneous increase in the electrical resistance and a decrease in the work function. This phenomenon is observed at coverages up to approximately one half of a monolayer ($N_2:Fe \approx 0.25$). Assuming that one N_2 molecule occupies 16 $Å^2$ and assuming a roughness factor of 1.7, a monolayer of N_2 has about 1×10^{15} N_2 molecules/cm^2 of geometric surface. The γ state has a desorption peak at 100 K. The calorimetrically determined heat of adsorption for this adsorption state is 5 kcal $mole^{-1}$. As more nitrogen is adsorbed the heat of adsorption decreases until a value ap-

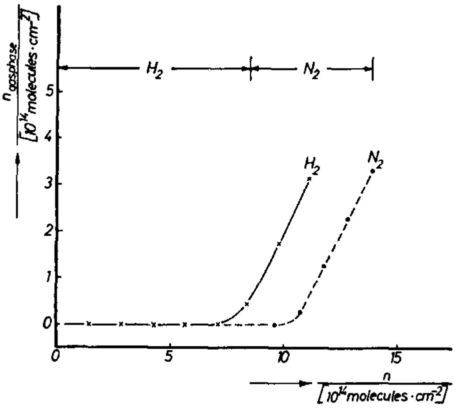

FIG. 2. Amount of H_2 and N_2 in the gas phase as a function of the amount added. $T = 77$ K.

proaching the heat of condensation is reached. The adsorption of nitrogen into this state, δ, causes the electrical resistivity to increase again and the work function continues to decrease. The δ-nitrogen can be quantitatively removed by pumping at 77 K. Therefore, a peak corresponding to the δ state does not appear in the desorption spectrum. On the other hand, at coverages greater than one half of a monolayer, a peak β_2 is observed in the desorption spectrum at 350 K. However, this peak can only be due to a very small amount of nitrogen.

Isotopic exchange experiments have shown that the nitrogen is not dissociated in its adsorbed states at temperatures below 400 K.

IV. COADSORPTION OF H_2 AND N_2 ON IRON

In all of the experiments discussed in this section the adsorption of the nitrogen on the iron was carried out under an equilibrium pressure of less than 10^{-3} Torr. In order to achieve enough adsorption of the nitrogen, the iron film was cooled to 77 K before the gas was added. The desorption spectra were taken in the range from 77 to 500 K.

1. Adsorption of N_2 on Iron Films after Preadsorption of H_2

In Fig. 2 the amount of gas remaining in the gas phase is plotted against the amount of gas admitted to the cell. The scale of the ordinate is the coverage that would be found if the amount remaining in the gas phase were quantitatively adsorbed. It can be seen that hydrogen is quantitatively adsorbed on clean films up to a coverage of 7×10^{14} molecules of hydrogen cm^{-2}. When additional hydrogen is admitted to the cell, very little is adsorbed and the excess gas remains exclusively in the gas phase. After removing the hydrogen by pumping, 8.5×10^{14} molecules cm^{-2} remain on the film (indicated with double arrows $\leftarrow H_2 \rightarrow$). This corresponds to one monolayer on clean iron. The subsequent adsorption of nitrogen results in the quantitative adsorption of only the first dose. Beginning with the third dose the nitrogen added remains completely in the gas phase. Although the equilibrium pressure of nitrogen was raised to 3×10^{-4} Torr, only 2×10^{14} molecules cm^{-2} were adsorbed, whereas under the same pressure approximately 8×10^{14} molecules cm^{-2} were adsorbed on a clean iron film. However, it must be realized that the nitrogen is adsorbed on an iron film completely covered with hydrogen. The results of the mass spectrometric analysis show that no adsorbed hydrogen is displaced by nitrogen. This is reasonable when one considers the fact that the heat of adsorption of nitrogen on iron is 5 kcal $mole^{-1}$ and the heat of adsorption of hydrogen on iron has been measured to be 23 kcal $mole^{-1}$.

After subsequent removal of the gas phase by pumping, approximately 0.3×10^{14} molecules of N_2 cm^{-2} remain on the film.

The change in the resistance, ΔR, and in the resistivity, $\Delta\rho$, of the iron film measured as the gas is adsorbed is plotted against the amount adsorbed in Fig. 3. In the case of hydrogen the curve we observe has the same shape as was found previously (*17*). The addition of nitrogen results only in a small increase of 0.03 Ω in the resistance of the film. A corresponding amount of nitrogen adsorbed on a clean iron film would have caused the resistance to increase by approximately 0.2 Ω.

A desorption spectrum in which the partial and total pressures are given is shown in Fig. 4. It can be seen that nitrogen is only present in the γ state. The adsorption sites on which the nitrogen is adsorbed in the β_1 and β_2 states (desorption temperatures 200–250 and 350 K, respectively) are apparently blocked by the hydrogen. The γ peak is approximately an order of magnitude smaller than the peak due to nitrogen adsorbed on clean iron (*15*). The hydrogen desorption spectrum consists of the normal peaks (β_1 and β_2). The intensities of these peaks are approximately equal to those obtained from hydrogen adsorbed on clean iron. The small γ peak ($p \approx 5 \times 10^{-9}$ Torr at 90 K) found in the absence of nitrogen (see Sect. III) cannot be observed. The binding state of the chemisorbed hydrogen is not noticeably influenced by the subsequent adsorption of nitrogen.

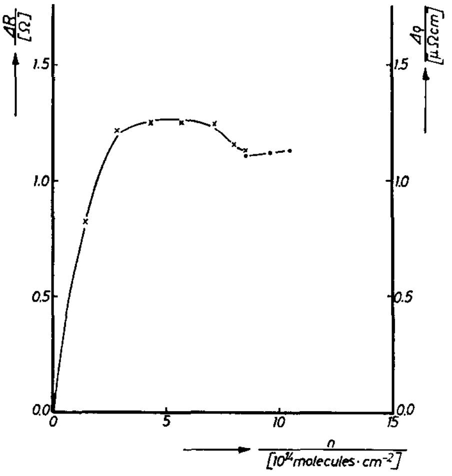

FIG. 3. Influence of the adsorption of H_2 (×) and N_2 (●) on the resistance R and on the resistivity ρ. T = 77 K; d = 88 Å.

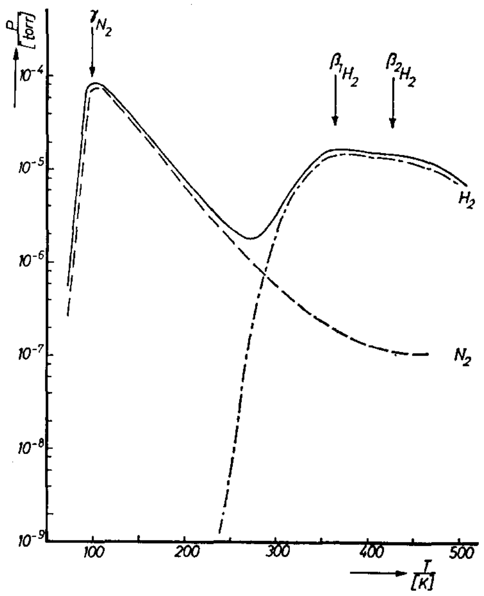

FIG. 4. Thermal desorption of N_2 and H_2 from Fe film after preadsorption of H_2.

2. *Adsorption of H_2 on Iron Films after Preadsorption of N_2*

The results obtained when hydrogen is adsorbed on a film already covered with a monolayer of nitrogen are strikingly different from the results described above. This can be seen by comparing Figs. 5 and 2. Nitrogen is quantitatively adsorbed on a clean iron film until the amount adsorbed approaches 6×10^{14} molecules cm^{-2}. As additional nitrogen is admitted (extended curve, filled circles) the equilibrium pressure increases simultaneously with the the adsorbed amount. The amount adsorbed at a pressure of 3×10^{-4} Torr is

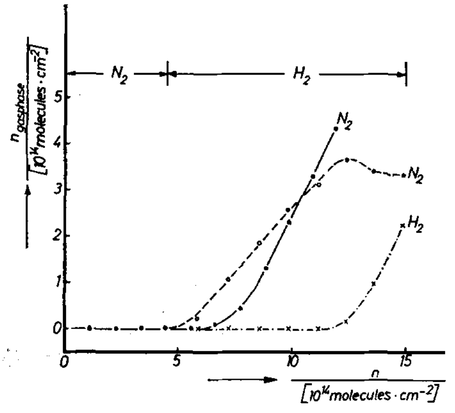

FIG. 5. Amount of N_2 (●) and H_2 (×) in the gas phase as a function of the amount added and displacement of N_2 (○) due to a subsequent H_2 (×) adsorption. T = 77 K.

8×10^{14} molecules cm^{-2}. A decrease in the equilibrium pressure of the reversibly adsorbed nitrogen to 3×10^{-6} Torr causes a decrease in the nitrogen coverage to 4.5×10^{14} molecules cm^{-2} (double arrows $\leftarrow N_2 \rightarrow$).

Hydrogen which is subsequently admitted to the cell (Fig. 5, crosses and dot-dashed curve) is initially quantitatively adsorbed until 7.5×10^{14} molecules cm^{-2} are adsorbed. This approximately corresponds to a monolayer of hydrogen adsorbed on a clean iron film. The total amount of hydrogen adsorbed under a higher pressure ($p = 5 \times 10^{-4}$ Torr) is approximately 8.5×10^{14} molecules cm^{-2}.

It is particularly interesting to note that the first dose of hydrogen leads to a desorption of nitrogen (Fig. 5, open circles, dashed curve), even though one half of the surface is uncovered. This is quite contrary to the observations made on the $Ni/H_2 + CO$ (*23*) system. In this system the CO displaced the hydrogen only after the total coverage of the hydrogen and carbon monoxide corresponded to one monolayer. In a broad range of coverage extending to nearly a monolayer (based on adsorption of $N_2 + H_2$) 1 hydrogen molecule displaces an average of 0.5 nitrogen molecules. The opposite behavior of the $Fe/N_2 + H_2$ and $Ni/H_2 + CO$ is logical if one considers that only the nitrogen adsorption on iron is strongly face specific (*15*). At the prevailing pressures the uncovered portion of the iron surface is not able to adsorb nitrogen. Taking the large heat of adsorption of hydrogen into consideration, it is reasonable to assume that any hydrogen molecule striking the surface will be adsorbed, regardless of whether the adsorption site is empty or occupied by a nitrogen molecule. In the first case no further interactions appear. In the latter case the nitrogen is displaced, without being able to become adsorbed on another site. In the $Ni/H_2 + CO$ system the tightly bound CO displaces the adsorbed hydrogen from its adsorption site. However, in this system the hydrogen can be adsorbed on another site as long as the total coverage has not reached one monolayer.

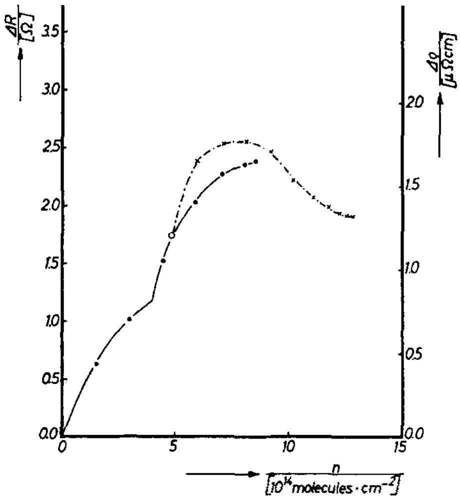

FIG. 6. Influence of the adsorption of N_2 and H_2 on the resistance R and on the resistivity ρ. T = 77 K; d = 62 Å. (●) Adsorption of N_2; some N_2 then desorbed, as far as (○); (×) subsequent addition of H_2.

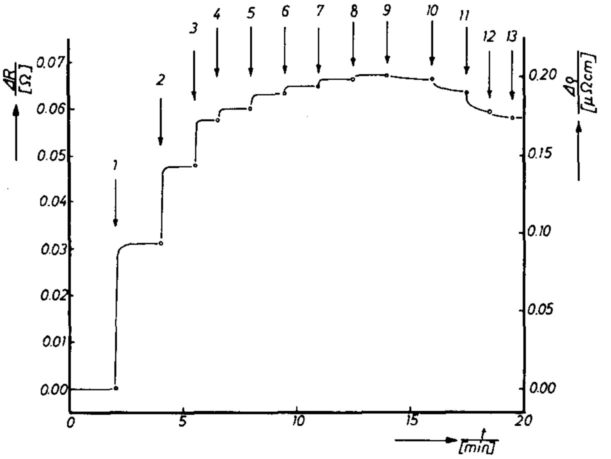

FIG. 7. Kinetics of the change of resistance R or of resistivity ρ due to the adsorption of H_2 on a clean Fe film at 77 K; $d = 262$ Å. The arrows indicate the addition of a new dose of H_2.

A slight readsorption of nitrogen is observed on iron films which are covered with a monolayer of hydrogen (Fig. 5 for n up to 12×10^{14} molecules cm^{-2}).

The change in resistivity measured in a corresponding experiment is given in Fig. 6. The initial adsorption of nitrogen causes the resistivity of the film to increase and, as previously observed, the curve splits into two branches. The first branch corresponds to nitrogen in the β_1 and γ states, and the second branch is due to nitrogen reversibly adsorbed in the δ state. The nitrogen adsorbed in the δ state can be totally desorbed by extended pumping at 77 K. In the case illustrated in Fig. 6 the pumping was stopped when a coverage of 4.8×10^{14} N_2 molecules cm^{-2} was reached. The subsequent addition of hydrogen caused the resistance to increase. After passing through a maximum the resistance decreased.

The change in resistivity due to the subsequent adsorption of hydrogen (Fig. 6) is clearly different from that due to the adsorption of hydrogen on a clean iron film (see Fig. 3). The reason for this difference can be seen from a comparison of Figs. 7 and 8. The time dependency of the change in the resistivity during the addition of hydrogen on a clean film is shown in Fig. 7. The arrows indicate the times at which the hydrogen was admitted to the cell. It can be seen that the resistance changes rapidly until the resistance maximum is approached. In this coverage range the kinetics of the process are predominantly determined by the diffusion of the gas from the pipette through the tubes of the apparatus to the film and not by the actual adsorption. When the coverage exceeds the amount corresponding to the resistance maximum the adsorption process itself requires a noticeable amount of time. This is presumably due to a reorientation of the β_2 phase into the β_1 phase (*16, 17, 24–27*).

Figure 8 shows the kinetics of the hydrogen adsorption on an iron film already covered with nitrogen as monitored by the change in resistivity. The adsorption of the first doses of hydrogen leads to a very rapid increase in the resistance, which can certainly be ascribed to the adsorption of hydrogen. This initial sharp increase in the resistivity is followed by a slow decrease; this is due to the desorption of the nitrogen which caused an increase

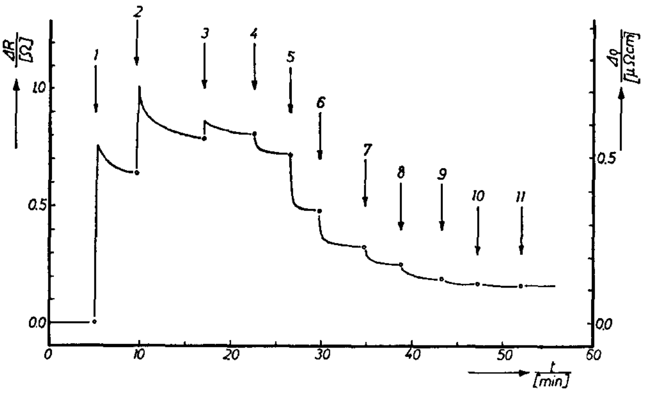

FIG. 8. Kinetics of the change of resistance R or of resistivity ρ due to the adsorption of H_2 on Fe film after preadsorption of N_2 at 77 K; d = 62 Å. The arrows indicate the addition of a new dose of H_2.

in the resistance during the adsorption process. The decrease in the resistivity due to the displacement of the nitrogen predominates already after four additions of hydrogen.

According to the arguments given above the final state of the hydrogen in the experiments with subsequent nitrogen adsorption (Fig. 3) should be approximately the same as the final state of hydrogen adsorbed on iron precovered with nitrogen (Fig. 6). A comparison of the two figures does indeed show that the changes of the specific resistivities ($\Delta\rho$) are approximately equal (1.12 and 1.32 μΩ cm for Figs. 3 and 6, respectively).

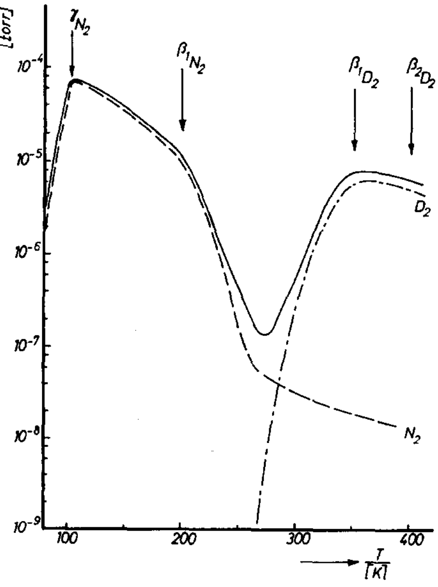

FIG. 9. Thermal desorption of N_2 and D_2 from Fe film after preadsorption of N_2.

Figure 9 corresponds to Fig. 4 and gives the desorption spectrum which is obtained after hydrogen has been adsorbed on iron precovered with nitrogen. For reasons given below the hydrogen isotope deuterium has been used. In contrast to the experiments in which nitrogen was adsorbed on iron films precovered with hydrogen (Fig. 4), one now (Fig. 9) observes the appearance of a peak which must be assigned to the β_1 nitrogen state. The height of the shoulder (β_1 in Fig. 9) is only slightly smaller than the shoulder in the spectrum from pure nitrogen adsorption.

However, the height of the γ peak in Fig. 9 is, as in Fig. 4, approximately an order of magnitude smaller than in the spectrum from pure nitrogen adsorption. This shows that the γ nitrogen is predominantly displaced by the hydrogen. In addition, the heights and positions of the peaks in the deuterium desorption spectrum correspond to those obtained from pure deuterium adsorption.

After the coadsorption of nitrogen and hydrogen, small peaks at masses 12, 15 and 16 always appear in the desorption spectrum. Of these, masses 15 and 16 could indicate the formation of N–H adducts on the iron film. In order to decide whether this was actually the case or whether the formation of these adducts took place at the tungsten cathode of the quadrupole mass spectrometer, the film was covered with nitrogen and deuterium. As can be seen in Fig. 10, masses 15 and 16 still appear. However, mass 18 was not observed. If the adducts were formed on the film, mass 18 should appear instead of mass 16. The formation of the adducts with masses 15 and 16 probably occurs in the mass spectrometer in which a small partial pressure of hydrogen is always present. This argument is supported by the fact that the partial pressures of masses 15 and 16 follow the same pattern as the desorption spectrum of nitrogen. The appearance of mass 20 (CD_4) is also attributed to a reaction at the cathode.

3. Alternative Adsorption of Hydrogen and Nitrogen

The coadsorption experiment was carried out by alternatively adsorbing small amounts of nitrogen and hydrogen on the film. Figure 11 shows the dependence of the amount of nitrogen in the gas phase on the amount of hydrogen and nitrogen admitted to the sample. Two different coordinate scales, which differ by an order of magnitude, are used. At coverages up to approximately 6×10^{14} molecules cm^{-2} both hydrogen and nitrogen are adsorbed. At higher coverages the partial pressure of nitrogen increases as a result of an addition of hydrogen as well as an addition of nitrogen. When the total coverage of 6×10^{14} molecules cm^{-2} is exceeded, no more nitrogen is adsorbed. As shown in Fig. 5, excess hydrogen added to the sample displaces the adsorbed nitrogen.

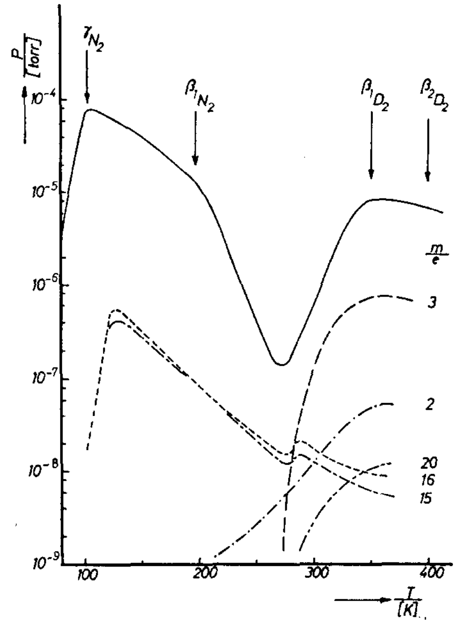

FIG. 10. Thermal desorption spectra after the adsorption of N_2 and D_2 on Fe at 77 K. (——) Total pressure; (— —) partial pressures.

Experiments using films with preadsorbed nitrogen have shown that approximately one half (A) of the surface area can be covered with nitrogen adsorbed in the γ state (adsorption on the other

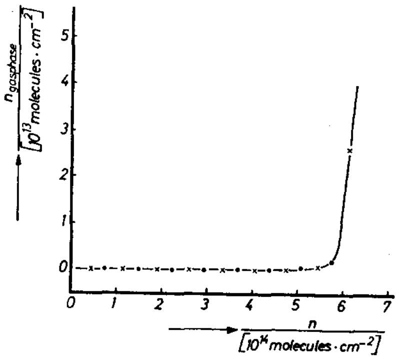

FIG. 11. Amount of N_2 in the gas phase as a function of alternatingly added amounts of N_2 (●) and H_2 (×).

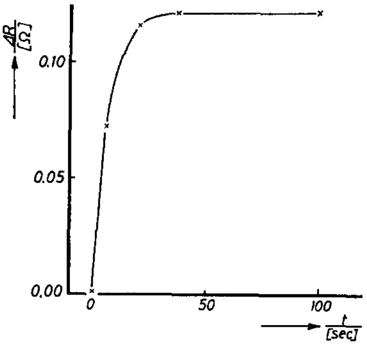

FIG. 12a. Kinetics of the change of resistance R due to the adsorption of N_2 on Fe film. $T = 77$ K; $d = 105$ Å.

half (B) is only observed under higher pressures and as reversible δ-state nitrogen). When small amounts of hydrogen and nitrogen are added to the sample, the hydrogen is distributed over the entire surface area (A and B) (hydrogen adsorption being hardly face specific) whereas nitrogen, which is face specifically adsorbed, can only be adsorbed on half (namely, part A) of the surface area. The amount of hydrogen added with each dose in Fig. 11 is 0.4×10^{14} molecules. Of this amount 0.2×10^{14} molecules are adsorbed on part A of the surface. The amount of nitrogen added with each dose is 0.3×10^{14} molecules and this amount was totally adsorbed on part A of the film. If the model described above is correct then approximately after the addition of 9 doses of hydrogen and 9 doses of nitrogen part A of the film should be completely covered (4.5×10^{14} molecules cm^{-2}) and there should be 1.8×10^{14} molecules of hydrogen cm^{-2} on part B. Additional doses of either gas should lead to a sharp increase in the partial pressure of nitrogen. As can be seen from Fig. 11 this is exactly what happens. As soon as the total coverage reaches 6×10^{14} molecules cm^{-2} the partial pressure of nitrogen increases sharply.

4. Study of the Adsorption and Displacement Kinetics

As shown in earlier work (*28, 29*) the change in resistivity which instantaneously accompanies the adsorption, can be used in the study of the kinetics of the adsorption process. It therefore seemed promising to study the exchange process (Fig. 8) using this method.

It has been stated in Sect. IV.3. that the kinetics observed with the adsorption of a pure gas are solely determined by the diffusion of the gas from the gas pipette to the film. This process would correspond to a first order reaction.

The time dependence of the change in electrical resistivity during one of the initial additions of nitrogen to a clean iron film is shown in Fig. 12a. The difference in the change in resistivity at time $t = \infty$ (ΔR_∞) and time $t = t$ (ΔR_t) can be obtained from Fig. 12a. A plot of the logarithm of this difference versus time yields a straight line as shown in Fig. 12b. This shows that the process observed is a first order reaction with a rate constant k_{N_2}. It follows that if the kinetics are determined by the diffusion of the gas through the tubes of the apparatus then the reaction rate constant for hydrogen adsorption should be larger by a factor $(M_{N_2}/M_{H_2})^{\frac{1}{2}} = (14)^{\frac{1}{2}}$. Using this rate constant $[k_{N_2}\cdot(14)^{\frac{1}{2}}]$ the change in resistance

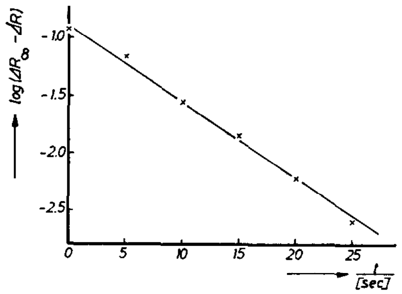

FIG. 12b. Plot of log ($\Delta R_\infty - \Delta R$) vs t to demonstrate the first order mechanism of the change of resistance shown in Fig. 12a.

due to hydrogen adsorption has been calculated (circles in Fig. 13). These circles fit very well the curve from the hydrogen adsorption which is obtained by a direct measurement of the change in resistance with a recorder.

In order to study the kinetics of the displacement reaction the decrease in the resistance as shown in Fig. 8 and observed with similar experiments were evaluated. Because the final value of the resistance, ΔR_∞, was not reached during the time in which the data were taken, the reaction order was not determined using the integrated differential equation *(30)*:

$$\log(\Delta R_\infty - \Delta R) = -k_1 \cdot \log e \cdot t + \log \Delta R_\infty \qquad \text{(1st order)} \quad (1)$$

or

$$\frac{1}{\Delta R_\infty - \Delta R} = \frac{k_2}{\Delta R_\infty} t + \frac{1}{\Delta R_\infty} \qquad \text{(2nd order)} \quad (2)$$

but by using the differential equation itself in the form

$$\frac{\Delta(\Delta R)}{\Delta t} = k_1'(\Delta R_\infty - \Delta R) \quad \text{(1st order)} \qquad (3)$$

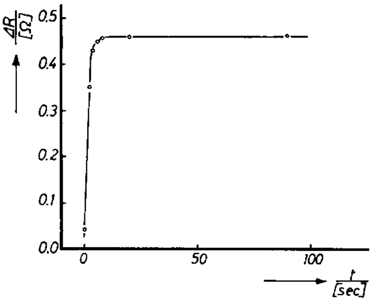

Fig. 13. Kinetics of the change of resistance R due to the adsorption of H_2 on a clean Fe film. $T = 77$ K; $d = 88$ Å. (——) experimental curve; (○) calculated values.

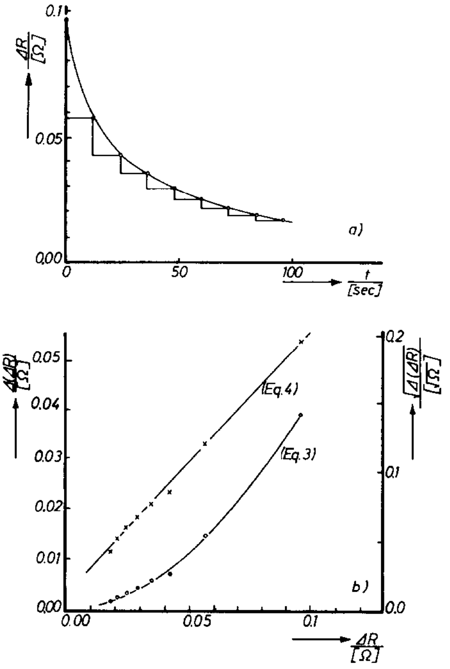

Fig. 14. Kinetics of the change of resistance R due to the second addition of H_2 on an iron film precovered with N_2 (see Fig. 8). (a) Experimental curve; (b) plot of $\Delta(\Delta R)$ vs ΔR [Eq. (3)]; and of $[\Delta(\Delta R)]^{\frac{1}{2}}$ vs ΔR [Eq. (4)].

or

$$\frac{\Delta(\Delta R)}{\Delta t} = k_2'(\Delta R_\infty - \Delta R)^2 \qquad \text{(2nd order)} \quad (4)$$

by plotting $\Delta(\Delta R)$ vs ΔR for the first order case or $[\Delta(\Delta R)]^{\frac{1}{2}}$ vs ΔR for the second order case for constant values of Δt.

The results of all of the evaluations have shown that Eq. (4) is valid and not Eq. (3), as long as the amount of nitrogen adsorbed is large compared to the amount of hydrogen available for an exchange process, i.e., in the initial steps of the exchange process. An example is given in Fig. 14. Using an enlarged scale Fig. 14a shows the decrease in resistance observed after the first addition of hydrogen in Fig. 8. The values of $\Delta(\Delta R)$, or $[\Delta(\Delta R)]^{\frac{1}{2}}$

taken from Fig. 14a are plotted versus ΔR in Fig. 14b. A second order reaction is also found for the subsequent additions of hydrogen up to the sixth addition in Fig. 8.

The reaction of the intermediate exchange steps 7–11 are found to be neither first order nor second order, whereas the reaction of the final steps approaches third order.

In the interpretation of the results it must be remembered that Eq. (4) assumes that the reaction partners determining the order of the reaction have the same initial concentration. It should also be pointed out that nitrogen is not present in the dissociated state (*15*) (see Sect. IV.5). Because hydrogen chemisorbed at 77 K cannot freely move on the surface of the film (*31*) only the hydrogen adsorbed on those faces which can also adsorb nitrogen must be considered.

A possible interpretation for the observed kinetics is given in Eq. (5).

$$N_{2(ads)} + H_2 \xrightarrow{\text{fast}} N_{2(ads)} + 2H^* \xrightarrow{\text{slow}} 2H_{(chem)} + N_{2(gas)}. \quad (5)$$

Hydrogen is very rapidly adsorbed in an atomic state (H*). However, at this stage the hydrogen atoms are not in the energetically most favorable state because the corresponding sites are initially blocked by nitrogen. In the slow reaction two hydrogen atoms displace one adsorbed nitrogen molecule and are thus transformed into their final chemisorbed state. The following equation is in agreement with the observed relations

$$\frac{dn_{H(chem)}}{dt} = k(n_{N_{2(ads)_0}} - 2n_{H(chem)}) \times (n_{H_0^*} - n_{H(chem)})^2, \quad (6)$$

where the $n_{N_{2(ads)_0}}$ and $n_{H_0^*}$ are the number of particles at the beginning of each exchange step, $dn_{H(chem)}$ is proportional to $d\Delta R$. Because of the large excess of nitrogen present in the initial exchange steps the term $(n_{N_{2(ads)_0}} - 2n_{H(chem)})$, in the first approximation, can be considered constant. This results in a second order reaction. After several exchange steps have occurred the concentration of the nitrogen has decreased to such an extent that the change in the nitrogen concentration during an exchange step must be taken into account. The reaction is now no longer second order. In the final exchange steps the amount of adsorbed nitrogen is approximately equal to the amount of hydrogen available for the exchange process. Therefore, the kinetics approaches a third order reaction in which the initial concentrations of the reaction partners are equal.

5. *Isotopic Exchange Studies of* $^{14}N_2$–$^{15}N_2$ *in the Presence of* H_2

It has been shown in a preceding work (*15*) that the isotopic equilibrium for nitrogen adsorbed on clean iron films was not established at temperatures below 400 K and at a nitrogen pressure of 10^{-4} Torr. This was also true when a red glowing iron wire was used as a catalyst. The same iron wire had been used to evaporate the films under ultrahigh vacuum conditions. Before the evaporation of the films the wire has been heated at dark red for 1 hr in a hydrogen pressure of 10 Torr. The surface area of the wire was about 0.1 cm². Even after 11 hr glowing no change in the isotopic composition of the N_2 gas (10^{-4} Torr) could be observed. From this work the authors have concluded that nitrogen is not dissociatively adsorbed on the clean iron surfaces employed.

The question has been raised whether the isotopic equilibrium of nitrogen can be established by the presence of hydrogen.

A possible intermediate for this process could be the $N_2 \ldots H$ adducts. Experiments show that in a $^{14}N_2$–$^{15}N_2$ mixture with a partial pressure of $p = 6 \times 10^{-4}$ Torr in the presence of hydrogen with a partial pressure of $p = 4 \times 10^{-4}$ Torr the formation of $^{15}N^{14}N$ cannot be detected over a clean iron film at 373 K even after 15 hr. The same result is obtained when a clean iron wire coil (see above) is kept glowing at a dark red color for 20 hr in a cell containing 3.5×10^{-4} Torr of hydrogen and 5.5×10^{-4} Torr of the $^{14}N_2$–$^{15}N_2$ mixture.

However, when the iron wire coil is replaced by a tungsten coil with a similar surface area, keeping the other experimental conditions constant, the formation of $^{14}N^{15}N$ from the $^{14}N_2$ and $^{15}N_2$ molecules is detected after a few minutes. This indicates that the absence of equilibration with the red glowing iron wire cannot be explained by inadequate experimental conditions such as pressure, surface area, temperature or sensitivity.

The experimental results presented in this paper do not support the theory that the isotopic equilibrium of nitrogen can be established by the presence of hydrogen as far as the low pressure range is concerned.

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