

THE INTERACTION OF NITROGEN WITH TUNGSTEN AND IRIDIUM

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The interaction of an iridium filament with nitrogen, thermally activated at the tungsten filament, was studied at low pressures. The activated nitrogen is chemisorbed at iridium and at room temperature it reacts with hydrogen, yielding ammonia.

The interaction of nitrogen with tungsten is described in a number of papers¹⁻³, while the system nitrogen-iridium has drawn much less attention. The physical adsorption of nitrogen at iridium has been described in literature⁴⁻⁶, in contrast to the chemisorption of the nitrogen molecules which does not occur^{5,7}. Mimeault and Hansen⁸ have observed nitrogen adsorption at iridium, at room temperature, when the ionization gauge with a tungsten filament was kept in operation. The authors attributed this adsorption to atomic nitrogen formed by thermal splitting at the tungsten filament of the vacuumeter. The formed atoms are transported to the iridium filament either through the gas phase or along the glass walls by surface diffusion. Thermal dissociation of the nitrogen molecules at the tungsten filament, in the temperature range 1700–2800 K, has been described by several other authors⁹⁻¹¹.

In the following text, the interaction of the thermally activated nitrogen with iridium is described in more detail. Nitrogen was thermally activated at the tungsten filament in the pressure range $1.3 \cdot 10^{-6}$ –5 Pa. The filament was placed in direct view of the iridium filament. The behaviour of nitrogen bound at the iridium surface was studied in the pressure range $1.3 \cdot 10^{-6}$ – $1.3 \cdot 10^{-3}$ Pa. The properties of the adsorbate were characterized by means of the thermal desorption and the reactivity towards deuterium.

EXPERIMENTAL

The all glass apparatus¹² was separated from the pumps and gas reservoirs by means of the metal valves. The volume of the apparatus was 2400 cc. The system consisted of a vessel with the tungsten and the iridium filament placed in a crosswise position, further of a Bayard-Alpert ionization gauge, a freezing finger and an omegatron detector (ZD PIE Warszawa). The detector

was connected to the apparatus with a tube 45 cm long and 20 mm in diameter. The final background ($2.6 \cdot 10^{-7}$ Pa) was achieved by pumping with the diffusion and the ion pump, applying the following procedure: The apparatus was heated at 670 K during 6–8 hours and then left overnight to cool down slowly under uninterrupted pumping. After that, all filaments were degassed for several hours (tungsten at 2 070 K, iridium at 1 770 K, the anode of the ionization gauge was heated by electron bombardment).

The filaments used for the thermal activation of nitrogen and for the chemisorption experiments had the following dimensions: tungsten – 22 cm long, 0.1 mm in diameter; iridium – 18 cm long and 0.2 mm in diameter. Nitrogen and deuterium were supplied by Technische gas, Leipzig (puriss.), and they were purified by a freeze-out in liquid nitrogen only.

After evacuation of the system and measurement of the mass spectrum of the residual gas, nitrogen was introduced at the chosen pressure. The nitrogen was then activated for 10 minutes by contact with the tungsten filament kept at 2 360 K and during that time the activated nitrogen was adsorbed at the iridium filament. Before the beginning of the activation, the iridium filament was purified by a one minute heating at 1 770 K. During the activation, the iridium filament was kept at room temperature. After the evacuation and a new measurement of the mass spectra of the residual gas, the system was ready for the thermal desorption. The latter was carried out in the presence of the residual gas or of deuterium. The heating voltage during the thermal desorption was applied either instantaneously or it was changed linearly with time.

For the latter case of the time dependent heating voltage, it is possible to obtain, from the energy balance, an approximate time dependence of the filament temperature

$$\log T = 0.5 \log t + 2.5. \quad (1a)$$

This equation is in good agreement with our empirically obtained expression (Fig. 1)

$$\log T = 0.5 \log t + 2.1. \quad (1b)$$

The apparatus used was not originally built for the TDS measurements¹² and therefore the distance between the sample and the mass spectrometer ion source did not permit¹³ to assign the temperature value obtained for the peak maximum, to the temperature of the maximum rate of desorption. For this reason, it was necessary to correlate the scale of the peak temperatures with the known values from the literature^{3,14,15} (Fig. 2). The “temperatures” obtained in this way can be used for the approximation of the activation energy of desorption E (kcal/mol), by means of the equation^{7,24}

$$E = 0.06T_m. \quad (2)$$

This expression is a rough approximation obtained from the equation for the first or second order desorption¹⁶. The same relation has been found empirically for the desorption of hydrogen¹⁷.

RESULTS AND DISCUSSION

Interaction with the Iridium Filament

In the applied pressure range, no molecular nitrogen adsorption was observed at room temperature, both at the clean surface or after the pre-adsorption of hydrogen. The nitrogen, which was thermally activated at the tungsten filament, was adsorbed at iridium in the amount which went up with the increasing pressure of activa-

tion. Our findings here differ from those ones of Mimeault and Hansen⁸ who have found that nitrogen which had been activated at the tungsten cathode of the ionization manometer, was adsorbed at the iridium filament at pressures as low as $5 \cdot 10^{-5}$ Pa. In our work, under comparable time and pressure conditions, the extent of sorption of the activated nitrogen was negligible even at pressures by one order of magnitude higher. It seems that in the above cited paper, the nitrogen molecules were additionally activated by electron bombardement¹⁸. In our experimental arrangement, the major part of nitrogen activations was carried out at pressure 5 Pa. This pressure guaranteed enough coverage to distinguish two energy forms in the course of the subsequent time programmed desorption. The shape of the desorption curve at the frequency 350 kHz (atomic mass 14, corresponding to the ion N^+) during the programmed heating is shown in Fig. 3. The first sharp peak is probably connected with desorption of the nitrogen from the surface. The second, broader peak, appearing at higher temperature, is probably related to the desorption of the particles diffusing towards the surface, from the sub-surface region of the iridium filament. A similar effect was described also for the system: atomic nitrogen–nickel (ref.¹⁹). The form of the above desorption curve (Fig. 3) strongly depends on the preceding treatment of the iridium filament: *a*) The first peak is not observed in a repeated desorption if the interval of cooling, measured from the previous heating to high temperature (which is required for the formation of a flat peak) is less than 20 seconds; *b*) A flat peak is obtained only after the filament has been warmed up by several successive heatings and not left cooling for more than 15 minutes. The first peak is evidently connected with the transport of nitrogen from the interior of the solid and with the formation of the nitrogen reserve in the sub-surface layer. This reserve consists of nitrogen which had not enough time to recombine and desorb

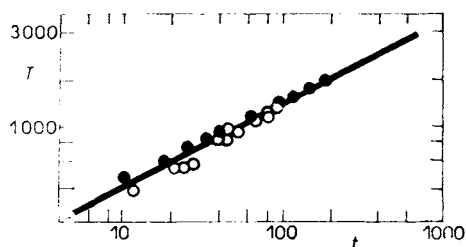


FIG. 1

The dependence of the filament temperature T (K) on duration of the programmed heating t (s), for tungsten and iridium; ● tungsten, ○ iridium

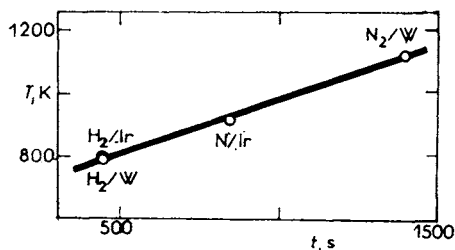


FIG. 2

Correlation of the maximum peak temperatures T (K), observed in this work and t (K), observed for the same system in literature^{7,26-28}

during the cooling of the filament from the high temperature. Molecular nitrogen itself cannot exist at the iridium surface at temperatures higher than 250 K (ref.²⁰). The second peak is probably connected with the formation of the stationary reservoir of subsurface nitrogen which, according to the observed effects, should be able to emerge at room temperature at the surface, recombine to a molecule, desorb, and in this way deplete the sub-surface reserve for the subsequent high-temperature desorption.

Interaction with the Tungsten Filament

The course of the 350 kHz signal in the nitrogen atmosphere ($> 1.3 \cdot 10^{-4}$ Pa), after the on and off switching of the tungsten filament, shows a typical adsorption and desorption behaviour (Fig. 4). The chosen apparatus arrangement, however, does not permit to distinguish the different adsorbed states by means of the thermal desorption. After the thermal activation of nitrogen (5 Pa, 2370 K, 10 minutes), part of the nitrogen is released from the tungsten filament only after the desorption peak, at higher temperatures, giving a very broad maximum (Fig. 5).

The desorption spectrum with a programmed heating resembles in this case the behaviour of the iridium filament, with the difference that in the case of the tungsten filament, the high temperature part of the adsorbate is independent of the preceding thermal treatment and is probably related to the formation of a surface nitride.

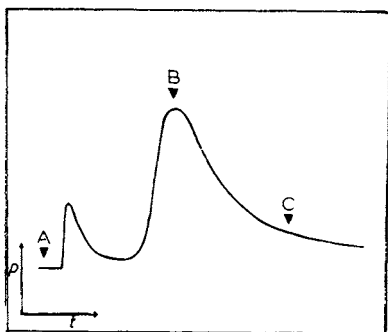


FIG. 3

The course of the nitrogen signal in the programmed heating of the iridium filament, after the nitrogen thermal activation at tungsten ($p_{\text{tot}} = 3 \cdot 10^{-5}$ Pa). A—B: temperature increase, B—C: temperature decrease; maximum temperature of the iridium filament 1720 K

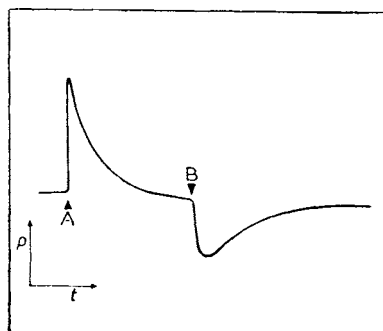


FIG. 4

The course of the nitrogen signal after switching on A and switching off B the tungsten filament heating, in the nitrogen atmosphere at 2000 K ($p_{\text{tot}} = 1.3 \cdot 10^{-4}$ Pa)

Deuterium Interaction with the Nitrogen at the Filaments

If after the thermal activation, nitrogen is pumped away and deuterium introduced instead (at room temperature and pressure $> 10^{-4}$ Pa), the partial pressure of nitrogen goes up very rapidly, evidently as the result of the displacement process. After that, the signal intensity at 247 kHz (mass 20) slowly increases, which in this case can be assigned to the formation of ND_3 . This seems reasonable because without the preliminary nitrogen activation, the signal at mass 20 (possibly D_2O) remains unchanged. If nitrogen is removed after the thermal activation from the iridium filament surface by thermal desorption, ammonia is not formed at room temperature. The ammonia synthesis can be therefore attributed not to the tungsten but to the iridium surface, in agreement with the data in the literature^{3,21}. The participation of the iridium filament in the ammonia synthesis is further suggested by the marked change of the desorption spectra of nitrogen (mass 14) from iridium, in the course of the reaction. It has been found that after the ammonia synthesis, a third peak with a relatively flat top appears between the two above described peaks. After a longer preliminary deuterium contact with iridium, this third peak is split into two peaks (Fig. 6). Simultaneously, the area of the two original peaks has decreased.

It has been found that in the opposite arrangement of the experiment (*i.e.* where deuterium was brought to the surface in its atomic form and only then molecular

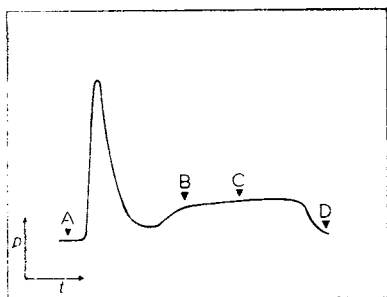


FIG. 5

The course of the nitrogen signal during the programmed heating of the tungsten filament, after the thermal activation of nitrogen ($p_{\text{tot}} = 1 \cdot 10^{-4}$ Pa). A—B: temperature increase, B—C: temperature of the constant maximum input (2 100 K). C—D: temperature decrease

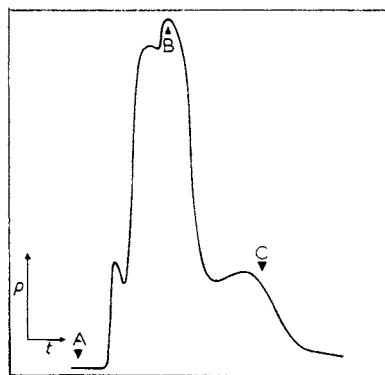


FIG. 6

The course of the nitrogen signal in deuterium ($p_{\text{tot}} = 1.5 \cdot 10^{-3}$ Pa) during the programmed heating of the iridium filament, after the reaction of the adsorbed nitrogen with deuterium. A—B—C: see Fig. 3; maximum temperature of the filament 1 720 K

nitrogen admitted at room temperature to the iridium filament), the signal at mass 20 remains at 300 K unchanged. The presence of the tungsten filament has no influence, independently whether this filament is cool or heated at 2 000 K.

Besides the direct reaction of nitrogen with deuterium, nitrogen changes also the reactivity of both filaments towards the same gas. At tungsten, after the heating of the filament has been switched off, nitrogen suppresses the formation of the peak of cooling¹² during the deuterium desorption. At iridium, nitrogen reduces the steepness of the signal decrease of deuterium in the region of the maximum power input at the filament. Both effects can be suppressed by repeated heatings of the filament in the presence of deuterium ($>10^{-4}$ Pa), under the same temperature conditions. Fig. 7 illustrates the effect of the presence of nitrogen (and of its removal), on the course of the deuterium desorption from iridium. Nitrogen was removed from the surface by two subsequent heatings. The time dependence of the partial pressure of deuterium during the heating is plotted together with the dependence of the total pressure (*i.e.* the pressure of the mixture of deuterium and nitrogen). During the programmed heating of the filaments, following their interaction with the activated nitrogen and deuterium, both gases are desorbed from the tungsten separa-

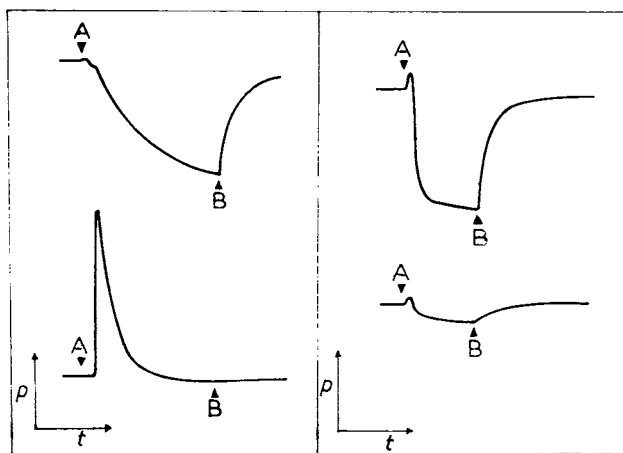


FIG. 7

The effect of the adsorbed nitrogen on the thermal desorption and atomization of deuterium at iridium ($p_{\text{tot}} = 6.7 \cdot 10^{-4}$ Pa); the filament temperature 1 600 K. The upper curves: the courses of the partial pressure of deuterium after switching on B the filament heating; the omega-gatron readings are in arbitrary units. The lower curves: the courses of the total pressure after switching on A and switching off B the filament heating; the ionization manometer readings are in arbitrary units; left hand: filament with adsorbed nitrogen; right hand: filament after the removal of nitrogen

tely, forming two peaks at the curve of the total pressure. The temperatures of the maxima of these peaks are 700 K for deuterium and 1 120 K for nitrogen. In the case of iridium, the temperatures of the maxima are mutually closer: 800 K for deuterium and 910 K for nitrogen. On the curve of the total pressure, both maxima merge into one peak.

As it is shown on the correlation straight line in Fig. 2, the value of the desorption temperature of nitrogen from iridium (910 K) agrees well with the value found by Gorodetskii (850 K). In the latter case, nitrogen was adsorbed at iridium at low temperature and then dissociated at the surface by electron bombardement⁷. It is interesting to note that the approximated relation (2) can be used for rough estimation of the activation energy of desorption, even for systems where the adsorption in the atomic form has been proved^{11,17,22,25}, so that a second order kinetics is indicated. This is probably due to the fact that the present experimental technique of the determination of E_{des} cannot distinguish between the cases of the first and second order desorption. On the other hand, the applicability of Eq. (2) may also suggest an attractive interaction between the dissociated particles at the surface. In such a case, the atoms formed by dissociation do not behave as independent particles, but act more like precursors of the molecules. This pairwise interaction can be either direct or intermediated by the metal. The nature of the intermediates in the molecular mechanism of the ammonia synthesis is a problem yet to be solved. These intermediates can be formed either by hydrogenation of the chemisorbed nitrogen molecule¹ (yielding hydrazine type species) or by the hydrogenation of the atoms of nitrogen¹ (giving species NH_x ($x = 1, 2, 3$)). The elimination of the energetically demanding step (dissociation of the nitrogen molecule at the metal surface), which has been adopted in this work, enables to follow separately only one of the mentioned mechanisms, *i.e.* the chemical reactivity of the chemisorbed nitrogen atoms. Similar approach has been already done in the system Pd/N₂/H₂, where the preadsorbed nitrogen atoms were formed by electron bombardement^{18,23}. In this case, the reaction proceeded at room temperature, only to the stage NH_x ($x = 1, 2$), as found by the analysis of the surface layer by high-resolution¹⁸ Auger spectroscopy (HRAES). The release of ammonia into the gas phase required higher temperature²³ (484 K). In our system with iridium, the same product appeared in the gas phase already at room temperature.

CONCLUSIONS

It is usually assumed in the ammonia synthesis that the most difficult reaction step is the dissociation of the nitrogen molecule. In the present paper, the N—N bond was split thermally in the gas phase and the properties were studied of the nitrogen atoms chemisorbed at the iridium surface, with special attention to their reactivity towards deuterium and to their thermal desorption. When the influence of the

dissociative nitrogen adsorption on the temperature dependence of the total reaction was eliminated, this reaction proceeded at iridium even at room temperatures and at low pressure. Similarly, it has been shown that the adsorption of thermally activated nitrogen at iridium yields two forms differing in bond strength. The weaker bonded form is chemisorbed while the more strongly bound nitrogen is apparently incorporated.

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