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# The Mechanism of the Reaction of Hydrogen with the Metals of the Iron Sub-group

L.V.Babenkova, N.M.Popova, and I.N.Blagoveshchenskaya

The results of quantum-chemical studies of the mechanism of formation of the metal-hydrogen adsorption bond and the solution of hydrogen in group VIII metals, and the results of experimental studies of the chemisorption properties of metals of the iron sub-group with respect to hydrogen, have been reviewed. The experimentally observed regular features of the change in the bond strength and the concentration of different forms of chemisorbed hydrogen agree with the results of the quantum-chemical calculations.
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## I. INTRODUCTION

Extensive experimental and theoretical material has now been accumulated in the study of the adsorption of hydrogen on transition metals.[1-8] A number of problems related to the nature of the adsorption bond, the structure of the surface centres, etc. have not yet been resolved, however. The application of modern physical methods of study (low-energy electron diffraction (LEED), ultraviolet spectroscopy, energy-loss spectroscopy (ELS), etc.) and quantum-chemical methods to the study of the reaction of hydrogen with transition metals has made it possible to approach an understanding of the mechanism of the chemisorption of hydrogen and the relationship between the adsorbing power of metals and their electronic structure.

Recent studies illuminating the role of *d* and *sp* electrons in the adsorption of hydrogen, the influence of the structure of the active centre on the chemisorption of hydrogen, and various models of the dissociative chemisorption of hydrogen on 3*d* transition metals will be reviewed.

## II. THE NATURE OF THE METAL HYDROGEN ADSORPTION BOND

### 1. The Role of *d* and *sp* Electrons in the Adsorption of Hydrogen on 3*d* Metals

In the first papers proposing models of the surface active centres in the chemisorption of hydrogen on transition metals,[6,9,10] it was assumed that the adsorption of hydrogen involves only *d* electrons, and that the directions in space and the splitting of the *d* orbitals with respect to energies are preserved for the surface atoms of the metal (Goodenough's model of the electronic structure of transition

metals[11] was used). It was shown that several types of chemisorption active centres may be formed on the (111), (110), and (100) crystallographic faces of single crystals of nickel and platinum as a result of the emergence of the corresponding $e_g$ or $t_{2g}$ orbitals on to the surface.

Modelling adsorption complexes in accordance with Goodenough's theory of the electronic structure of transition metals gives satisfactory correlations between the experimental and calculated values of the kinetic and thermodynamic parameters of adsorption. A large amount of data on the change in the electronic state of metal and hydrogen atoms during chemisorption, obtained in the last ten years using modern physical and quantum-chemical methods of study, however, indicate that not only the *d* orbitals, but also the *sp* orbitals, of transition metals are involved in the formation of the H–M bond.[12–28]

The principal results of the study of the adsorption of hydrogen on transition metals, obtained using cluster models of adsorption[12,13] and semi-empirical methods of calculation, taking account of the contribution of both the *d* and the *sp* orbitals of the metal to the formation of the H–M bond can be considered.

Calculations by the extended Hückel method (EHM) of the energy of adsorption of a hydrogen molecule on the cluster formed by two neighbouring atoms in a metal lattice (M = Cu, Ni) have shown that the interaction of the 1*s* orbitals of the hydrogen molecule with the $3d_{z^2}$ orbitals of $Ni_2$ leads to the activationless dissociation of the hydrogen molecule with the subsequent localisation of the H atoms on the $3d_{z^2}$ centres of of nickel; the 4*s* orbitals of nickel and copper can form bonds only with hydrogen atoms.[14]

The simultaneous participation of the 3*d*, 4*s*, and 4*p* electrons of the nickel atom in the chemisorption of atomic hydrogen with allowance for the influence of the nearest neighbouring metal atoms in the lattice has been examined by the EHM in Ref.15 (3*d* and 4*s* electrons) and in Refs.16 and 17 (3*d*, 4*s*, and 4*p* electrons). The adsorption was calculated for surface clusters consisting of 8, 9, or 10 nickel atoms, arranged in such a way that the metal atom interacting with hydrogen had the complete immediate environment corresponding to its position on the (100), (110), or (111) faces of a face-centred cubic (f.c.c.) lattice. The most satisfactory agreement between the calculated and experimentally determined values of the H–M bond energies (290 kJ $mole^{-1}$ [29]) was observed when the simultaneous contributions of both the 3*d* and the 4*s* surface states of the nickel atom were taken into account in the calculation.[15] The population of the $3d_{z^2}$ orbital of the nickel atom interacting directly with the hydrogen atom changed during adsorption from 1.904 to 0.972, and that of the 4*s* orbital from 0.468 to 0.368. The changes in the populations of the $3d_{x^2-y^2}$, $3d_{xy}$, $3d_{xz}$, and $3d_{yz}$ orbitals, and also the 4*p* orbitals of the given atom, and the 3*d* and 4*sp* orbitals of the metal atoms surrounding the active centre, were found to be slight for all types of cluster examined.[15–17]

The preferred participation of the 4*s* orbitals of Ni in bond formation with molecular forms of hydrogen has been demonstrated.[18] A semi-empirical MO LCAO calculation of the adsorption of a hydrogen molecule on a centre formed by two neighbouring nickel atoms (Ni–Ni bond length 2.49 Å), with allowance for the contribution to the bond of the 1*s* orbital of hydrogen and the $3d_{z^2}$ and 4*s* orbitals of the metal, on the energy surface of the dissociative chemisorption revealed three states corresponding to two molecular[18,30] and one atomic[18] form of chemisorption. When only the 3*d* orbitals of nickel were involved in the $H_2$–$M_2$ interaction, one state, corresponding to the adsorption of atomic hydrogen, was detected.[18]

The complete neglect of differential overlap (CNDO) showed that, irrespective of the structure of the crystallographic face, the extent of the participation of the 4*s* orbitals in bond formation is much greater than that of the 3*d* orbitals.[20]

Calculations of the change in the density of the surface *d* and *sp* states of transition metals (M = Ni, Pd, W) in an $M_9$ cluster with the (100) structure of an f.c.c. lattice during the chemisorption of atomic hydrogen, carried out by the $X_\alpha$ discrete variation method, made it possible to reach various conclusions about the mechanism of the interaction of a hydrogen atom with a metal surface.[19] As a hydrogen atom approaches an $Ni_9$ cluster, as a result of Coulombic interaction with the cluster, the energy of the 1*s* level of the hydrogen atom is lowered considerably, and approaches the energies of the 4*sp* levels of nickel. Thus the interaction of the 1*s* orbital of the hydrogen atom takes place primarily with the molecular orbital of the $Ni_9$ cluster situated at the bottom of the valence zone and including mainly the 4*s* and 4*p* orbitals of the nickel atom (Fig.1). This leads to the formation of two new levels: a bonding $1a_1$ and a hypothetical antibonding $2a_1'$; the latter interacts with the 3*d* orbitals of nickel, leading to the production, in the valence zone of the cluster, of a $2a_1$ level (with an energy ~4 eV lower than the Fermi level), characteristic of the H–M bond.[19] The formation of a new level situated 5.9 eV (Ni [31]) or ~5.6 eV (Fe [32]) below the Fermi level has been detected in an ultraviolet spectroscopic study of the adsorption of hydrogen.

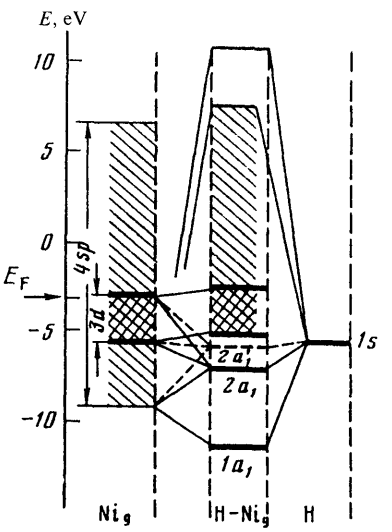



**Figure 1.** Schematic diagram of the interaction of the 1*s* orbital of a hydrogen atom with the 4*sp* and 3*d* orbitals of an $Ni_9$ cluster[19] ($E_F$ is the Fermi level).

As a result of the formation, in the valence zone of the metal, of the antibonding $2a_1'$ level, produced as a result of the interaction of the 1s(H) and 4s(Ni) states[19] (see Fig.1), the population of the Ni–Ni bond becomes negative, leading to repulsion of neighbouring nickel atoms and to a decrease in the strength of the M–M bond in the lattice. It should be noted that in calculations of the adsorption of hydrogen on Pd and W [19] in the valence zone of the cluster H–$M_9$ only the

formation of the bonding level was observed; this is due to the differences in the electronic structures of Ni (the lowest occupied energy levels of the 3*d* zone are appreciably higher than the bottom of the 4*sp* zone) and Pd (the positions of the bottoms of the 4*d* and 5*sp* zones coincide). These data are in good agreement with the fact that nickel hydride, unlike palladium hydride, is unstable.[19]

The participation of both the *d* and *sp* surface states of transition metals in H–M bond formation was also detected experimentally in a study of the state of the surface of a solid during the adsorption of hydrogen.[33–36] The use of NMR [33] to study the adsorption of hydrogen on polycrystalline Cu, Pt, and W made it possible to reveal two adsorption states on the surface of Pt and W specimens, characterised by differences in the magnitude and direction of the resonance shift, and one adsorption state for Cu; the latter is a consequence of the participation of only the 4s orbitals of the metal in H–M bond formation.

Comparison of the directions of the resonance shifts in the adsorption of hydrogen on Pt and W with that obtained for Cu [33] shows that both the 5*d* and the 6*s* electrons take part in H–M bond formation. For Pt, the contribution of the 5*d* states to the production of both types of adsorption is much greater than that of the 6*s* states, whereas for W, predominant participation of the 5*d* orbitals is observed only for one less mobile (that is more firmly bound) adsorption state.

The predominant role of the 4*sp* states of the metal in H–M bond formation was detected in a study of the adsorption of hydrogen on the (111) face of a single crystal of nickel by photoelectron spectroscopy.[34] Comparison of the photoemission spectra obtained with gradual decrease in the degree of covering of a nickel surface with hydrogen (Fig.2) shows that the surface states of the metal are displaced to higher energies and gradually quenched in the range of energies corresponding to the 4*sp* zone of Ni (~0.25–0.50 eV below the Fermi level, see Fig.2). At the same time, the surface 3*d* states of nickel undergo practically no changes with increase in the time of exposure of the specimen in hydrogen.[34]

The predominant participation of the *sp* orbitals for Ni [34,36] and of the *d* orbitals for Pt and Pd [33] in H–M bond formation has been related to the differences in the electronic structures of these metals.[33,34]

According to quantum-chemical data, the H–M bond energy is determined by the extent of the participation of the surface *d* and *sp* states of the metal in the interaction with hydrogen, which in turn is determined by the structure of the chemisorption active centre.[15–17,20,22] Calculated data obtained by the extended Hückel method on the extent of the participation of the valence 3*d* and 4*s* electrons in the adsorption of atomic hydrogen on different crystal faces of nickel show that the role of the 4*s* orbitals of the metal increases with increase in the strength of the H–M bond, whereas the contribution of the 3*d* orbitals is greater for weak interactions with hydrogen; thus the population of the overlap of the 1*s* orbital of the hydrogen atom with the $3d_{z^2}$ and 4*s* orbitals of nickel changes as follows in the series of faces (110), (100), (111) (with decrease in the strength of the bond): 0.0452, 0.0526, and 0.0600 for the $3d_{z^2}$ orbital, and 0.1589, 0.1479, and 0.1399 for the 4*s* orbitals.[15]

The same regular features are observed for the chemisorption of molecular hydrogen.[21] For weak chemisorption of a hydrogen molecule (long H–Ni bond and short H–H bond) for the periodic model of the surface [an ideal crystal lattice, containing 250 atoms, with the f.c.c. structure, (100) face], the greatest contribution to bond formation is made by the 3*d* orbitals of nickel (Table 1), whereas with increase in the strength of the H–Ni bond, the participation of the 4*sp* states of the metal in adsorption predominates. For the cluster model of chemisorption, irrespective of the size of the particle, the 3*d* states of the metal make a smaller contribution to bond formation than the 4*sp* states (Table 1). The contribution of the *d* or *sp* orbitals of the metal to the interaction with hydrogen is determined by the structure of the chemisorption active centre.[15–17,22,25,37]

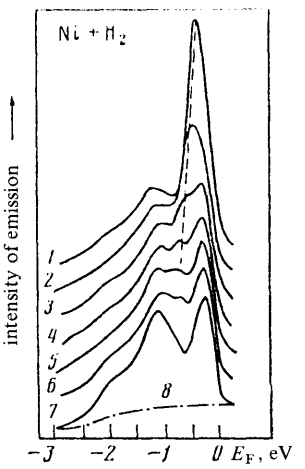



**Figure 2.** Photoelectron spectra of the (111) face of a single crystal of nickel for different degrees of covering of the surface by hydrogen:[34] *1*) original specimen; *2*) specimen kept in $H_2$ at 0.2 Langmuir; *3*) at 0.4; *4*) 0.6; *5*) 0.8; *6*) 1.0; *7*) 1.2; and *8*) (spectrum corresponding to complete saturation of the surface with hydrogen) 10.0 Langmuir (1 Langmuir = $10^6$ mmHg). The broken line shows the displacement of the surface states with increase in the degree of covering of the surface.

**Table 1.** Contribution of the surface 3*d* and 4*sp* states of nickel to the formation of the $H_2$–M bond.[21]*

| r (Ni–Ni), Å | r (H–H), Å | Ni–H bond population | | r (Ni–Ni), Å | r (H–H), Å | Ni–H bond population | |
|---|---|---|---|---|---|---|---|
| | | 3*d* | 4*sp* | | | 3*d* | 4*sp* |
| Periodic model of the surface | | | | $Ni_8$ cluster | | | |
| 2.0 | 0.74 | 0.410 | −1.355 | 2.0 | 1.20 | 2.015 | 5.147 |
| 2.0 | 1.00 | 1.027 | −0.010 | $Ni_{14}$ cluster | | | |
| 2.0 | 1.20 | 3.096 | 2.830 | | | | |
| 1.5 | 1.20 | 7.764 | 8.455 | 2.0 | 1.20 | 2.463 | 5.857 |

*The calculations were carried out by the extended Hückel method.

The EHM has been used to calculate the values of the energy of adsorption of atomic hydrogen and the population of the overlap of the 1*s* orbital of hydrogen with the 3*d* and 4*sp* orbitals of nickel for 11 different types of adsorption complex ("surface molecules").[16,17] Comparison of the energies of adsorption $\Delta E_{ads}$ obtained for the restricted periodic model of the surface and for the cluster model shows that on all crystallographic faces, the bond between the

hydrogen atom and one nickel atom (position *A*) is preferred ($\Delta E_{ads}$ has values from −2.80 eV to −2.46 eV) to the formation of multicentre bonds with the hydrogen atom situated between two (position *B*, $\Delta E_{ads}$ between −2.60 eV and −2.23 eV), three, or four (position *C*, $\Delta E_{ads}$ between −2.38 eV and −2.24 eV) nickel atoms. Irrespective of the number of bonds formed by the hydrogen atom with the metal atoms, the 4*sp* states of nickel play the greatest part in the interaction. The adsorption of hydrogen on all types of centre is accompanied by the formation of a negatively charged form of hydrogen;[15–17] the magnitude of the charge is determined by the structure of the active centre, and amounts to −0.35 e for centres of type *A*, −0.30 e for centres of type *B*, and −0.25 e for centres of type *C*.

Analogous data on the strength of the bond formed by a hydrogen atom adsorbed on a nickel surface in positions *A*, *B*, or *C* were obtained in Ref. 22, again by the EHM; the maximum displacement of charge from the metal to the hydrogen atom (−0.725, −0.605, and −0.536 e), the greatest population of the bond between the hydrogen atom and the nearest nickel atom (0.428, 0.317, and 0.237), and the maximum decrease in the total energy of the H–M system (−1118.445, −1118.080, and −1117.599 eV for adsorption on the centres *A*, *B*, and *C* respectively) correspond to the adsorption of the hydrogen atom on the centre of type *A*.

On the other hand, calculations of the stability of the multicentre bond of the chemisorbed hydrogen atom on nickel, carried out by the CNDO [20,38] and Wolfsberg–Helmholtz MO [6] methods for the adsorption of atomic hydrogen on the *A*, *B*, and *C* centres of the (100), (110), and (111) faces of a single crystal of nickel showed that an increase in the number of metal atoms taking part in bond formation with the hydrogen atom is accompanied by a significant increase in the bond energy: −1.6, 2.8, 3.2, and 3.0 eV for an H atom combined with one, two, three, and four nickel atoms.[38] Irrespective of the type of adsorption centre and crystallographic face, however (as in Refs. 15 and 17), negative charge is displaced from the metal to hydrogen (0.2 e); the magnitude of the charge changes little with change in the structure of the active centre.

Evidence of the preferential adsorption of hydrogen on centres formed by three, four, or five metal atoms (centres of type *C*) is also provided by the results of an experimental study of the chemisorption of hydrogen by low-energy electron diffraction,[39–46] energy-loss spectroscopy,[40] and inelastic neutron spectroscopy,[46,47] which showed that best agreement between the experimental and calculated data on the change in the structure and electronic state of the metals during the chemisorption of hydrogen is observed when multicentre models of chemisorption ($H–M_n$) are used.

## 2. Model of the Dissociative Chemisorption of Hydrogen

Quantum-chemical calculations of the energy of interaction in an $H_2–M_n$ system (where M = Ni, Pt, Pd) make it possible to reach various conclusions about the mechanism of the dissociative chemisorption of hydrogen and to determine the reasons for the production and to predict the relative height of the energy barrier to rupture of the H–H bond.[12,14,18,22,48]

The interaction of the molecular orbitals of hydrogen with the molecular orbitals of an $Ni_{13}$ cluster (adsorption at the centre of the crystallographic (111) face of an icosahedron) leads to an appreciable change in the electronic structure of the metal (Fig. 3). At the bottom of the 3*d* zone, a new band $\phi^*$ (−9.571 eV) appears, formed mainly by the contribution of the antibonding $1s\sigma_u$ state of hydrogen and the valence level of the metal, including an appreciable proportion of the *d* state. The production, in the valence zone of the cluster, of a level containing antibonding states of hydrogen, and the appreciable transfer of electrons to this level from the *d* zone of the metal (−0.19 e) leads to a significant decrease in the strength of the H–H bond and is responsible for the dissociation of the hydrogen molecule.[22]

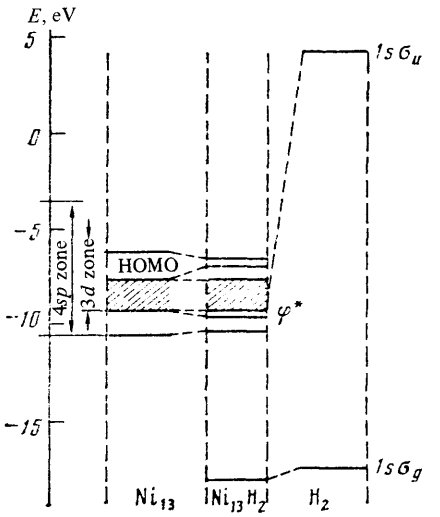



**Figure 3.** Schematic diagram of the interaction of the electron levels of the hydrogen molecule and an $Ni_{13}$ cluster.[22]

A similar mechanism for the dissociation of molecular hydrogen in its adsorption on transition metals of the fourth period (Ti–Ni) was proposed[12] on the basis of MO LCAO calculations of the adsorption of a hydrogen molecule on a cluster formed by two metal atoms (M–M distance 2.5 Å). Since the hydrogen molecule does not have electron levels situated close to the 3*d* zone of the metal† (the magnitude of the 1s(H)–3d(Ni) overlap integral is ~0.1, whereas for 1s(H)–4s(Ni) it is ~0.5), the adsorption of molecular hydrogen takes place as a result of the donor–acceptor interaction of the occupied 1*s* orbital of hydrogen with the unoccupied bonding 4*s* orbitals of the metal.[12] The hydrogen molecule is positively charged.[12,27] The subsequent movement of the hydrogen molecule along the reaction coordinate (that is decrease in the H–M distance) is accompanied by the interaction of the antibonding 1*s* and 4*s* orbitals of the hydrogen molecule and the metal atom, leading to the formation of a new level in the valence zone of the $H_2–Ni_2$ cluster and the transfer of the 3*d* electrons of nickel to this level.[12]

The height of the energy barrier to the dissociation of molecular hydrogen is determined by the position of the 4*s* antibonding and 3*d* levels of the metal;[12] the higher these

†According to Ref. 22, the 3*d* zone of nickel in the $Ni_{13}$ cluster lies in the energy range from −9.232 eV to −7.652 eV, and the *sp* zone in the range from −10.624 eV to −4.488 eV, whereas the bonding and antibonding levels of the hydrogen molecule have energies of −17.56 eV and 4.17 eV respectively.

levels on the energy scale, the more closely they approach the antibonding 1*s* levels of the hydrogen molecule, and hence the more readily the antibonding 1s(H) and 4*s*(M) states interact and the more readily the 3*d* electrons of the metal are transferred to the newly formed molecular orbital.

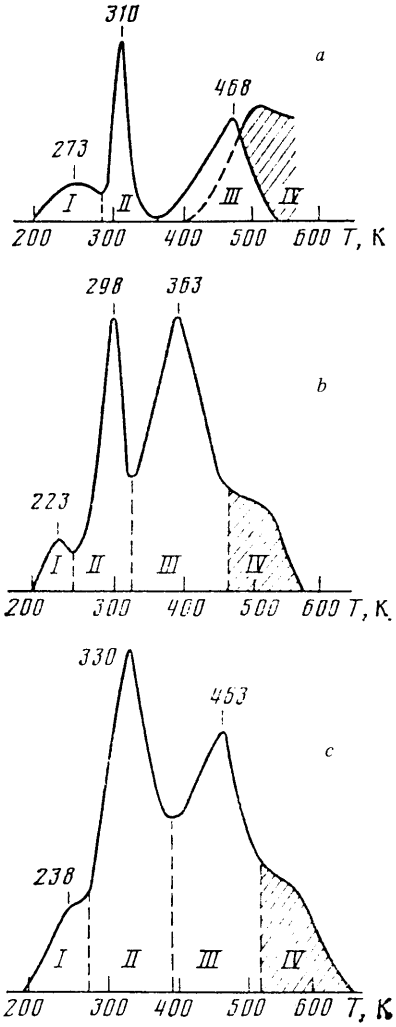



**Figure 4.** Spectra of the desorption of hydrogen from α-Fe (*a*), α-Co (*b*), and Ni (*c*) blacks ($T_{ads}$ = 573 K);[50,52,54] *I,II,III*) forms of adsorbed hydrogen; *IV*) (hatched region) dissolved hydrogen.

Thus an analysis of theoretical and experimental studies of the mechanism of the chemisorption of hydrogen on transition metals of period IV shows that the adsorption of hydrogen takes place as a result of the interaction of the 1*s* states of the hydrogen molecule with the surface 4*sp* and 3*d* states of the metal atoms, with the preferential participation of the *sp* states. This interaction leads to the formation, in the valence zone of the metal, of a new level containing an appreciable proportion of the antibonding states of hydrogen and the 4*s* states of the metal, and to the transfer of the 3*d* electrons of the metal to this level, and hence to the dissociative chemisorption of hydrogen on the surface of the transition metals. The nature and strength of the H–M bond formed is determined by the extent of the participation of the 4*sp* and 3*d* states of the metal in the interaction; the greater the contribution of the *sp* states, the stronger the resulting H–M bond. The contribution of the *d* or *sp* states of the metals to the interaction in turn is determined by the electronic structure of the metal and the structure of the adsorbed complex.

The above data on the mechanism of the chemisorption of hydrogen on transition metals can be compared with the results of the study of the state of hydrogen in metal blacks of the iron sub-group (Fe, Co, Ni), obtained by temperature-programmed desorption.[49–54]# The reaction of hydrogen with these metals leads to the production of four forms of hydrogen, due to the existence of different types of adsorption complexes on the surface of the blacks studied (Fig.4). From the kinetics of the desorption, forms I and II were classified as molecular, and form III as an atomic form of chemisorption. The energetic uniformity of the most strongly bonded hydrogen of form IV, detected for Fe, Co, and Ni (the complete removal of the hydrogen of form IV under isothermal conditions at the temperature of the start of the desorption of the hydrogen of this form), together with published data on the solution of hydrogen in metals of the iron sub-group, made it possible to classify the hydrogen of form IV as hydrogen dissolved in the bulk of the metals studied;[50,53,54] the regular features of the solution of hydrogen will be examined in the next section.

A study of the distribution with respect to the activation energy of desorption of the hydrogen adsorbed in forms I, II, and III showed that part of the atomic hydrogen of form III (~40–50%) is characterised by similar values of the activation energy of desorption. The energetic uniformity of this fraction of the atomic hydrogen of form III on the surface of non-noble metals is due to the adsorption of hydrogen on centres of a single type (possibly one-centre adsorption), whereas the firmly bound and energetically less uniform fraction of the hydrogen of form III corresponds to the adsorption of hydrogen atoms on centres of different types (a multicentre bond of the form $H–M_n$, where $n$ = 2, 3, 4, 5). Thus data on the state of hydrogen on the surface of non-noble metals (Fe, Co, Ni), obtained by thermal desorption, provide evidence of the greater strength of the multicentre $H–M_n$ bonds.

Comparison of the thermal desorption characteristics of hydrogen for the series Fe, Co, Ni (Table 2) shows that the strength of the bond produced by molecular forms of hydrogen tends to increase along the period; there is an increase in the temperature at which desorption is complete and in the proportion of molecular adsorption. The observed increase in the strength of the bond and increase in the proportion of molecular adsorption on going from Fe to Ni correlates with the change in the radius of the metal atoms along the period, leading to a downward displacement, on the energy scale, of the unoccupied bonding 4*s* levels of the metal, and to their maximum approach to the bonding 1*s* level of the hydrogen molecule. This last feature leads to a lowering of the energy barrier to the formation of the

#The Ni and Co black specimens studied were obtained by the reductive decomposition of the formates in a stream of $H_2$ at 573 K and 623 K. Fe black was prepared by decomposing iron nitrate and then reducing the oxides in $H_2$ at 773 K (30 h).

adsorbed complex $H_2$–$M_n$(Table 2).[12,18,26,27] The relative concentration and bond strength of the atomic adsorbed hydrogen on Fe, Co, and Ni blacks, on the other hand, decreases slightly from Fe to Ni (Fig.4 and Table 2). According to calculated data,[12,26,27] this may be due to an increase in the energy difference between the antibonding 1*s* level of hydrogen and the 4*s* antibonding and 3*d* levels of the metals involved in H–M bond formation, leading to an increase in the energy barrier to the dissociation of the hydrogen molecules (Table 2).

**Table 2.** Experimental[49–54] and calculated[26,27] characteristics of different forms of hydrogen on Fe, Co, and Ni.

| M | *r*, Å | $T_{end\ des.}$, K | [$H_2$], % | $E(H_2\text{–}M)$*, kJ mole$^{-1}$ | $l_{H_2\text{–}M}$, Å | $E_{des.\ at.}$, kJ mole$^{-1}$ | [H], % | $E_{diss}$ ($H_2$–M), eV |
|---|---|---|---|---|---|---|---|---|
| Fe | 1.26 | 343 | 39.1 | −128.04 | 1.95 | 56.8 | 60.9 | 7.94 |
| Co | 1.25 | 313 | 44.4 | −149.47 | 1.81 | 47.2 | 55.6 | 9.14 |
| Ni | 1.24 | 393 | 56.8 | −172.35 | 1.75 | 45.2 | 43.2 | 10.95 |

Notes: *r* is the atomic radius; $T_{end\ des.}$ the temperature of the end of the desorption of molecular hydrogen; [$H_2$] the fraction of molecular hydrogen; $E(H_2\text{–}M)$ the energy of the complex $H_2$–M; *l* the equilibrium length of the $H_2$–M bond; $E_{des.\ at}$ the activation energy of the desorption of the atomic hydrogen of form III; [H] the fraction of atomic hydrogen; and $E_{diss}(H_2\text{–}M)$ the dissociation energy of the complex $H_2$–M.

*Calculated data.

Thus the experimental data on the variety of forms and the change in the quantity and bond strength of molecular and atomic hydrogen in the series Fe, Co, Ni [49–57] agree with the results of quantum-chemical calculations on the chemisorption of hydrogen, taking account of the electronic structure of both hydrogen and the metals.[12,13,15–22,27,30,58]

## III. SOLUTION OF HYDROGEN IN METALS

### 1. Dependence of the Solubility of Hydrogen on the Electronic Structure of Transition Metals

The study of the solubility of hydrogen in the metals of the iron sub-group (Fe, Co, Ni) is of considerable practical importance. A number of monographs and reviews have been devoted to the problem of the solution of hydrogen in massive specimens (films, membranes, wires, etc.),[59–65] but published data on the solubility of hydrogen in dispersed metals are few and contradictory.[66–70] Since Fe, Co, and Ni are used as catalysts mainly in the dispersed state, it is of interest to determine the quantitative characteristics of the solubility of hydrogen in these metal blacks.

The main regular features of the solution of hydrogen in transition metals can be examined first. In recent years, increasing attention has been paid to the search for correlations between the ability of transition metals to dissolve hydrogen and their electronic structure.[67–72] Attempts are being made to establish the relationship between the solubility of hydrogen and the difference in the electron densities of the metal and hydrogen,[73] the concentration of valence electrons,[73,74] the density of states on the Fermi surface of the metal,[74,75] etc.

The main regular features of the change in the structure of the valence zone of the 3*d* and 4*d* transition metals with increase in the number of hydrogen atoms introduced into the lattice are qualitatively similar, as shown by calculations of the electronic structures of the hydrides of these metals with the stoichiometric composition, containing hydrogen as the proton.[71,76] On going from the pure metal to the compound containing 5 at.% hydrogen in the bulk of the metal ($MH_{0.05}$), a new metal–hydrogen level is produced, which lies below the conductivity zone and which is formed by the *s* states of hydrogen and hybridised *s*–*d* states of the metal;[71,76] further increase in the hydrogen concentration in the bulk of the metal is accompanied by broadening of the metal–hydrogen level.[71] Comparison of the electronic structures of pure palladium and the palladium–hydrogen system[75] indicates that the Fermi level is displaced to higher energies; the density of states on the Fermi surface decreases considerably.

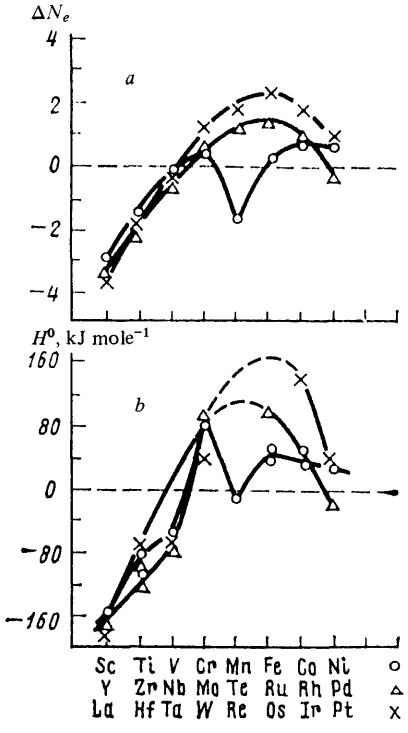



**Figure 5.** Change in the difference in the electron density $\Delta N_e$ on the metal and hydrogen atoms (*a*) and the heat of solution $H^0$ of hydrogen (*b*) along the 3*d*, 4*d*, and 5*d* periods[73] (the unit of density is ~6 × $10^{22}$ electron cm$^{-1}$).

Data obtained in calculations of the change in the electronic structure of transition metals during their saturation with hydrogen[71] have made it possible to estimate the heat of formation of the hydrides of 3*d* and 4*d* transition metals $\Delta E$ as the difference between the total energies of the zones of the

pure metal and compounds with different stoichiometric compositions. The stable hydrides of elements from the left-hand side of the fourth period (Sc, Ti, V) are formed with the liberation of considerable quantities of heat (from −40 kJ mole$^{-1}$ to −200 kJ mole$^{-1}$). The formation of the products of the interaction of hydrogen with metals from the right-hand side of the period (Fe, Co, Ni, Cu; Fig.5*b*) is accompanied by the absorption of heat (from +40 kJ mole$^{-1}$ to +90 kJ mole$^{-1}$).[71]

According to Ref.73, the transition metals which lie at the start of the 3*d* and 5*d* periods and which have a lower electron density than that on the hydrogen atom are also capable of dissolving hydrogen exothermally to give stable hydrides (Figs.5*a* and 5*b*). Metals with a higher electron density than that on the hydrogen atom dissolve only small quantities of hydrogen, with the absorption of heat (Figs.5*a* and 5*b*).[73]

According to Ref.74, depending on their position in the periodic system, the transition metals can be divided into two groups differing in the influence of dissolved hydrogen on the strength of the bonds formed by the atoms in the metal lattice: 1) metals whose *d* level is less than half filled; and 2) metals containing more than six valence electrons.

The introduction of the 1*s* electron of the hydrogen atom into the electron zone of metals of the first type increases the strength of the bond formed by the atoms in the lattice, leading to the formation of stable hydrides [60,71,73] (the metals of sub-groups III–V of the periodic system); the strength of the bond between the atoms in the lattice of metals of the second type (the transition metals of sub-groups VI–VIII) decreases when the 1*s* electron of the hydrogen atom is introduced (hydrogen brittleness). According to the Engel–Brewer theory,[77,78] this influence of dissolved hydrogen on the strength of the bond formed by the metal atoms in the crystal lattice is due to a change in the number of unpaired *d* electrons in the transition metals. The additional 1*s* electron of the hydrogen atom increases the number of unpaired electrons in metals whose valence zone is less than half filled, leading to an increase in the strength of the bond between the atoms in the lattice. For metals of the second type, whose outer level contains more than six electrons, the 1*s* electron of the hydrogen atom lowers the total number of unpaired electrons, leading to a decrease in the strength of the M–M bond in the crystal.

The dependence of the quantity of dissolved hydrogen on the number of unpaired *d* electrons in the outer level of the metal atom is clearly observed for transition metals with a small number of *d* electrons ($d^2$–$d^4$; Ti, Zr, V, La, Hf, etc.); the element with the smallest number of *d* electrons corresponds to the highest solubility of hydrogen and the greatest increase in the strength of the M–M bond.[74]

For metals with a valence level which is more than half filled (Fe, Co, Ni, Ru, Rh, Pd, etc.), best agreement between the calculated and experimental data on the extent of the solution of hydrogen is obtained using a model which relates the ability to dissolve hydrogen to the density of states on the Fermi surface of the given metal;[74] a higher density of states (Fig.6*a*) corresponds to a greater ability to dissolve hydrogen. These models have been used[74] to calculate the magnitude of the change in the strength of the M–M bond when the 1*s* electron of the hydrogen atom is introduced into the valence zone of the metal. The introduction of the additional electron increases the strength of the Ti lattice (ground state $3d^24s^2$) by 7.1%, whereas the bond between the atoms in the Ni lattice (ground state $3d^84s^2$) is weakened by 8.57%.

Comparison of calculated data on the extent of the disordering of metal lattices when hydrogen is absorbed[74] (Fig.6*b*) with the heats of solution of hydrogen[73] (Fig.5*b*) shows a distinct correlation between these quantities: the greater the decrease in the strength of the interaction between the metal atoms when the 1*s* electron of hydrogen is introduced (Fig.6*b*), the greater the endothermic effect of solution (Fig.5*b*).

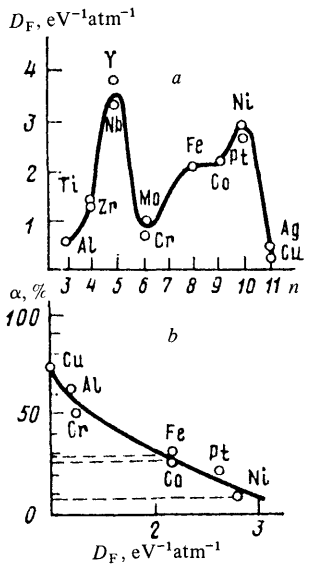



**Figure 6.** Density of states $D_F$ on the Fermi surface (*a*) and extent of the disordering of the lattice α for 3*d* transition metals when hydrogen is dissolved in them (*b*) [74] (*n* is the number of electrons in the outer levels).

## 2. Influence of the State of the Surface on the Extent of the Penetration of Hydrogen into Metal Lattices

A significant unsatisfactory feature of theoretical methods for studying the solution of hydrogen by transition metals is the fact that no account is taken of the contribution of processes taking place on the metal surface during the solution of hydrogen. The absorption of hydrogen by the bulk of the metal is a complex multistage process, involving the adsorption and dissociation of the hydrogen molecule, the penetration of hydrogen atoms into the bulk, and diffusion in the volume of the metal.[59,61,63] Calculations[79] have shown that for metals characterised by an exothermic effect for the solution of hydrogen, the heat liberated during adsorption is sufficient for the penetration of the hydrogen atom into the bulk of the metal.

When hydrogen dissolves in metals for which this process is endothermic (Fe, Co, Ni), the heat liberated during the adsorption of hydrogen is insufficient for the penetration of the hydrogen atom into the bulk of the metal; penetration can take place only at high temperatures, when the adsorbed hydrogen atom acquires sufficient energy to overcome the energy barrier to penetration into the bulk of the metal.[79]

Analysis of the influence of various factors on the rates of the processes taking place on the surface of iron, nickel, and other transition metals during the solution of hydrogen in them[61] shows that change in the extent of the defect character (disperse nature) of the surface (plastic deformation,

the application of strokes, scratches, polishing, sintering at high temperatures[80-83]), its chemical composition (surface coatings[81,84,85]), or temperature[62,80,86-90] leads to a considerable change in the rate of penetration of H atoms into the bulk.

The rate of the penetration of hydrogen atoms into the bulk ($v$) at high temperatures (>670 K) obeys the law $v \sim p^{1/2}$ (where $p$ is the hydrogen pressure), indicating that solution is preceded by dissociation of the hydrogen molecule.[59,63,64] At temperatures <670 K, deviation from the $v \sim p^{1/2}$ relationship is observed, and the kinetic curves show inflections in the temperature range ~470–670 K [61,62,80,86-90] (Figs.7 and 8). According to Ref.61, the existence of the inflection is due to a change in the mechanism of solution; at temperatures <670 K (before the inflection), the surface reactions involving the dissociation of molecular (or the recombination of atomic) hydrogen take place at slow rates, that is they determine the rate of penetration; the activation energy of the penetration of hydrogen in this temperature range is high (107.0 kJ mole$^{-1}$ for Fe). At temperatures >670 K (after the inflection), when the surface reactions take place readily and do not limit the rate of penetration of hydrogen, the activation energy of this process is only 37.6 kJ mole$^{-1}$ (Fe) and practically coincides with the activation energy of diffusion.[87]

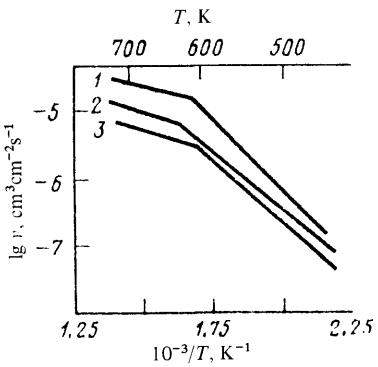



**Figure 7.** Temperature dependence of the rate of penetration of hydrogen $V$ through iron membranes of different thickness $l$:[87] 1) $l$ = 0.25 mm, 2) $l$ = 0.5 mm, 3) $l$ = 1.0 mm.

The role of the atomisation of molecular hydrogen in the process of solution in metals has been clearly demonstrated in a study of the permeability of a nickel membrane for deuterium previously ionised under gas-discharge conditions and for deuterium from the molecular state.[88] For the ionised deuterium, the temperature dependence of the rate of penetration (Fig.8) does not show an inflection (curve *1* in Fig.8), whereas for the non-ionised deuterium, at temperatures >630 K, as in Ref.87, a change in the rate of penetration of deuterium atoms into the bulk of the metals takes place (an inflection is observed; curve *2* in Fig.8). The activation energy of the penetration of deuterium is 61 kJ mole$^{-1}$ at $T$ < 630 K, and 10.5 kJ mole$^{-1}$ at $T$ > 630 K.[88]

The position of the point of inflection on the curve giving the temperature dependence of the rate of penetration of hydrogen depends markedly on the extent of the defect character (disperse nature) of the metal surface;[61,80-83,91] with change in the surface structure of the specimen, for example as a result of plastic deformation,[80] the inflection (~660 K) is displaced to higher temperatures (~790 K).

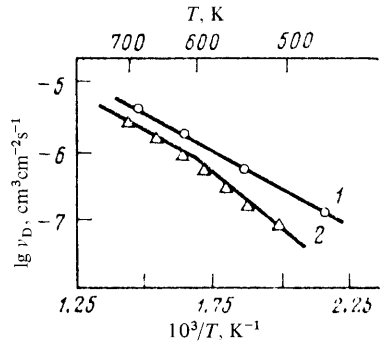



**Figure 8.** Temperature dependence of the rate of penetration of deuterium $v_D$ through a nickel membrane under gas-discharge conditions (*1*) and from the molecular phase (*2*).[88]

Change in the chemical composition of the surface layer of the specimen is also reflected in the rate of penetration of hydrogen into the bulk of the metal.[81,84,85] Covering an iron membrane with a thin layer of palladium[81] or other materials highly active in the atomisation of hydrogen (Ni and Pd blacks) leads to a marked increase in the rate of the penetration of hydrogen, whereas layers of Cu or Ag on an iron membrane surface decrease the magnitude of the hydrogen flux.[84] The application of thin coatings changes the electronic structure of metal surfaces, leading to an increase or a decrease in the rate of the dissociation or recombination of hydrogen;[61] for example, a gold membrane, which is practically impermeable to hydrogen, begins to allow it to pass freely if its inner surface is covered with a thin layer of nickel (thickness ~1 × 10$^{-5}$ cm).[85]

Thus the dissolution of hydrogen in metals at temperatures <670 K is limited by surface reactions (adsorption, dissociation; recombination, desorption). The deviation of the values of the rate of penetration from the $v \sim p^{1/2}$ law at $T$ < 670 K has been related[61] to a decrease in the number of active centres on the surface with decrease in the degree of dispersion of the metal, to the shielding action of surface impurities inactive with respect to the dissociation of hydrogen, and to the presence on the surface of chemisorbed hydrogen which does not have a sufficient reserve of energy for penetration into the metal lattice.[61]

The decrease in the rate of the stage involving the recombination of atomic hydrogen (or the dissociation of molecular hydrogen on the surface of nickel films, accompanied by an increase in the activation energy of the process at low temperatures, has been attributed[62,92] to the formation of a nickel hydride β-phase, whose catalytic activity in the recombination of atomic hydrogen is ~3 times lower than that of pure nickel.[92,93] Calculation of the standard free energy ($G^0$) of the H–M system for the reaction

$$4M + H_2 \rightarrow 2M_2H$$
$$M = Ni, Pd$$

has shown, however, that the formation of nickel hydrides at atmospheric pressure and relatively low temperatures is thermodynamically unlikely, since under these conditions the

value of $G^0$ for the NiH system is +23.6 kJ mole$^{-1}$, whereas for the formation of stable hydrides PdH, $G^0 = -11.8$ kJ mole$^{-1}$.

The preparation of stable hydrides of iron, cobalt, and nickel by the direct reaction of the metal with hydrogen is possible only under extremely severe conditions, at hydrogen pressures >10–20 thousand atm and temperatures >500 K.[62, 65,94] A study of the solubility of hydrogen in palladium and nickel, carried out using calculation methods,[95] showed that the formation of stoichiometric nickel hydrides (H/Ni = 1) is possible at hydrogen pressures not less than 28 thousand atm.

The study by various modern methods (X-ray diffraction, NMR, magnetic methods, etc.) of the state of hydrogen in the volume of metals which absorb it endothermally has indicated that the hydrogen atom transfers the 1s electron to the unfilled *d* zone of the metal, and is present in the lattice as a proton.[59,60,63,79,97] According to calculations,[96] the effective charge of the hydrogen atom is +0.45 e in the Pd lattice, +0.53 e for Ni, and +0.26 e for Fe.

There are at present two widely encountered views on the equilibrium position of a hydrogen atom introduced into a metal lattice. The authors of Refs.63 and 98, who used the precision method of secondary X-ray spectra to study the state of iron saturated with hydrogen, concluded that the hydrogen endothermally absorbed by the metal is present as a proton, inserted into the electron cloud of the metal atoms ("proton gas"). On the other hand, the theoretical calculation of the equilibrium positions of hydrogen atoms in metals which crystallise with a face-centred cubic lattice shows that in a structure of this type, the particles introduced occupy octahedral vacancies.[99,100] Experimental neutron diffraction studies of the structure of the products of the reaction of palladium and nickel with hydrogen also indicate that the protons occupy octahedral positions in the f.c.c. lattice.[101,102]

Calculation of the positions of hydrogen atoms introduced into the body-centred cubic lattice of α-Fe, Ta, V, and Nb [103] showed that in α-Fe the hydrogen atoms occupy only octahedral positions, in Ta and Nb the hydrogen can occupy octahedral and tetrahedral positions, and in V it occupies only tetrahedral lattice positions.

It is of considerable interest to identify the surface active centres by means of which the hydrogen atoms penetrate into the metal lattice. Kinetic and thermodynamic calculations[104,105] have shown that for metals which dissolve hydrogen exothermally (for example Pd), the heat of the adsorption of hydrogen on the centres responsible for its solution should not exceed ~68 kJ g-atom$^{-1}$, so that more firmly bound forms of chemisorption cannot be in equilibrium with absorbed hydrogen.[104] Experimental confirmation of the suggestion that hydrogen penetrates into the bulk of palladium via centres which chemisorb hydrogen with a relatively low bond energy is provided by data obtained by thermal desorption.[79, 106,107] The first portions of hydrogen are adsorbed on a Pd wire (104–306 K) on centres with a high M–H bond energy (heat of adsorption 60–120 kJ g-atom$^{-1}$); solution of hydrogen does not take place. Dissolved hydrogen appears in the desorption spectrum only when hydrogen covers the regions of the surface with a low heat of chemisorption (30–60 kJ g-atom$^{-1}$) (this is the low-temperature range of hydrogen desorption, characterised by a high energetic uniformity).

The authors of Ref.106, who used a micro-gravimetric method to study the kinetics of the sorption and desorption of hydrogen, concluded that the penetration of hydrogen into the palladium lattice takes place via regions which adsorb weakly bound forms of hydrogen (heat of adsorption 7 kJ g-atom$^{-1}$). Calculation of the thermal effects of all stages of the sorption of hydrogen showed that the movement of hydrogen from the state preceding the penetration of hydrogen into the bulk of palladium is energetically more favourable (activation energy of absorption 15 kJ g-atom$^{-1}$) than its migration along the surface to centres with a high heat of adsorption (activation energy of migration 55 kJ g-atom$^{-1}$).[106]

The conclusion that the desorption of absorbed hydrogen takes place via adsorption centres with a low hydrogen–metal bond energy was also previously reached for dispersed Pd,[107] Ta, and W.[108]

The solution of hydrogen in dispersed Fe, Co, and Ni was studied by temperature-programmed desorption[49,50,53,54] to determine the temperatures of the start of the solution and the removal of dissolved hydrogen from the bulk of metals; to differentiate adsorbed and dissolved forms of hydrogen according to the temperature ranges and activation energies of desorption; to estimate quantitatively their concentrations in the metals; and to study the influence of the surface adsorbed forms on the removal of hydrogen from the lattices of these metals.

Dissolved hydrogen appears in α-Fe black at $473 < T \lesssim 573$ K, in α-Co black at 373–423 K, and in Ni black at 298 to 373 K, that is on going from one metal to another along this triad, the temperature of the start of the solution (curve *3* in Fig.9) and the activation barrier to this process decrease; $E_{abs}$ for α-Co black is 18 kJ mole$^{-1}$,[52] whereas for Ni black this energy is 2.5 kJ mole$^{-1}$.[50] In accordance with the model relating the solubility of hydrogen in transition metals to their electronic structure,[74] the minimum heats of the endothermic solution are observed for metals which have the maximum density of states on the Fermi surface. For nickel, which has the highest density of states on the Fermi surface (curve *1* in Fig.9) and the lowest heat of solution (curve *2* in Fig.9), the absorption of hydrogen requires the minimum expenditure of energy compared with Fe and Co (curve *3* in Fig.9).

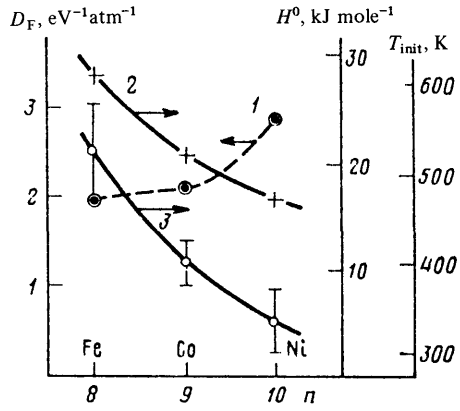



**Figure 9.** Correlation between the heat of solution $H^0$ (*2*),[73] the temperature of the start of the solution of hydrogen $T_{init}$ (*3*),[53,54] and the density of states on the Fermi surface $D_F$ (*1*)[74] for the metals of the first triad of Group VIII of the periodic system (n is the number of outer electrons).

Comparison of the solubility of hydrogen in α-Fe, α-Co, and Ni blacks shows that the absorption capacity of α-Fe black with respect to hydrogen is $10^3$ times greater than that

for α-Co and Ni blacks; the ratio of the number of hydrogen atoms absorbed by the metal to the total number of metal atoms in the specimen is ~1 for α-Fe black, $1.7 \times 10^{-3}$ for α-Co black, and $1.4 \times 10^{-3}$ for Ni black. The sharp decrease in the quantity of dissolved hydrogen in the order Fe > Co > Ni is evidently also due to differences in the electronic structures of the metals. The solubility of hydrogen is higher, and the solution takes place with an exothermic effect, in those transition metals on whose atoms the electron density is lower than that on hydrogen atoms.[73] In metals which dissolve hydrogen with an endothermic effect, the electron density on the metal atoms is generally higher than that on hydrogen atoms.[73] For iron, however, the difference in the electron density on the Fe and hydrogen atoms is much lower than that for Co and Ni (see Fig.6a), and this is apparently responsible for the higher solubility of hydrogen in iron. The high absorption capacity of α-Fe with respect to hydrogen (specimen saturation temperature 773 K) is quantitatively comparable with that of Pd [1,2,8,107,109,110] (saturation temperature ~298 K), in good agreement with the similarity in the values of the electron density on the α-Fe and Pd atoms.[73]

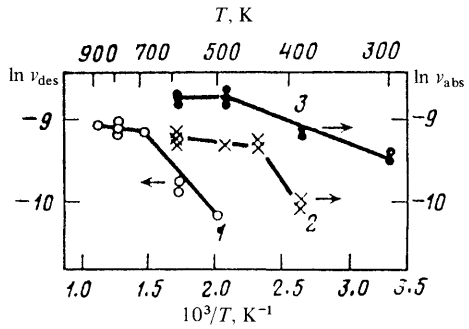



**Figure 10.** Temperature dependence of the rate of desorption of dissolved hydrogen from α-Fe black (*1*) and the rate of adsorption of hydrogen by α-Co (*2*) and Ni (*3*) blacks.[52,54]

In the determination of the activation energy of the desorption or absorption of dissolved hydrogen, the curves giving the temperature dependence of the rate of desorption (α-Fe black, Fig.10) [53,54] or absorption of hydrogen (α-Co and Ni blacks, Fig.10, see Ref.111 for the method of calculation) showed inflections at temperatures of 673 K for α-Fe, 423 K for α-Co, and 473 K for Ni. At low temperatures (before the inflection), the activation energy for the desorption of hydrogen from α-Fe black is 14.6 kJ $mole^{-1}$; $E_{abs}$ for hydrogen for α-Co and Ni blacks is 18.0 kJ $mole^{-1}$ and 2.5 kJ $mole^{-1}$ respectively. At high temperatures (after the inflection), the slope of the straight lines decreases, and the values of $E_{des}$ and $E_{abs}$ indicate that the processes take place with practically no activation barrier; $E_{des}$ for α-Fe black is 2.5 kJ $mole^{-1}$, and $E_{abs}$ has the values ~0.4 kJ $mole^{-1}$ and <0.1 kJ $mole^{-1}$ for α-Co and Ni blacks respectively. Comparison of the temperatures of the liberation of adsorbed (Fig.4) and dissolved (Fig.4 and curve *3* in Fig.9) forms of hydrogen from α-Fe, α-Co, and Ni blacks indicates that the absorption or desorption of dissolved hydrogen with low activation energies takes place at a temperature above that corresponding to the complete removal of adsorbed forms of hydrogen from the surface.[49-54]

Data on the temperature boundaries of the liberation of adsorbed and dissolved forms of hydrogen and the start of the desorption and solution of hydrogen in the bulk of Fe, Co, and Ni blacks, which dissolve hydrogen endothermally (Figs.4 and 9), indicate that, in contrast to metals which dissolve hydrogen exothermally (Pd, Ta, W),[105-108] the removal of hydrogen dissolved in Fe, Co, and Ni takes place on the sections of the surface which chemisorb firmly bound forms of hydrogen.

Thus the systematic study of the processes involved in the chemisorption of hydrogen for metal blacks of the iron subgroup has revealed the regular features of the change in the strength of the bonds formed by atomic and molecular hydrogen, and also the absorption power of the blacks, and has made it possible to relate these characteristics to the positions of the metals in the periodic system. The data obtained on the concentration, forms, and bond energies ($E_{des}$) of hydrogen, which is one of the components of catalytic processes, can be used to develop active catalytic systems and to determine their mechanism of action.

Moreover, the quantitative characteristics obtained for the desorption of dissolved hydrogen from dispersed Fe, Co, and Ni may be useful in the development of processes preventing the corrosion breakdown of these metals.

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Institute of Organic Catalysis and
Electrochemistry of the Academy
of Sciences of the Kazakh SSR,
Alma-Ata