

PHYSICAL PREREQUISITES, MECHANISMS, AND KINETICS OF FORMATION OF Pd₂⁺ MOLECULAR COMPLEXES IN METALLIC PALLADIUM

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UDC 541.183.1

The issue of whether Pd₂⁺ molecular complexes can be formed in metallic palladium has been considered. It has been shown that in the structure of the face-centered cubic palladium crystal lattice, there are the energy and geometric prerequisites for the formation, from the atoms at the centers of adjacent lattice faces, of Pd₂⁺ molecular complexes with a hole in the 4d shell of one atom. The average content of these complexes and holes per palladium atom has been evaluated. Possible mechanism and kinetics of formation of Pd₂⁺ molecular complexes in metallic palladium have been considered.

Keywords: atom, hydrogen degradation, heterogeneous catalysis, face-centered cubic, crystal lattice, kinetics, metallic palladium, mechanism, palladium molecular complex, shielded hydrogen complex.

Introduction. By analyzing the experimental dependence of the sublimation energy (integral interatomic-bonding energy) in palladium on the relative atomic concentration of the hydrogen absorbed in it, it has been shown in [1] that this energy may decrease on the initial portion of the plot presumably when Pd₂⁺ molecular complexes in metallic palladium that interact with shielded hydrogen complexes (H⁺)_{sh} disintegrate. However, the issues of the physical (energy and geometric) prerequisites, mechanism, and kinetics of formation of Pd₂⁺ complexes were not considered in [1] in detail.

Formulation of the Problem. Our objective is to investigate in greater detail the issues of the physical prerequisites, mechanism, and kinetics of formation of Pd₂⁺ molecular complexes in metallic palladium.

Solution of the Formulated Problem. From the general courses in chemistry and physics, it is known that palladium belongs to the group of the so-called transition d metals. Also, it is known that observance of the Pauli principle and the principle of minimum energy in the ground state in filling the shells of palladium atoms leads to the following anomaly in the energy-level distribution:

$$5s < 4d < 5p .$$

The existence of such anomaly energetically offers the possibility of the palladium-atom electrons shifting spontaneously to higher levels, i.e., from the 4d level to a 5s level to form a hole in the 4d shell of palladium.

It is noteworthy that holes are formed in atomic shells only in the metal state and not in the gaseous state where the atoms are "isolated" from each other. From a course in secondary school, it is known that when the metal state is formed only one electron from the 4d shell of each palladium atom is collectivized; these electrons together with the gas-forming free electrons ensure the existence of metallic interatomic-bonding forces.

The presence of holes in the shells of transition-metal atoms, which create new hybridized electronic states in the atoms, can change such important physical properties of these metals as electrical conductivity, heat capacity, etc. Therefore, in the physics of transition metals, it is necessary to know the average number of holes per atom for adequate description of their properties.

The analysis [1] of publications on this issue has shown that for metallic palladium, there are at least three values of the average number of holes per atom at present: 0.36 (36%), 0.6 (60%), and 0.72 (72%) [2–4].

*Deceased.

The effort made to explain this result has led us to the following conclusion. Metallic palladium under normal conditions has two phase states: the α phase with a crystal lattice in the form of a face-centered cube and a lattice constant $a_\alpha \approx 3.89$ Å and the β phase with the same lattice structure but with a lattice constant $a_\beta \approx 4.05$ Å [3, 5].

The β phase exists independently only when stabilized by hydrogen which is to be found predominantly in octahedral palladium interstices, according to neutron-graphic measurements [6].

The relation $a_\alpha/a_\beta = 4.05/3.89 \approx 1.041$ shows that on transition from the α phase to the β phase, in interaction of palladium with hydrogen, the distance between palladium atoms increases by nearly 4.1%. The relation $(a_\alpha/a_\beta)^3 = (4.05/3.89)^3 \approx 1.128$ shows that on α -to- β phase transition, the lattice volume must increase by nearly 12.8%. The local volume in which the interacting hydrogen and palladium atoms are contained must increase by the same value, too. However it has experimentally been established that in interaction of a hydrogen atom with a palladium atom having a hole in the 4d shell, when a neutral molecule of palladium hydride PdH is formed, the volume of the local region in which this molecule is to be found increases by a value of the order of 20% [7].

The relation of the two values of the same quantity (obtained experimentally (20%) and by calculation (12.8%)), which is equal to 1.5625 and is closer to two rather than to unity, has led us to the conclusion that two palladium atoms, one having a hole in the 4d shell, participate in the formation of the palladium-hydride molecule. This conclusion is also confirmed by our calculations.

As is well known, in the structure of the face-centered cubic crystal lattice of metallic palladium, for one lattice there are four atoms, on the average, three of which are at the centers of the faces and one is at the apex of the lattice. In each palladium unit cell consisting of three lattices in each of the three coordinates and with an edge dimension $3a_\alpha$, three atoms at the centers of adjacent lattice faces can form, on the average, 1.5 pairs of atoms bonded by covalent forces (in what follows, covalent-bonded atoms). The atoms at the apices of the cells, which have nearest neighbors, can also form pairs of covalent-bonded atoms. The atom at the opposite apex counteracts their necessary approach. There are no such counteractions for the atoms at the centers of adjacent faces of the lattice. Therefore, for each atom in a unit cell of palladium, there are, on the average, $\approx 1.5 : 4 \approx 0.375$ (37.5%) pairs of covalent-bonded atoms; this corresponds to nearly the same value of the number of holes in the 4d shells of the atoms (0.36 or 36.0%), which has been obtained experimentally in investigating the de Haas–van Alphen effect [3].

The possibility of the covalent bonding force occurring between two palladium atoms arranged at the centers of adjacent lattice faces is also confirmed geometrically, if it is taken into account that the distance between these atoms in the palladium's α phase (d_α) is

$$d_\alpha = a_\alpha/\sqrt{2} \approx 3.89/1.41 \approx 2.76 \text{ \AA} ,$$

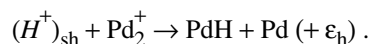
which, with allowance for errors in determining it, corresponds to the tabular value of the palladium-atom diameter [8]:

$$D_{\text{Pd}} \approx 2r_{\text{Pd}} \approx 2 \cdot 1.37 \approx 2.74 \text{ \AA} .$$

Thus, it is our opinion that metallic palladium in the α phase consists of covalent-bonded pairs of palladium atoms to the extent of 36.0–37.5% and of the same number of holes in the 4d shells of these pairs arbitrarily called Pd_2^+ molecular complexes. The maximum energy of covalent interatomic bonding E_c in a Pd_2^+ complex is $E_c = 2\varepsilon_c \approx 2 \cdot 3.1 \approx 6.2$ eV [1].

According to the energy-conservation law, the generation of negative covalent-interatomic-bonding energy in the atomic system must be accompanied by the release of positive energy, e.g., additional kinetic energy imparted to an electron that leaves a palladium atom. As a result the electron leaving the palladium atom on formation of a hole in it may possess an energy sufficient for attaining the level of Fermi-gas conductivity (Fermi level) in palladium.

Values of 0.6 and 0.72 of the average number of holes in the 4d shells of palladium atoms, which have been obtained experimentally in investigating the paramagnetic susceptibility and superconductivity of palladium [2, 4], reflect, in our opinion, the result of formation and then decay of the subsequent generations of Pd_2^+ molecular complexes in hydrogen-palladium interaction; this interaction can be described by the following equation [1]:



Indeed, if we consider a hypothetical situation in which there are initially 36 pairs of covalent-bonded atoms of the first generation, the interaction of hydrogen atoms with these palladium atoms can produce 36 palladium-hydride molecules and 36 free palladium atoms arranged at the centers of adjacent faces of the crystal lattice. From these 36 free palladium atoms, there can be formed 18 new covalent-bonded pairs of palladium atoms of the second generation. In the same manner, 9 covalent-bonded pairs of palladium atoms of the third generation, 4.5 pairs of palladium atoms of the fourth generation, etc. can further be formed.

Using the formula for the sum of the terms of an infinitely decreasing geometric progression (S) for calculation of the total number of pairs of palladium atoms of all generations, we obtain

$$S = a_1 / (1 - q) = n_1 / (1 - 0.5) = 36 / 0.5 = 72 ,$$

where $a_1 = 36$ is the value of the first term of the progression and $q = 0.5$ is the denominator of the progression (because of a decrease of 2 times in the initial number). This means that in experiments longer than those on investigating the paramagnetic susceptibility and superconductivity of palladium [2, 4], we can establish that the total disappearance of paramagnetic susceptibility in palladium or the disappearance of the number of holes in palladium atoms is attained for a relative atomic concentration of absorbed hydrogen of 0.72 (72%) instead of a concentration of 0.6 (60%) observed in the experiment. We note that if measurements of paramagnetic susceptibility are discontinued during the appearance of third-generation holes ($0.36 + 0.18 + 0.09$), as was the case in actual practice during the experiment, we obtain a value of 0.63, i.e., the number close to 0.6.

Also, it is noteworthy that the limiting value of the average number of holes in palladium atoms per atom (0.72) was obtained experimentally, as follows from [4], when the phenomenon of superconductivity in palladium was investigated.

The proposed mechanism of formation and disintegration of Pd_2^+ molecular complexes in metallic palladium and, possibly, in other transition d metals enables us to draw a certain conclusion in the field of both heterogeneous catalysis on these metals and hydrogen degradation of structural materials most of which represent transition d metals or their alloys.

A Pd_2^+ complex with a hole in the 4d shell is of high free energy and, being arranged on the metallic-palladium surface, can initiate a chemical reaction in interaction of adsorbate molecules from the gaseous phase with it in catalysis, i.e., be an active catalytic center. The formation of Pd_2^+ complexes increases the integral interatomic-bonding energy in transition d metals or their alloys, ensuring high physical and mechanical properties for them.

Disintegration of Pd_2^+ complexes under the action of high-mobility complexes $(\text{H}^+)_{\text{sh}}$, which is accompanied by the formation of the β phase (this phase has a higher value of the lattice constant and lower physical and mechanical properties than the initial α phase), involves all stages of hydrogen degradation of structural materials: strengthening (cold hardening), creep (increase in the lattice volume), and destruction (embrittlement, hydride corrosion).

NOTATION

a_1 , value of the first term of an infinitely decreasing geometric progression; a_α , crystal-lattice constant of the α phase of palladium, Å; a_β , crystal-lattice constant of the β phase of palladium, Å; E_c , maximum energy of covalent interatomic bonding in the Pd_2^+ complex, eV; d_α , distance between the atoms at the centers of adjacent faces of the crystal lattice of the palladium α phase, Å; D_{Pd} , diameter of a palladium atom, Å; r_{Pd} , radius of a palladium atom, Å; S , sum of the terms of an infinitely decreasing geometric progression; q , denominator of an infinitely decreasing geometric progression; α , alpha phase of metallic palladium; β , beta phase of metallic palladium; ϵ_c , energy of covalent bonding forces of the atom pair in the Pd_2^+ complex per Pd atom, eV; ϵ_h , thermal effect of the reaction of formation of palladium hydride, kcal/mole. Subscripts: 1, number of the term of an infinitely decreasing geometric progression; c, covalent; h, heat; sh, shielded.

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