THE PECULIARITIES OF HYDROGENATION OF PLATINUM FULLERIDES

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The statistical theory of processes of phase transformations realized by hydrogenation of metalfulleride has been developed in present paper. Such reaction was studied experimentally for fullerides of palladium and platinum [1, 2]. In the case of platinum the chemical reaction proceeds by the scheme:

$$\Phi Pt + \frac{1}{2}xH_2 \rightarrow \Phi PtH_{x_1} + \frac{1}{2}(x - x_1)H_2 \rightarrow \Phi H_x + Pt \quad (1)$$

where Φ=C_{60}, C_{70}. At first, the hydrofulleride ΦPtH_x is formed over the temperature range of 400-550K and thereafter with increased temperature in the range from 600 to 700K the formation of ΦH_x hydrofullerite phase occurs and the pure platinum stands out.

The performed calculations give an insight and substantiation into the phase transformations caused by rise in temperature in the fulleride-hydrogen system. For solving the problem the free energies f_i (i = 1, 2, 3) of respective ΦPt, ΦPtH_x, ΦH_x phases have been calculated using the average energies method, their dependences on temperature, the c_1, c_2, x concentrations of C_{60}, C_{70} fullerenes and hydrogen, the order parameter η in distribution of fullerenes over the lattice sites and energetic constants have been defined. The simplified approximations have been taken in calculations: the fcc lattice of $L1_2$ type is proposed to be geometrically ideal, the interactions of fullerenes, platinum atoms and hydrogen are taken into consideration for the nearest neighbours and in this case the approximation of spherically symmetric rigid balls is assumed, the correlation in substitution of sites and interstitial sites by fullerenes and platinum atoms and hydrogen is not taken into consideration. It is expected also that the arrangement of platinum and hydrogen atoms takes place in interstitial sites of crystal lattice of fullerite. As this takes place, the platinum atoms are arranged in octahedral O interstitial sites of ΦPt, ΦPtH_x phases and hydrogen atoms occupy the tetrahedral Θ and trigonal Q positions in the ΦPtH_x phase, when it is considered that radiuses of H and Pt atoms and Φ = C_{60}, C_{70} molecules are equal respectively 0,46; 1,3875 and 7,1Å. The disposition of hydrogen atoms in octahedral O interstitial sites can be nonequilibrium by virtue of their sizable volume. Several hydrogen atoms can arrive at octahedral interstitial sites. Because of this, it is suggested that in the ΦH_x phase the hydrogen atoms occupy the tetrahedral and trigonal interstitial sites forming the dumb-bells along the spatial diagonals of cube of fullerite elementary cell. Several hydrogen atoms find themselves in the octapositions and make up the dumb-bells allong the axises parallel to edges of lattice cell volume, i.e. in octahedral interstitial sites the hydrogen clasters (D_1, D_2 positions) are formed, as shown in Fig. 1.

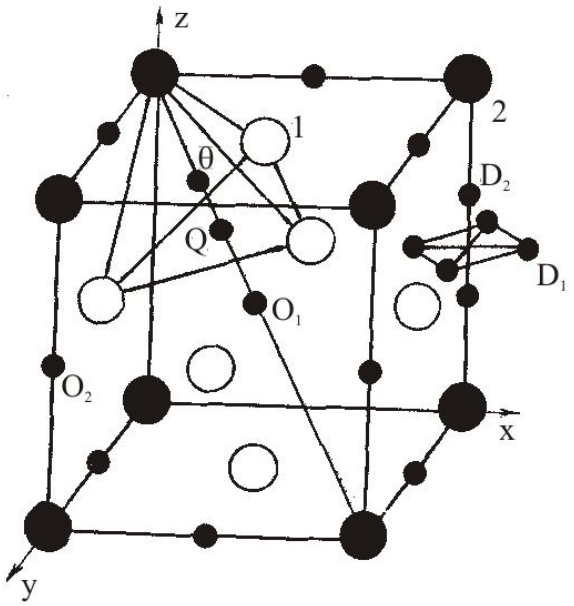

Fig. 1. The fcc lattice of $L1_2$ hydrofullerite.
○ ● – the sites of first and second type of Φ_1, Φ_2 fullerenes,

● – the interstitial sites (octahedral O_1, O_2, tetrahedral Θ, trigonal Q and clasteral D_1, D_2).

The evaluation of energetic constants of all components of the chemical reaction (1) has been performed with the use of experimental data on temperature ranges of phase transformations at different steps of the reaction.

The plots of free energies of ΦPt, ΦPtH_x, ΦH_x phases have been constructed as a function of concentration for different temperatures. The phase diagram has been constructed by intersection points of these plots and with the use of method of total tangent lines to them. This diagram defines the temperature and concentration regions of forming of all phases of chemical reaction.

The solubility of hydrogen in the ΦPtH_x, ΦH_x phases has been calculated, it is determined by the equilibrium concentration of hydrogen atoms in relation to the temperature. The formulae of these dependences take the forms:

$$x = 4\left[\frac{1}{\lambda}\exp\frac{-(\omega_2\eta+\varepsilon_2)}{kT}+1\right]^{-1} \quad \text{for } \Phi PtH_X \text{ phase} \tag{2}$$

$$x = 10\left[\frac{1}{\lambda}\exp\frac{-(\omega_3\eta+\varepsilon_3)}{kT}+1\right]^{-1} \quad \text{for } \Phi H_X \text{ phase,} \tag{3}$$

where λ is the activity of hydrogen atoms, ω_i, ε_i (i =2,3) are energetic parameters of named phases, k is the Boltzmann's constant, T is the absolute temperature. From formulae (2), (3) it follows that with increase in temperature the hydrogen concentration in the ΦPtH_x phase tends to the four ($x_0 = 4$), but in the ΦH_x phase it approaches the ten ($x_0 = 10$) (Fig. 2). In this case all interstitial sites in these phases are filled with the hydrogen atoms and the ΦPtH_4 and ΦH_{10} compounds are formed with the great content of hydrogen.

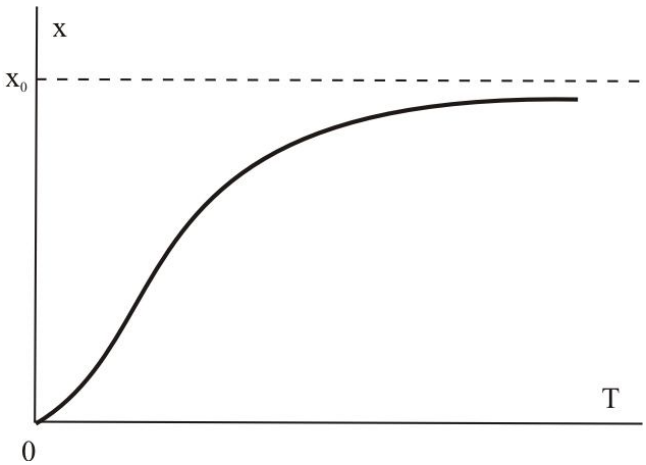

Fig. 2. The character of temperature dependence of hydrogen solubility at the negative value of energetic parameter in exponent.

$x_0 = 4$ for the ΦPtH_x phase, $x_0 = 10$ for the ΦH_x.

References

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