

Hydrogen Adsorption on and Solubility in Graphites¹.

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Abstract

The experimental data on sorption and solubility of hydrogen isotopes in graphite in a wide ranges of temperature and pressure are reviewed. The Langmuir type adsorption is proposed for the hydrogen - graphites interaction with taking into account dangling sp^2 -bonds relaxation. Three kinds of traps are proposed: carbon interstitial loops with the adsorption enthalpy of -4.4 eV/ H_2 (Traps 1); carbon network edge atoms with the adsorption enthalpy of -2.3 eV/ H_2 (Traps 2); basal planes adsorption sites with enthalpy of $+2.43$ eV/ H_2 (Traps 3). The sorption capacity of every kind of graphite could be described with its own unique set of traps. The number of potential sites for the "true solubility" (Traps 3) we assume as $1E+6$ appm, or $H/C=1$, but endothermic character of this solubility leads to negligible amount of inventory in comparison with Traps 1 and Traps 2. The irradiation with neutrons or carbon atoms increases the number of Traps 1 and Traps 2. At damage level of ~ 1 dpa under room temperature irradiation the number of these traps was increased up to 1500 and 5000 appm respectively. Traps 1 and Traps 2 are stable under high temperature annealing.

Introduction

The graphite is proposed for application in thermonuclear fusion reactors due to its low atomic number and excellent thermal characteristics. However, some disadvantage feature of this material such as high hydrogen inventory needs some attention to details of hydrogen-carbon interaction [1].

Below we shall use the term "hydrogen" for all isotopes except of the specially mentioned cases.

Last ten years a number of experimental data for the hydrogen occlusion in graphite in a wide ranges of partial pressures ($0.66\text{-}10^5\text{Pa}$) and temperatures (600-1800K) have been reported [1-3].

In [3,4] the authors have proposed a Sievert's law for the hydrogen exothermic solution in graphite ($T=1123-1323$ K, $p=10^4$ Pa) with the following expression: $S=S_0 p^{1/2}$, where

$$S_0 = 64.4 \cdot \exp(+0.2 \text{ eV}/kT) \text{ appm/atm}^{1/2}$$

However, in a recent work [4] it was reported the endothermic value of 0.1 eV/H₂ for ISO-88 graphite solution enthalpy.

An alternative approach to the problem was proposed by E.Hoinkis [2] who was suggested that the hydrogen - graphite interaction could be described in the terms of chemisorption ($T=1173$ K, $p=1-100$ Pa). The Langmuir type isotherms for the dissociative adsorption was calculated with the assumption of $\Delta H = -2.5$ eV/H₂ adsorption enthalpy. Like a majority of the other authors [5,6] he considered a network carbon edge atom as a site for chemisorption. Contrary to H. Atsumi [3], who did not observed any deviation from linearity of concentration versus square root of pressure, E.Hoinkis reported that hydrogen concentration was saturated at 140 appm level.

One more possibility for the hydrogen to interact with graphite is trapping with high binding energy. This trapping becomes apparent at high temperatures under low pressures and was investigated mainly by R.Causey [1]. He reported an existence of 17 appm deep traps with 4.3eV/H binding energy in POCO AXF-5Q graphite (T=1400-1800 K, p=0.66-133 Pa). The interstitial loops of carbon atoms [7] were proposed to be responsible for this trapping.

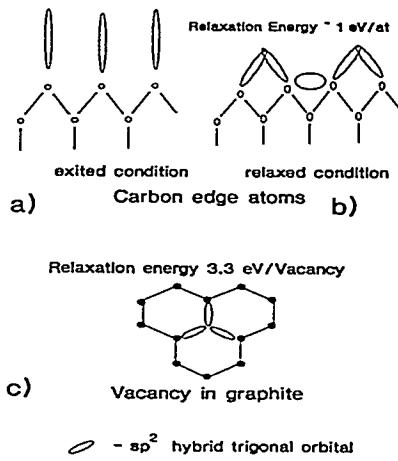
Below we shall describe hydrogen-graphite interaction on the basis of hydrogen chemisorption on different sites of graphite network.

2. Hydrogen-carbon interaction energetic.

The network edges of graphite are known to contain dangling bonds, binding hydrogen atom to carbon atom. The energy, calculated for the bond of a hydrogen atom to a benzene ring is $E_{CH} = 4.45 \text{ eV}$; the dissociation energy of H_2 is $E_D = 4.5 \text{ eV}$. Therefore the exothermic adsorption enthalpy ΔH should be estimated as:

$$\Delta H = 4.5 \text{ eV} - (4.45 \text{ eV} + 4.45 \text{ eV}) = -4.4 \text{ eV/H}_2$$

Contrary to the above estimation, the experimental value of the hydrogen adsorption enthalpy was found in the range of $-2.1 \div -2.5 \text{ eV/H}_2$ [5,6]. The difference one could explain due to the relaxation of edge atoms on the graphite hexagonal network. Indeed, carbon dangling bonds are known to interact each other with forming relaxed surface structure (Fig. 1a,b).



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Fig. 1. Scheme of relaxation process for carbon edge atom (a,b) and vacancy (c).

This relaxation energy is calculated by quantum-mechanical methods [8]. The special feature of a single adsorption act is an essential deformation of surface electron spectrum, when hydrogen atom adsorbs. This

process is known also for the hydrogen adsorption on diamond surfaces [9].

Returning to the interstitial loops of carbon atoms between graphite layers it is reasonable to propose the absence of carbon atoms relaxation; that leads to the adsorption enthalpy of $\Delta H = -4.4 \text{ eV}/\text{H}_2$.

Taking into account the variety of real graphites microstructure one could propose that the real hydrogen adsorption enthalpy should be distributed between -2.1 and $-4.4 \text{ eV}/\text{H}_2$. For the reason of simplicity further we assume that there are exist only two kinds of carbon edge atoms with the adsorption enthalpies of $-2.3 \text{ eV}/\text{H}_2$ (relaxed atom) and $-4.4 \text{ eV}/\text{H}_2$ (unrelaxed atom) respectively. Hydrogen adsorption energetic is shown on Fig.2.

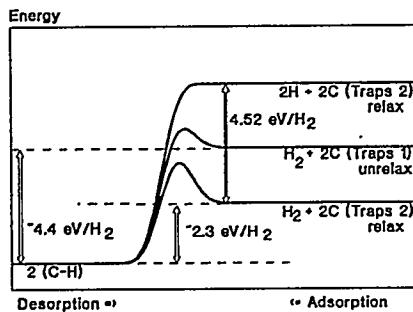


Fig.2. Hydrogen adsorption energetic for Traps 1 and Traps 2.

There are two other possibilities for hydrogen atoms to locate on the graphite network. A vacancy is a first one.

According to [8,10] a graphite vacancy contains three singly-occupied sp^2 - trigonal hybrid orbitals (1, 2 and 3 in Fig.1c). The interaction between these orbitals results in the release of vacancy stabilization energy $E_V^{\text{Rel}} = 3.3 \text{ eV}$.

Since the adsorption of hydrogen atom in a vacancy has to disturb two of three relaxed bonds, the enthalpy of two VH-complexes should be:

$$2E_{\text{VH}} = E^{\text{D}} + 2/3 \cdot 2E_V^{\text{Rel}} - 2E_{\text{CH}} = 4.5 + 4.4 - 8.8 = +0.1 \text{ eV}/\text{H}_2.$$

We should pointed out that the interaction of hydrogen atom with a vacancy is slightly endothermic reaction. Additionally, the number of vacancies we propose is much lower than other traps, so we exclude vacancies from the consideration of hydrogen occlusion.

The last possibility for hydrogen location is the adsorption on the basal planes (0001) of graphite network. We do not exclude this hydrogen "true solubility". It should be responsible for the hydrogen transgranular diffusion and should not be depended upon the real graphite structure. The most probable reaction for the "true solubility" we propose the reaction between hydrogen atom and basal plane carbon atom with $\text{sp}^3\text{-C} - \text{s-H}$ chemical bonding. In this case the carbon atom

should be displaced normal to the basal plane, while the rest neighbor carbon atoms keep their places. The possibility of such reaction was proposed in [11]. One can call it the local $\text{sp}^2\text{-sp}^3$ transition. These transitions are discussed in [12].

Our consideration shows that solution of hydrogen in the graphite is endothermic process ($\Delta H = 2.46 \text{ eV}/\text{H}_2$) and the amount of hydrogen "true dissolved in the graphite" is negligible by comparison with this caused by adsorption on the traps.

3. Adsorption isotherms

The hydrogen-carbon interaction energetic described previously allows us to propose that hydrogen inventory in graphites is caused only by dissociative adsorption. Following by E.Hoinkis [2] we suppose Langmuir adsorption for every type traps.

$$\Theta = \frac{\sqrt{k^A p}}{1 + \sqrt{k^A p}}.$$

This equation gives the relation between the total fraction coverage of graphite adsorption sites Θ and the hydrogen gas pressure p .

The adsorption constant is $k^A = \exp(-\Delta G^0/RT) = k^A_0 \exp(-\Delta H^0/RT)$, where ΔG^0 -is a standard free energy variation at gaseous hydrogen adsorption on graphite. Gaseous pressure of $p=1 \text{ Pa}$ we define as the standard. By the definition, $\Delta G^0 = \Delta H^0 - T\Delta S^0$, where ΔH^0 and ΔS^0 are standard enthalpy and entropy variations respectively, so k^A can be written as:

$$k^A_0 = \exp(\Delta S^0/R).$$

We assume that the main variation of entropy under adsorption is caused by escaping of translation and rotation parts of gaseous hydrogen entropy and appearing of adsorbed hydrogen oscillation entropy. With the help of statistical thermodynamic it is possible to write

$$k^A_0 = \exp(-7/2) \cdot \left(\frac{2\pi mkT}{h^2} \right)^{-3/2} \cdot (kT)^{-1}$$

$$\cdot (\theta_{\text{rot}}/T) \exp\left(2\frac{h\nu}{kT} \frac{\exp(-\frac{h\nu}{kT})}{1 - \exp(-\frac{h\nu}{kT})}\right) / (1 - \exp(-\frac{h\nu}{kT}))^2 \quad (1)$$

where m -mass of hydrogen atom, θ_{rot} is characteristic temperature for rotation of hydrogen molecule, ν is vibration frequency of adsorbed hydrogen atom, all the rest symbols are in their usual meaning.

This approach is very similar to E.Hoinkis [2] one. Additionally we include the entropy of adsorbed

hydrogen atom. For deuterium k_A^0 is equal $(6.6-2.3) \cdot 10^{-14} \text{ Pa}^{-1}$ at the temperature range of 1000-2000 K.

4. Discussion

4.1. Trapping features

With the formalism developed above we describe hydrogen inventory in a wide ranges of temperatures and pressures. Our proposals are summarized as follows:

1. There exist at least two kinds of adsorption sites in graphite that are responsible for the hydrogen inventory. They are:

-carbon interstitial loops with the adsorption enthalpy of -4.4 eV/H_2 , (Type 1, unrelaxed carbon atoms). These sites are located between graphite layers and are hardly accessible for hydrogen at low temperatures. Transgranular diffusion is necessary for reaching this traps. R.Causey experiments showed that at temperature of 1473 K one hour is necessary for saturation Traps 1 with hydrogen, while this time has been increased up to ~ 20 hours for saturation at temperature of 1373 K.

-carbon network edge atoms with the adsorption enthalpy of -2.3 eV/H_2 (Type 2, relaxed carbon atoms). These sites are easy accessible for hydrogen because they are located on the grain boundaries and hydrogen transport is assumed via rapid Knudsen diffusion through interconnected pores structure. But saturation of Traps 2 could be limited by adsorption kinetics. Hoinkis experiment showed that a hundred hours is necessary for equilibrium state at temperature of 1173 K.

2. These two kinds of traps have different enthalpies as well as different vibration modes. We propose that adsorbed benzene molecule is a good model for estimating the hydrogen vibration on carbon edge atoms (Type 1 and Type 2). It is known [14] that adsorbed benzene molecule has a vibration mode that corresponds to oscillation perpendicular to molecule plane with the frequency of $2E+13 \text{ sec}^{-1}$ (684 cm^{-1}). We will use this oscillation frequency for entropy factor estimation for the adsorption on Traps 1 and Traps 2.

3. We consider that every kind of graphite could be described with its own unique set of traps. From the R.Causey and E.Hoinkis experiments it is possible to estimate the number of Traps 1 as $\sim 0-50 \text{ appm}$ [1], Traps 2 as $\sim 0-200 \text{ appm}$ [2].

4. This approach proposes that irradiation with neutrons or carbon atoms increases the number of Traps 1 and Traps 2.

4.2. Unirradiated graphites.

With the above proposals the deuterium adsorption was calculated in the temperature range of 1473-1773 K under pressure 0.66 Pa (133 Pa). We have proposed 17 appm of Traps 1 and 200 appm of Traps 2. The comparison with [1] experimental values is given in Table 1. One can see that only Traps 1 are responsible for the hydrogen inventory at the conditions. There is a good fitting between calculated and experimental values at temperatures up to 1673 K. At higher temperatures

the calculated values are lower than experimental data. This could be explained with the assumption of existence of high temperature vibration mode ($\sim 3000 \text{ cm}^{-1}$) for adsorbed hydrogen. The values in brackets show the deuterium adsorption under the pressure of 133 Pa. Our calculation confirms the [1] result that the Traps 1 coverage fraction is weakly dependent upon the pressure at temperature of 1473 K.

Table 1. Comparison of experimental and calculated data for deuterium inventory

Temperature, K	Deuterium in Traps 1, appm	Deuterium in Traps 2, appm	Deuterium Total, appm	Experimental [1]
1473	14.27 (16.77)	0.26 (3.71)	14.55	15
1573	10.59 (16.30)	0.14 (2.01)	10.73	11.5
1673	6.35 (15.20)	0.08 (1.16)	6.43	8
1773	3.31 (13.20)	0.05 (0.71)	3.36	6

J.P.Redmond and P.L.Walker [5] have investigated the hydrogen sorption in a wide range of temperatures and pressures. The comparison between their experimental data at high temperatures (1608 K and 1768 K) and our calculations is presented on Fig.3.

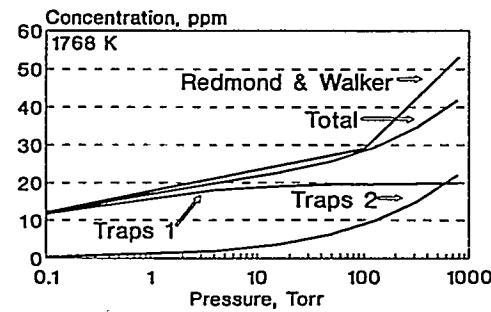
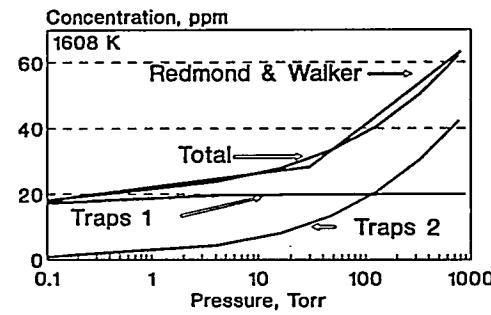


Fig.3. The comparison between experimental and calculated inventory at high temperatures.

To fit the experimental data and calculations we have proposed 20 appm of Traps 1 and 200 appm of Traps 2 for graphite TSP.

The hydrogen solubility in the number brands of graphite materials have been studied at 1273 K [15]. The experiments were provided under the pressures up to 10^4 Pa (0.1 atm) but reported the values for the solubility under 10^5 Pa (1 atm) pressure. The solubility reported differs significantly among the different samples and with exception of CFCs belongs mainly to the interval of 200-600 appm. This means that the real measured values for hydrogen inventory at the pressures of 10^4 Pa (0.1 atm) are equal to 60-200 appm.

We have plotted the hydrogen inventory versus square root of hydrogen pressure at the temperature range of 973-1473 K for the graphites with the same number of Traps 1 and Traps 2 as in the previous case. As one can see (Fig.4) in the range of 50-150 Pa $^{1/2}$ and temperatures higher than 1273 K, with taking into account the experimental errors, this curves could be represented as straight lines just as predicted by Sievert's law. To the other hand the extrapolation of this lines to the higher pressures gives the overestimation values for the solubility at one atmospheric pressure. To our opinion this could be the reason for why the hydrogen solubility in POCO AXF-5Q graphite measured one atmosphere [1] is three times lower than the value reported in [3].

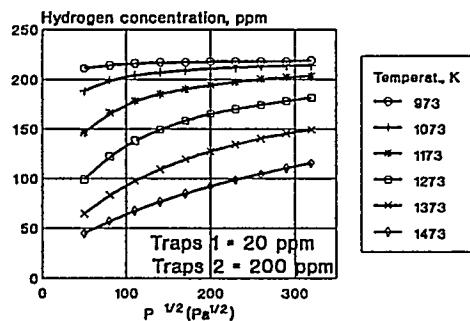


Fig.4. Sorption isotherms for hydrogen in graphites.

At temperatures lower than 1273 K the calculated hydrogen concentration depends weakly upon the pressure in the range of 0.2-1.0 atm (50-300 Pa $^{1/2}$). This is the result of adsorption sites saturation. This conclusion is in a contradiction with the recent H. Atsumi et al experiment at 973 K [4] that confirms Sievert's law for hydrogen solubility in the range of 10^4 - 10^5 Pa. To our opinion this result might be explained with very slow adsorption kinetics at this temperature. Although not stated in the paper, it appears the time for the adsorption was chosen as some tens of hours - the same time interval as in the previous H. Atsumi et al. experiments. It was shown by E. Hoinkis [2] that even at temperature of 1173 K there is necessary waiting for hundred hours to reach an equilibrium with the gas.

4.3. Irradiated graphites.

Neutron irradiation is known to increase the number of traps for hydrogen adsorption. The detailed information on hydrogen occlusion dependence upon the neutron irradiation is necessary for tritium inventory estimation for the first wall and divertor of tokamak. As it is in the case of unirradiated graphite the exact calculations need the exact energy distribution for hydrogen trapping. We propose that the nature of radiation induced traps and intrinsic traps is the same. The only difference is the number of Traps 1 and Traps 2 in irradiated and unirradiated graphites.

We made an attempt to estimate the number of Traps 1 and Traps 2 in radiation damaged POCO AXF-5Q graphite with the following experiment [16], Fig.6:

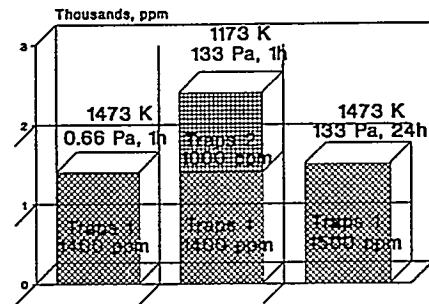


Fig 5. Hydrogen inventory in POCO AXF-5Q irradiated with 200 keV C $^{+}$ - ions.

1. Damage was produced at room temperatures by ion irradiation with 200 keV C $^{+}$ ions up to a damage dose of ~ 10 dpa.

2. Following irradiation, the sample was soaked in deuterium gas at a temperature of 1473 K under pressure of 0.66 Pa for 1 hour. The concentration of D in the damaged region (0.5 mkm) was then measured using nuclear reaction analysis. The D concentration increased with damage and saturated at a damage level of about one dpa. At saturation the D concentration was found as ~ 1400 appm. At these conditions Traps 2 are empty and consequently the number of Traps 1 could be estimated as 1400 appm.

3. Further this sample was soaked in deuterium gas at temperature of 1173 K under pressure of 133 Pa for 1 hour. The D concentration increased and was found as ~ 2400 appm. The increasing of adsorption time up to 24 hours did not lead to deuterium concentration increase in the damage region. It means that the equilibrium concentration was reached and the number of Traps 2 filled with deuterium was ~ 1000 appm. With eq. (1) it is possible to calculate the deuterium fraction coverage for the adsorption in graphite with enthalpy of 2.3 eV/H₂. This value for the above temperature and pressure is about 20%. So the total number of Traps 2 should be estimated as ~ 5000 appm. Also, the time independence of

adsorption at the conditions shows that Traps 2 are stable under the annealing at temperature of 1173 K.

4. At last the sample was soaked in deuterium gas again at a temperature of 1473 K under pressure of 133 Pa for 24 hours. The D concentration was decreased and found as ~ 1500 appm. This confirms the conclusion of Causey for weak pressure dependence for Traps 1 saturation in the range of 0.66 - 133 Pa and also shows that Traps 1 are stable under high temperature annealing.

H. Atsumi [15] have calculated the hydrogen solubility in graphites at 1273 K irradiated with neutrons. The hydrogen solubility proved to be saturated above the 0.3 dpa damage level. The values of hydrogen concentration were normalized under 1 atm (10^5 Pa) and was reported as 0.8 and 1 at.% (8000 and 10000 appm) for IG-430U and ETP-10 graphites respectively. Since the measurements were provided under pressure of 20 kPa it means that the measured concentrations were 3500 and 4500 appm.

Assuming the 1500 appm for Traps 1 and 5000 appm of Traps 2 quantities we have calculated the hydrogen adsorption at 1273 K under 20 kPa pressure. Our calculations give the value of 4700 appm for hydrogen concentration, that is in accordance with the data reported in [15].

5. Conclusions

1. The Langmuir type adsorption is proposed for the hydrogen isotopes - graphites interaction. The dangling sp^2 -bonds relaxation was taken into account, the value of hydrogen adsorption enthalpy depends upon the the nearest environment of carbon atom.

Three kinds of traps are proposed:

-carbon interstitial loops with the adsorption enthalpy of -4.4 eV/ H_2 ; (Traps 1) -carbon network edge atoms with the adsorption enthalpy of -2.3 eV/ H_2 ; (Traps 2) -basal planes adsorption sites with enthalpy of $+2.43$ eV/ H_2 (Traps 3).

2. Every kind of graphite could be described with its own unique set of traps. For instance POCO AXF-5Q has the Traps 1 and Traps 2 numbers of 20 and 200 appm respectively. The number of potential sites for the "true solubility" (Traps 3) we assume as $1E+6$ appm, or $H/C=1$, but endothermic character of this solubility leads to negligible amount of inventory in comparison with previous cases.

The irradiation with neutrons or carbon atoms increases the number of Traps 1 and Traps 2 while the number of Traps 3 remains practically constant. At damage level of ~ 1 dpa under room temperature irradiation the number of Traps 1 and Traps 2 was increased up to 1500 and 5000 appm respectively. Our adsorption experiments show that Traps 1 and Traps 2 are stable under high temperature annealing.

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