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Journal of Nuclear Materials 248 (1997) 52–59

journal of nuclear materials

Section 3. Hydrogen isotope effects in plasma surface interactions

Elementary processes near the interface between hydrogen gas and solid

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Abstract

Sorption–desorption processes at the interface between molecular hydrogen gas and solids are analyzed in the work. Various channels of post-dissociation and pre-recombination transitions are considered. Analytical expressions for concentrations and the 'effective recombination coefficient' in the steady-state conditions are obtained. © 1997 Elsevier Science B.V.

1. Introduction

A description of elementary processes near the solid–hydrogen gas interface is of interest for many applications, particularly for the assessment of tritium accumulation and leakage in thermonuclear reactors. An important aspect of the problem is how to calculate the desorption rate. It is usually assumed that the rate of hydrogen thermal desorption from the surface is proportional to the squared concentration of adsorbed atoms in the chemisorption sites on the surface. But for many applications it is assumed that in equilibrium, the surface concentration is proportional to that in the bulk of solid and, therefore, the rate of hydrogen thermodesorption from the surface is proportional to the square of the bulk concentration of hydrogen under the surface. The proportionality coefficient was named the recombination coefficient. Ali-Khan [1] introduced this approach and since then it has been widely used. Approaches to calculation of the recombination coefficient where proposed in Refs. [2–4] where atomic and molecular fluxes between gas, surface and bulk of the solid were considered in thermodynamic equilibrium. Analytical expressions were obtained in these works after different simplifying suggestions. Later these models were extended in Refs. [5,6].

In this work we perform analytical calculations of hydrogen concentrations, desorption rates and the effective recombination coefficients in equilibrium with gas and show that suggestions used in previous models often give wrong results.

2. Model

Let us consider the interaction of molecular gas with a solid. The flux of gas molecules onto the surface is $I_0 = p/\sqrt{2\pi mkT}$ (molecule/m^2 s), where p is the gas pressure (Pa), m is the mass of the hydrogen molecule (kg), T is the temperature and k is the Boltzman constant. The simplest potential diagram of a hydrogen atom near the interface between the hydrogen gas and the solid is shown schematically in Fig. 1. The diagram is just the same as in the previous works [2–4]. Two basic types of sites for hydrogen atoms are considered: chemisorption on the surface with concentration n (atoms/m^2) and absorption in the bulk of the solid with concentration u (atoms/m^3). The maximum concentrations are n_m and u_m, respectively. Physical adsorption as well as possible variation of the energetics of sites of the same type are not considered for simplicity.

The diagram in Fig. 1 shows eleven elementary transitions of hydrogen atoms between gas, surface and bulk of a solid. Their meaning is clear from the diagram and the rates of the processes are as follows:

$$J_1 = k_1 I_0 (1 - n/n_m)^2 \text{ (molecule/m}^2\text{ s)},$$

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PII S0022-3115(97)00201-8

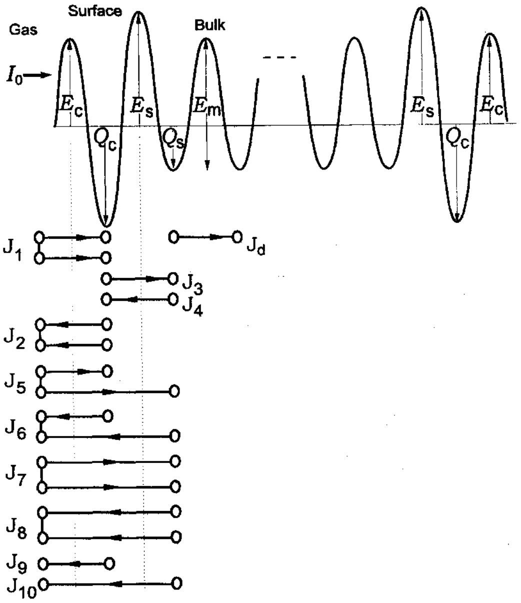

Fig. 1. Schematic diagram of the interaction of hydrogen gas with metal. Potential relief for the hydrogen atom and main fluxes are shown. E_c and E_s: the activation energies for chemisorption and direct absorption, respectively. Q_c and Q_s: the heats of chemisorption and solution. E_m: the activation energy for diffusion.

where

$k_1 = \exp(-2E_c/(kT))$;

$J_2 = k_2 n^2\ (\text{molecule/m}^2\ \text{s})$,

where

$k_2 = \nu\lambda^2 \exp(-2(E_c - Q_c)/(kT))$;

$J_3 = k_3 n(1 - u/u_m)\ (\text{at/m}^2\ \text{s})$,

where

$k_3 = \nu \exp(-(E_s - Q_c)/(kT))$;

$J_4 = k_4 u(1 - n/n_m)\ (\text{at/m}^2\ \text{s})$,

where

$k_4 = \nu\lambda \exp(-(E_s - Q_s)/(kT))$;

$J_5 = k_5 I_0(1 - n/n_m)(1 - u/u_m)\ (\text{molecule/m}^2\ \text{s})$,

where

$k_5 = \exp(-E_c/(kT)) \exp(-E'/(kT))$

and

$E' = \max(E_c, E_s)$;

$J_6 = k_6 nu\ (\text{molecule/m}^2\ \text{s})$,

where

$k_6 = \nu\lambda^3 \exp(-(E_c - Q_c)/(kT)) \exp(-E''/(kT))$,

and

$E'' = E' - Q_s$;

$J_7 = k_7 I_0(1 - u/u_m)^2\ (\text{molecule/m}^2\ \text{s})$,

where

$k_7 = \exp(-2E'/(kT))$;

$J_8 = k_8 u^2\ (\text{molecule/m}^2\ \text{s})$,

where

$k_8 = \nu\lambda^4 \exp(-2E''/(kT))$;

$J_9 = k_9 n\ (\text{at/m}^2\ \text{s})$,

where

$k_9 = \nu \exp(-(E_d - Q_c)/(kT))$,

where E_d is the dissociation energy of the hydrogen molecule in the gas phase;

$J_{10} = k_{10} u\ (\text{at/m}^2\ \text{s})$,

where

$k_{10} = \nu\lambda \exp(-(E_d - Q_s)/(kT))$;

$J_d = -D\, \partial u/\partial x\ (\text{at/m}^2\ \text{s})$,

where

$D = D_0 \exp(-E_m/(kT))$.

If the solid is in equilibrium with the gas, the net fluxes into the under-the-surface site and the chemisorption site are zero:

$$\lambda\, \partial u(x, t)/\partial t = 0 = J_3 - J_4 - J_d + J_5 - J_6 + 2J_7 - 2J_8 - J_{10}, \quad (1)$$

$$\partial n(t)/\partial t = 0 = -2J_2 + 2J_1 + J_4 - J_3 + J_5 - J_6 - J_9. \quad (2)$$

The flux of particles entering the solid (influx) is given by

$J_{in} = J_1 + J_5 + J_7\ (\text{molecule/cm}^2\ \text{s})$,

while the flux of particles leaving the solid (outflux) is given by

$J_{out} = J_2 + J_6 + J_8\ (\text{molecule/cm}^2\ \text{s})$.

Following the traditional approach, we denote the effective recombination coefficient K according to the formula $J_{out} = Ku^2$ (molecule/m^2 s).

3. Three traditional influx schemes

Eqs. (1) and (2) can be used for calculation of the concentrations, the desorption flux and the recombination coefficient K. In the earlier publications [2–4] these calculations were performed using different suggestions about the relation between J_1, J_5 and J_7 fluxes. Pick [2] assumed that after dissociation both atoms rest in the chemisorption sites first and only after thermalisation do they penetrate into the bulk, i.e., $J_1 \gg J_5$, J_7. Baskes [3] supposed that after dissociation one of the two atoms fills the chemisorption site, while another one penetrates directly into the bulk, i.e., $J_5 \gg J_1 J_7$. Richards [4] supposed that three processes can go in parallel: the two accepted in Refs. [2,3] plus the third one when both atoms after dissociation directly penetrate into the bulk, i.e., J_7 can be of the same order as J_1 and J_5.

In Refs. [2–4] the dilute solution $u \ll u_\mathrm{m}$ was suggested. Besides, in two earlier publications [2,3] it was accepted that the surface coverage $\theta = n/n_\mathrm{m} \ll 1$ and only Richards expression for K depends on Θ.

Let us analyze the three possible schemes where only one of the fluxes J_1, J_5, J_7 is significant. We shall not neglect Θ but assume that $u/u_\mathrm{m} \ll 1$. Usually it is assumed that $J_2 \gg J_4$, J_6 and $J_\mathrm{out} = J_2$. This was accepted both in Refs. [2,3]. Only Richards analyzed the J_6 and J_8 contribution, but he mentioned that J_6 and J_8 are significant only at high concentration. Therefore in writing the balance equations we consider first $J_0 = J_2$ for all the three approaches. Afterwards we analyze other possibilities for desorption.

(1) For the suggestion made by Pick [1] $J_1 \gg J_5$, J_7 the balances of fluxes near the surface (Eqs. (1) and (2) are

$$2k_1 I_0(1 - n/n_\mathrm{m})^2 - 2k_2 n^2 + k_4 u(1 - n/n_\mathrm{m}) - k_3 n = 0, \tag{3}$$

$$-k_4 u(1 - n/n_\mathrm{m}) + k_3 n = 0. \tag{4}$$

Denoting $n = n_1$, $u = u_1$, and $K = K_1$ for this case, one can find

$$n_1 = \frac{n_\mathrm{m}}{1 + n_\mathrm{m}\sqrt{k_2/(I_0 k_1)}}, \tag{5}$$

$$u_1 = (k_3/k_4)\sqrt{k_1 I_0/k_2}, \tag{6}$$

$$K_1 = \frac{k_2 k_4^2}{k_3^2}\left(1 - \frac{n_1}{n_\mathrm{m}}\right)^2. \tag{7}$$

If to accept that $n/n_\mathrm{m} \ll 1$ ($\theta = 0$) as it was done in Ref. [2], one can reduce Eqs. (5)–(7) to

$$n_1^0 = \sqrt{k_1 I_0/k_2} = \sqrt{I_0/(\nu\lambda^2)}\exp(-Q_\mathrm{c}/kT), \tag{8}$$

$$u_1^0 = (k_3/k_4)\sqrt{k_1 I_0/k_2}$$
$$= \left[1/\left(\sqrt{\nu\lambda^4}\sqrt[4]{2\pi mkT}\right)\right]\exp(-Q_\mathrm{s}/kT)\sqrt{p}, \tag{9}$$

$$K_1^0 = k_2 k_4^2/k_3^2 = \nu\lambda^4 \exp[2(Q_\mathrm{s} - E_\mathrm{c})/kT]. \tag{10}$$

It is easy to see that in Pick's approach, the concentration of hydrogen (Eq. (9)) has the form of Sieverts law with a square root dependence of solubility on pressure and an exponential dependence on the heat of absorption. That is, the equilibrium concentration in this case can be written in the form traditional for writing the solubility in solid in equilibrium with gas:

$$u_\mathrm{s} = u_\mathrm{s0}\exp(-Q_\mathrm{s}/kT)\sqrt{p},$$

if to denote

$$u_\mathrm{s0} = 1/\left(\sqrt{\nu\lambda^4}\sqrt[4]{2\pi mkT}\right).$$

This a very important point and a good support of the suggestion about the relations between J_1, J_5, J_7 used in Ref. [2]. Note also that Eq. (10) for K_1 coincides with Pick's expression K_P taken from Ref. [2] if we take the respective value for ν in Eq. (10).

(2) For the suggestion made by Baskes [3], $J_5 \gg J_1$, J_7 and $J_0 = J_2$, the balance of fluxes (Eqs. (1) and (2)) gives

$$k_5 I_0(1 - n/n_\mathrm{m}) - 2k_2 n^2 - k_3 n + k_4 u(1 - n/n_\mathrm{m}) = 0, \tag{11}$$

$$k_3 n - k_4 u(1 - n/n_\mathrm{m}) + k_5 I_0(1 - n/n_\mathrm{m}) = 0. \tag{12}$$

Denoting n, u, and K as n_5, u_5 and K_5 for this case, one can find

$$n_5 = k_5 I_0\left[\sqrt{1 + (4k_2 n_\mathrm{m}^2)/(k_5 I_0)} - 1\right]/(2n_\mathrm{m}k_2), \tag{13}$$

$$u_5 = [k_3 n_5 + k_5 I_0(1 - n_5/n_\mathrm{m})]/[k_4(1 - n_5/n_\mathrm{m})], \tag{14}$$

$$K_5 = J_0/u_5^2$$
$$= I_0 k_5(1 - n_5/n_\mathrm{m})^3 k_4^2/[k_3 n_5 + I_0 k_5(1 - n_5/n_\mathrm{m})]^2. \tag{15}$$

At the limit of low surface concentration accepted in Ref. [3]

$$n_5^0 = \sqrt{k_5 I_0/k_2} = n_1^0\exp[-(E' - E_\mathrm{c})/2kT], \tag{16}$$

$$u_5^0 = \left[k_3\sqrt{k_5 I_0/k_2} + k_5 I_0\right]/k_4, \tag{17}$$

$$K_5^0 = I_0 k_5 k_4^2/[k_3 n_5 + I_0 k_5]^2. \tag{18}$$

Eq. (17) for concentration u_5 in the steady state consists of two addends, the first of them is proportional to the square root of the gas pressure while the second one is proportional to gas pressure. Estimations show that the second addend is very small and

$$u_5^0 = \frac{k_3}{k_4}\sqrt{\frac{k_5}{k_2}}\sqrt{I_0}$$
$$= \sqrt{\frac{1}{\lambda\nu^4}}\exp\left(-\frac{Q_\mathrm{s}}{kT}\right)\exp\left(-\frac{E' - E_\mathrm{c}}{2kT}\right)\sqrt{I_0} \tag{19}$$

or

$$u_5^0 = u_1^0\exp[-(E' - E_\mathrm{c})/2kT]. \tag{20}$$

Eq. (18) for K_5 can be reduced to

$$K_5^0 = k_4^2 k_2/k_3^2 = K_1^0 = \nu\lambda^4\exp[2(Q_\mathrm{s} - E_\mathrm{c})/kT]. \tag{21}$$

At this point we must make the following three statements. First, the expression for K_5^0 (Eq. (21)) obtained in the Baskes's suggestion coincides with Eq. (10) for K_1^0 obtained in Pick's suggestion. Second, Eq. (21) for the effective recombination coefficient we have just obtained does not coincide with that given by Baskes in Ref. [3] though all the principal suggestions were identical. Third, the concentration in equilibrium with gas given by Eq. (20) depends not only on the heat of solution Q_s but also on the activation barriers E' and E_c. The latter strongly contradicts thermodynamics. Therefore, one can say that the basic suggestion $J_5 \gg J_1$, J_7 coupled with $J_0 = J_2$ postulate is invalid.

(3) Now consider the last case $J_7 \gg J_1, J_5$. Its possibility was admitted by Richards [4] in his model along with two other sorption channels accepted by Baskes and Pick. Again, we take here $J_{out} = J_2$.

Flux balance equations are

$$-2k_2n^2 - k_3n + k_4u(1 - n/n_m) = 0, \qquad (22)$$

$$k_3n - k_4u(1 - n/n_m) + 2k_7I_0 = 0. \qquad (23)$$

Denoting n, u and K as n_7, u_7 and K_7 for this case, we find

$$n_7 = \sqrt{k_7I_0/k_2} = n_1^0 \exp[-(E' - E_c)/kT], \qquad (24)$$

$$u_7 = \frac{2k_7I_0 + k_3n_7}{k_4(1 - n_7/n_m)},$$

$$K_7 = J_0/u_7^2 = I_0k_7/u_7^2.$$

Neglecting $2k_7I_0$ in comparison with k_3n we reduce

$$u_7 = \frac{k_3n_7}{k_4(1 - n_7/n_m)} \qquad (25)$$

and

$$K_7 = \frac{I_0k_7k_4^2}{k_3^2}\left(\frac{1 - n_7/n_m}{n_7}\right)^2. \qquad (26)$$

At low surface coverage

$$n_7^0 = n_7,$$

$$u_7^0 = \frac{k_3n_7}{k_4} = \frac{1}{\sqrt{\nu\lambda^4}}\exp\left(-\frac{Q_s}{kT}\right)\exp\left(-\frac{E' - E_c}{kT}\right)\sqrt{I_0}$$

or

$$u_7^0 = u_1^0 \exp[-(E' - E_c)/kT], \qquad (27)$$

and

$$K_7^0 = k_4^2k_2/k_3^2 = K_5^0 = K_1^0 = \nu\lambda^4 \exp[2(Q_s - E_c)/kT]. \qquad (28)$$

So, from the consideration performed for three approaches for incoming fluxes and desorption from the chemisorption sites, one can surprisingly see that all the three approaches give identical expressions (Eqs. (10), (21) and (28)) for the effective recombination coefficient. Also important is that approaches proposed by Baskes (J_5 is dominant) and Richards (J_7 can be significant) are invalid because the equilibrium concentrations in these cases have been found to depend on the activation barriers E' and E_c. Only if $E_c > E_s$ (in this case $E' = E_c$) do the concentrations not depend on the activation barriers and depend only on Q_s. Unfortunately, for many materials the activation barrier for chemisorption is supposed to be very small and the condition $E_c > E_s$ is not fulfilled.

4. Symmetric influx–outflux schemes

Disagreement between the concentrations obtained using the Baskes and Richards approaches and the Sieverts law is connected with the suggestion that the sites where incoming gas atoms accommodate after dissociation and the sites from which the atoms recombinate before leaving the solid are different. These were 'asymmetric' influx–outflux schemes. The contradiction can be eliminated if we accept 'symmetric' influx–outflux schemes. In these schemes the influx and outflux go via mutually reverse channels. That is, if the influx is given by J_5, the outflux must be given by J_6 (but not by J_2) or if the influx is given by J_7, the outflux must be given by J_8 (but not by J_2). In this determination Pick's model is a symmetric scheme ($J_{in} = J_1$, $J_{out} = J_2$).

Let us transform Baskes approach by making it symmetric: accept $J_{in} = J_5$ as Baskes did but take $J_{out} = J_6$. In this case one can re-write Eqs. (1) and (2) as

$$k_5I_0 - k_6nu - k_3n + k_4u = \partial n/\partial t = 0,$$

$$k_5I_0 - k_6nu + k_3n - k_4u = \partial u/\partial t = 0.$$

Note that from these two equations immediately follows the so-called local equilibrium condition between mutually reverse processes ($J_5 = J_6$ and $J_3 = J_4$) mentioned by Richards in Ref. [4]:

$$k_5I_0 = k_6nu,$$

$$k_3n = k_4u.$$

These relationships give

$$u_5 = u_s = \sqrt{\frac{k_3k_5I_0}{k_4k_6}} = \left(\frac{1}{\sqrt{\nu\lambda^4}}\right)\exp(-Q_s/kT)\sqrt{I_0}. \qquad (29)$$

It is easy to verify that the same expression for u can be obtained if we consider another symmetric influx–outflux scheme: $J_{in} = J_7$, $J_{out} = J_8$. That is, all the three symmetric schemes give exactly the same expression for equilibrium solubility (Eq. (29)) that agrees with the Sieverts law.

As for the effective recombination coefficients in the symmetric schemes, they differ. Recollect that for the ($J_1 - J_2$) scheme Eq. (21) gives

$$K_1^0 = \nu\lambda^4 \exp[(2Q_s - 2E_c)/kT].$$

One can show that for the (J_5–J_6) scheme

$$K_5^0 = \nu\lambda^4 \exp[(2Q_s - E_c - E')/kT],$$

and for the (J_7–J_8) scheme

$$K_7^0 = \nu\lambda^4 \exp[(2Q_s - 2E')/kT].$$

The tendency is obvious: the sum of the two highest barriers that must be overcome by two primary atoms entering the solid after dissociation appears under the exponent. The recombination coefficient is simply proportional to the product of the probabilities for two atoms to stick to the solid either on or under its surface.

This is not difficult to understand. If the concentration in the bulk does not depend on the surface barriers (as it does in a thermodynamic equilibrium with gas) and if the desorption flux equals the flux of gas particles entering either the adsorption or absorption sites, the increase in the probability of this primary sorption leads to a proportional increase in the 'effective recombination coefficient'.

5. Desorption of the under-the-surface atoms

It is interesting to find out when under-the-surface atoms can recombine to give a significant contribution to the net re-emission rate, i.e., when the contributions of J_6 and J_8 fluxes are important. Combining the respective expressions for J_6, J_8 and J_2 with the local equilibrium condition $J_3 = J_4$ one can obtain

$$\frac{J_6}{J_2} = \frac{1-(u/u_m)}{1-(n/n_m)} \exp\left(-\frac{E_s - E_c}{kT}\right),$$

$$\frac{J_8}{J_2} = \left(\frac{J_6}{J_2}\right)^2.$$

It is seen that both J_6/J_2 and J_8/J_2 depend on two parameters $\theta = n/n_m$ and $E_s - E_c$. The contribution of J_6 and J_8 fluxes in the net re-emission rate increases with an increase in the surface coverage. This is because $J_2 = k_2 n^2$ can be limited by n_{max}. Therefore, if the incoming flux is high, but the thermodesorption flux from the surface is limited, the only way to rise the desorption flux is to enhance $J_6 = k_6 nu$ and $J_8 = k_8 u^2$ by increasing u values. The latter is achieved due to diminution of J_4 transitions at high n_m.

The second factor is the E_s/E_c ratio. If $E_s > E_c$, then J_6/J_2 and J_8/J_2 are small, but if $E_s < E_c$, J_6/J_2 and J_8/J_2 can be very high. Note that the heats Q_s and Q_c do not participate in conditions for J_6/J_2 and J_8/J_2 ratios in equilibrium.

One must also mention the following: it is easy to show that $J_6/J_2 = J_5/J_1$ and $J_8/J_2 = J_7/J_1$. That is, J_6 and J_8 become high only when J_5 and J_7 are high if we compare with J_1. That happens when the E_s barrier is small. That agrees with the condition of equilibrium between reverse processes: $J_1 = J_2$, $J_5 = J_6$ and $J_7 = J_8$.

6. Calculations

Let us illustrate the tendencies in the $u(T)$ and $K(T)$ behaviour for Ni and Nb which are typical representatives of endothermal and exothermal occluders for hydrogen gas. The following parameters were taken:

For Nb: $Q_s = -0.366$ eV, $u_{s0} = 1.57 \times 10^{17}$ at./cm^3 Pa$^{-1/2}$, $n_m = 1.45 \times 10^{15}$ cm^{-2} and $D = 1.1 \times 10^{-3} \exp(-0.147/kT)$ cm^2/s.

For Ni: $Q_s = 0.15$ eV, $u_{s0} = 4.71 \times 10^{17}$ at./cm^3 Pa$^{-1/2}$, $n_m = 2 \times 10^{15}$ cm^{-2} and $D = 5.27 \times 10^{-3} \exp(-0.4/kT)$ cm^2/s.

Figs. 2 and 3 give the temperature dependencies of the equilibrium concentrations u_1, u_5 and u_7 obtained when the influx of particles is determined, respectively, by J_1, J_5 and J_7 processes while the desorption is determined by the J_2 process.

The high temperature parts of the curves are straight lines and the deviations observed at low temperatures are connected with an increase in the surface coverage. One can see that only $u_1(T)$ coincides with the Sieverts solubility u_s at any set of parameters. The Arrhenius plots for other approximations, u_5 and u_7, can even change the signs of their slopes ('effective heats of solution' are different). The 'effective solubilities' u_5 and u_7 depend on the activation barriers E_c and E_s, the effect one should not expect in equilibrium. Both E_c and E_s parameters are important in the calculation of u_5 and u_7. It is significant that at low surface coverage all the three schemes give equal concentrations $u_1 = u_5^0 = u_7^0$ and $n_1 = n_5^0 = n_7^0$ if $E_s < E_c$. But if $E_s > E_c$, then $u_5^0 > u_7^0$ and an increase in E_s leads to a decrease in $u_5^0 \neq u_7^0$ while an increase in E_c leads to an increase in u_5^0 and u_7^0.

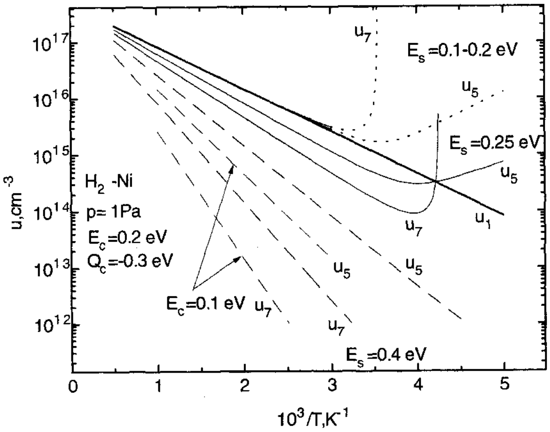

Fig. 2. Concentration of hydrogen in Ni in equilibrium with gas at $p = 1$ Pa in the assumption that the desorption rate $J_0 = J_2$, while the influx is determined by either J_1, J_5 or J_7. The respective concentrations are noted as u_1, u_5 and u_7. Sieverts solubility u_s coincides with u_1. Four values of E_s are used: 0.1, 0.2, 0.25 and 0.4 eV. Parameters: $Q_c = -0.3$ eV, $E_c = 0.2$ and 0.1 eV (two additional short curves).

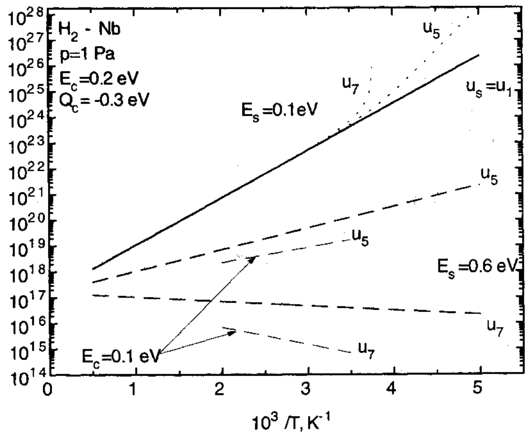

Fig. 3. Concentrations of hydrogen in Nb in equilibrium with gas at $p = 1$ Pa calculated in the assumption that the desorption rate $J_0 = J_2$, while the influx is determined by either J_1, J_5 or J_7. Denotations as in Fig. 2. Parameters: $Q_c = -0.3$ eV, $E_c = 0.2$ and 0.1 eV (additional short curves), two families are given for $E_s = 0.1$ and 0.6 eV.

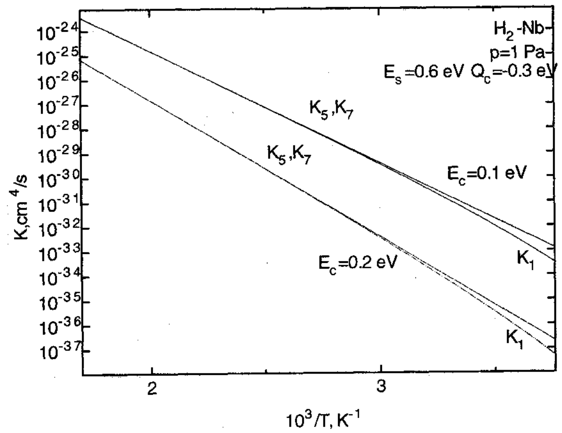

Fig. 5. The effective recombination coefficient for Nb calculated in equilibrium with gas at $p = 1$ Pa in the assumption that the desorption rate $J_0 = J_2$, while the influx is determined by either J_1, J_5 or J_7. Parameters: $Q_c = -0.3$ eV, $E_s = 0.6$ eV, $E_c = 0.1$ and 0.2 eV.

Figs. 4 and 5 show the 'effective recombination coefficients' for Ni and Nb. The most important statement here is that the effective recombination coefficients calculated at low surface coverage coincide at the same set of parameters independent of the suggestion of which of the three fluxes, J_1, J_5 and J_7, prevail. In other words, the value of K_{eff} must be the same in the models developed by Baskes, Pick and Richards though the concentrations are different. In the literature it has been discussed, that Pick's and Baskes's formula give absolutely different results. From our point of view, the reason is that the formula given in the original paper by Baskes is not correct. If we perform calculations more carefully, Baskes's approach ($J_5 \gg J_1$, J_7) and Pick's approach ($J_1 \gg J_5$, J_7) give the very same K^0 values! The same K^0 values as in the Richards' approach. There are two main parameters that determine $K^0(T)$ in the suggestion $J_0 = J_2 = k_2 n^2$: the heat of solution Q_s and the activation energy for chemisorption E_c.

An absolutely different situation arises in 'symmetric' schemes: the 'effective solubilities' coincide in different approaches while the 'effective recombination coefficients' differ as a function of temperature (Fig. 6).

The sign of the effective activation energy for recombinative desorption in the three original approaches $E_k =$

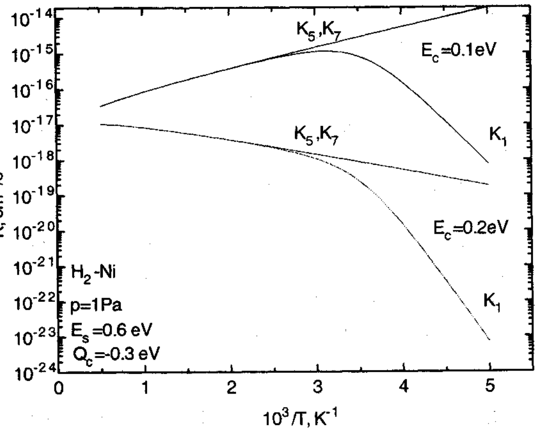

Fig. 4. The effective recombination coefficient for Ni calculated in equilibrium with gas at $p = 1$ Pa in the assumption that the desorption rate $J_0 = J_2$, while the influx is determined by either J_1, J_5 or J_7. Parameters $Q_c = -0.3$ eV, $E_s = 0.6$ eV, $E_c = 0.1$ and 0.2 eV (two families).

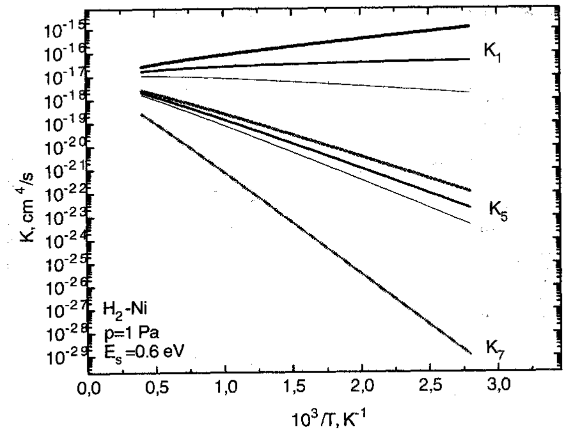

Fig. 6. The effective recombination coefficient for Ni calculated in equilibrium with gas at $p = 1$ Pa in symmetric influx–outflux schemes: $J_1 = J_2$, $J_5 = J_6$, $J_7 = J_8$. Parameters: $E_s = 0.6$ eV, $Q_c = -0.4$ eV, three families are given for every K: $E_c = 0.1$, 0.15 and 0.2 eV.

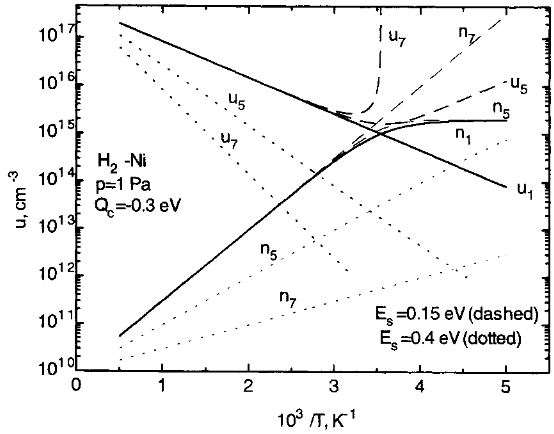

Fig. 7. Correlation between the bulk and surface concentrations in Ni for $E_c = 0.2$ eV, $Q_c = -0.3$ eV and two values of $E_s = 0.15$ and 0.4 eV.

$-2(Q_s - E_c)$ depends on the relation between Q_s and E_c. The curves for Ni in Fig. 4 are drawn for $E_c = 0.1$ eV $< Q_s = 0.15$ eV and $E_c = 0.2$ eV $> Q_s = 0.1$ eV. One can see that the slopes are very different in these two cases. For Nb (Fig. 5) Q_s is negative, therefore E_k is positive and K always rises with temperature.

An interesting and important aspect is the influence of the surface coverage on the concentrations and the recombination coefficients. Figs. 7 and 8 show $n(T)$, $u(T)$ and $K(T)$ dependencies for the case of $J_0 = J_2$. One can see from Fig. 7 that u_1 does not depend on θ even when $\theta \rightarrow 1$. For the other two cases the concentrations u_5 and u_7 strongly depend on the E_s barriers that determine the value of these concentrations. If E_s is high, the surface concentrations n_5 and n_7 are low and there is no effect of the surface population. But if E_s is low, the concentrations u_5 and u_7 both rise with θ when the surface coverage is higher then 0.05. The effect can be explained if we take into account that the concentrations n_5 and n_7 are determined by transitions from the bulk, while n_1 is determined by direct adsorption of atoms after dissociation. It is significant that in some cases the n_7 value is not restricted by the maximum available concentration n_m, as in Fig. 7. This is an additional indication that the respective model approach is invalid. Contrary to the concentrations, all the three $K(T)$ plots depend on θ (Fig. 8).

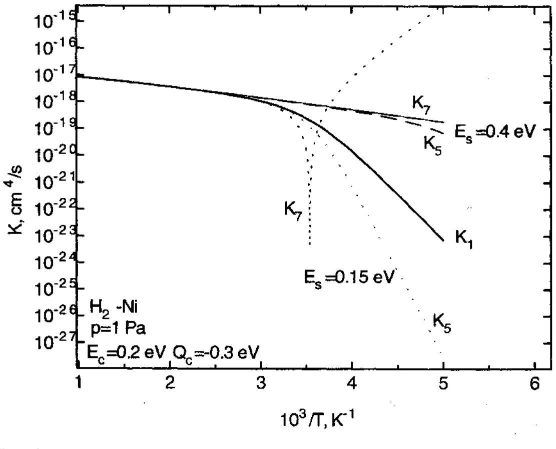

Fig. 8. Recombination coefficient in Ni for $E_c = 0.2$ eV, $Q_c = -0.3$ eV and two values of $E_s = 0.15$ and 0.4 eV.

7. Conclusion

The traditional scheme of elementary processes near the interface between the molecular hydrogen gas and solid is considered. After dissociation of a molecule, atoms may rest both at the surface and under the surface. Molecular desorption from the solid may result from the recombination of both on-surface and under-the-surface atoms. Various suggestions about dominating processes of dissociation giving the outflux of molecules were analyzed. A comparison of analytical solutions for concentrations and effective recombination coefficients in different assumptions in the steady state regime was performed. It has been shown that:

(1) If we accept the commonly used suggestion that molecular desorption is connected with the recombination of two chemisorbed atoms while absorption goes through one of the three channels considered by Pick, Baskes and Richards, one can show that only Pick's suggestion about post-dissociation behaviour of atoms (both sticking to on-the-surface sites) can give the classic Sieverts law for solubility at any set of parameters. Other suggestions proposed by Baskes and Richards that incorporated the idea about primary rest in the under-the-surface sites contradict thermodynamics, giving the equilibrium concentrations dependent on the surface barriers. At the same time, the three recombination coefficients obtained by using the Pick, Baskes and Richards approaches coincide in a very wide range of temperatures and parameters.

(2) If we accept the symmetric influx–outflux schemes that assume that two atoms desorb due to recombination from the sites of the same type as those where the primary atoms accommodate after dissociation, all the three models of primary sticking give the very same concentrations which coincide with the Sieverts solubility. But in these schemes the recombination coefficients strongly differ in the three models.

(3) In many situations the 'effective' recombination coefficient depends on the flux of primary sticking particles.

(4) The concentrations in the bulk of the solid are influenced by the surface coverage only at low temperatures and only in asymmetric influx–outflux schemes. The recombination coefficients are influenced by the surface

coverage mainly in the scheme of Pick with adsorption and desorption through the chemisorption sites.

(5) The influence of surface barriers for chemisorption and absorption is different under different conditions.

(6) Recombination processes with participation of the bulk atoms are important only in conditions when at least one of the incoming atoms after dissociation can penetrate directly into the bulk of solid.

Acknowledgements

The work was supported in part by the Russian Foundation for Fundamental Investigations (Grant RFFI 96-02-18706). Many thanks to Mrs E.N. Gordeeva for computations.

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