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On the possibility to increase efficiency of conditioning of vacuum surfaces by using a discharge in a hydrogen-noble gas mixture

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Abstract

Because of using the carbon-based wall protection in fusion devices, many surfaces of inner components, remote from plasma, become to be coated with carbon film. Between components subjected to C film deposition are elements of plasma diagnostics, e.g., in-vessel mirrors and windows of laser and optical methods. From time to time these elements have to be cleaned from the contaminating films. One possible method is to use a cleaning discharge with low temperature plasma ($Te \leq 5$ eV) however, at that the efficiency of removal of hydrocarbon film molecules is quite small, ~2-3 %. The rate of C film cleaning could be significantly increased by providing discharge in oxygen (with efficiency up to 30%), but the use of this gas is impossible in fusion devices. The alternative method to enhance the efficiency of C film cleaning is to use the plasma produced by discharge in mixture of hydrogen with one of heavy rare gases, as was suggested in [4]. This approach is not in contradiction with the general conception of the fusion reactor project, where the addition of a rare gas (heavier than helium) is considered as a real method to control the periphery plasma parameters.

In the present paper we analyze the published data on all important reactions in a low-temperature plasma produced in mixture of hydrogen with rare gases: Ne, Ar, Xe, Kr. The main peculiarity of such plasma is the appearance of a group of hydride ions, namely NeH^+, ArH^+, XeH^+, KrH^+, which probably is the main factor leading to increase of the rate of removing C film from contaminated surfaces compare to pure hydrogen plasma but practically do not exist as neutrals. The comparison data on cross sections of different reactions demonstrates clearly that between all rare gases, the highest concentrations of hydride ions would be in the Ar-H_2 mixture plasma.

Keywords

Cleaning of in-vessel components, glow discharge, hydrocarbon film removal, mixture of hydrogen with rare gases, hydride ions

Introduction

In fusion devices under operation to exclude an influx of metallic impurities into the confined plasma, the protective tiles fabricated of carbon-based materials are widely used (e.g., [1]). Correspondingly, the carbon is the main component in the production of erosion. It is transported inside the vacuum vessel and deposits on surfaces remote from locations of the strongest plasma impact. The appearance of deposit on the inner elements of optical and laser diagnostics, i.e., on windows and mirrors, is one of negative consequences of mass-transport of the eroded material resulting in gradual degradation of their optical properties [2]. This process can become much more serious for the inner optical components assigned for plasma diagnosing in a fusion reactor, e.g., in-vessel mirrors and especially for mirrors used in diagnostic schemes to observe the divertor plasma. Time to time the in-vessel mirrors have to be cleaned from a carbon-containing deposit, possibly by means of a discharge organized locally in the nearest vicinity of the mirror working surface. Important to note that during the cleaning procedure oxygen cannot be used as a working gas in spite that the plasma of an oxygen discharge is the most effective method to clean metal surfaces from carbon-containing films: the effectiveness of C film removing reaches ~30% [3], compare to 2-3 % for hydrogen (deuterium) plasma.

The methods of surface cleaning from a carbon film are based on high chemical activity of hydrogen (deuterium) atoms and ions. As a result of this, the volatile molecules of hydrogen with carbon (mainly CH_4) and with oxygen (H_2O) are created, which can be evacuated out of the vacuum vessel by standard pumping equipment. The probability to create the molecules containing atoms of light impurities (C, O) is proportional to the flux of hydrogen atoms and ions to contaminated surface that has to be cleaned. However, the rate of surface cleaning depends not only on the probability of creation of volatile impurity-containing molecules but on the probability of their desorption, which depends on surface temperature, and on the speed of molecules evacuation from the vacuum vessel.

One possible way to increase significantly the efficiency of cleaning the vacuum vessel surfaces in fusion devices from carbon-containing contaminating films is to use for conditioning the discharge in mixture of hydrogen (deuterium) with one of heavy noble gases (Ar, Kr, Xe), as was shown for the first time in paper [4]. Such approach does not contradict the common conception of the project of a fusion reactor, where the addition of small amount of a noble gas is being suggested as one of possibilities to control the parameters of the periphery plasma [5].

In this paper the attempt is made to give an explanation of the mechanism which provides an increase of the efficiency of cleaning observed in of [4]. With this purpose we compared the rate coefficients of different processes that take place in the plasma when discharge is organized in the mixture of hydrogen with a noble gas.

History of the question

In 1990 Lianghua Yao et al suggested [4] the method based on the use of gas mixture (H_2 and noble gases Kr, Xe, Ne) for increasing the rate of conditioning the vacuum chamber of the LH-1 tokamak. During conditioning procedure the plasma was produced by Ohmic discharge by applying the alternating current of industrial frequency (50 Hz) of 1.5-5.0 kWA power to the primary circuit of the tokamak transformer. With toroidal magnetic field strength B=0.085 T and gas pressure $(2.0\text{-}20)\cdot 10^{-3}$ Pa the plasma density and electron temperature varied in the range $n_e=(3\text{-}10)\cdot10^{16}$ m^{-3}, T_e=2-10 eV with degree of ionization of the working gas 0.1-0.4 %. In the course of experiment a substantial rise of partial pressures of carbon-containing compounds and water (atomic masses 15, 16, 17, 18, and 28) was observed when discharge was organized in the mixture of hydrogen and a noble gas. The effect was strongly different when different noble gases were added to hydrogen, Ne, Kr, or Xe. Besides, the partial pressures of impurity-containing molecules in plasma, as well as the rate of conditioning, depended on the composition of mixture (i.e., on ratio of densities of noble gas molecules to hydrogen molecules). As a result, the time for conditioning procedure was shortened remarkably. Table 1 shows the ratios of partial pressure of indicated masses during discharges with noble gas addition to the corresponding values without noble gas, i.e., when discharge with approximately similar characteristics was provided in pure hydrogen (these data are taken from Fig. 7 of paper [4], shown here as Fig. 1). It is seen that between noble gases tested the addition of krypton was demonstrated to give the highest efficiency of conditioning. For the krypton-hydrogen mixture the effect on the rise of partial pressure of impurities (masses 16, 18 and 28) was an increasing function of Kr/H_2 concentration ratio from zero to ~ 0.6 (Fig. 4 in [4]).

However, the physical principle of increasing the conditioning efficiency with addition of the noble gas was not clearly explained in the paper [4]. Besides, the experiments with Ar-H_2 mixture were not provided. As a result, impossible to make a conclusion on the optimal choice of the rare gas – hydrogen mixture from the experimental data presented. Meanwhile, as can be shown by analyzing published experimental and theoretical data on processes occurring in plasma in mixture of hydrogen with noble gas, the most promising effect on conditioning efficiency increase should be just when argon is added to hydrogen (or to deuterium). Below the results of such a detail analysis are presented.

Reactions in the plasma of hydrogen-noble gas mixture

Let us examine the most important reactions that occur in rather cold plasma with low ionization degree produced by any discharge in the mixture of noble gas with hydrogen:

$$X^+ + H_2 \rightarrow XH^+ + H, \quad (1)$$
$$H_2^+ + X \rightarrow XH^+ + H, \quad (2)$$
$$XH^+ + H_2 \rightarrow H_3^+ + X. \quad (3)$$
$$X^+ + H_2 \rightarrow H_2^+ + Ar, \quad (4)$$
$$H_2^+ + Ar \rightarrow Ar^+ + H_2 \quad (5)$$
$$H_2^+ + H_2 \rightarrow H_3^+ + H, \quad (6)$$
$$H_3^+ + X \rightarrow XH^+ + H_2, \quad (7)$$

Here X means the chemical symbol of a noble gas, i.e., X= He, Ne, Ar, Kr, Xe.

Apparently, the distinctive feature of such plasma is that it contains a group of quite long-living ions of noble gas hydrides, XH^+, which disintegrate quickly after the ion becomes to be neutral. A priory, we may suppose that just existence of noble gas ions, X^+, and noble gas hydride ions, XH^+, does determine, to a considerable degree, the increase of the conditioning efficiency in comparison with the case when during conditioning procedure the plasma of discharge in a monocomponent gas (hydrogen or deuterium) is in use. If so, for increasing the efficiency of conditioning one has to reach the maximal concentration in the discharge just of these ions.

Making use the theoretical calculations by P.J.Kuntza and A.C.Roach [6], let us examine the conditions for reactions (1) and (2) to be realized and the probabilities of their realization. In Fig. 2 the potential curves in the entrance valley are shown for the molecular ions: H_2^+, NeH^+, ArH^+, and KrH^+. It is seen from the graphs that the pseudo-crossing of curves for noble gases with the curve for hydrogen takes place at increasing H-H distance as one goes in X from Ne to Ar and Kr.

For Ne the crossing of curves occurs at very short distance and at a quite high energy, what means that formation of NeH^+ molecular ion according to reaction (1) in its ground state will be difficult. This reaction is exothermic with energy excess of ~6 eV. This energy is much higher than the energy of dissociation of the NeH^+ ion that equals to 2.15 eV [7], thus much portion of the hydride ions have to disappear just after reaction (1). In contrast, reaction (2) is endothermic with 0.5 eV deficit of energy, therefore it can be realized only if H_2^+ reactant will be in vibrational states $v \geq 2$. The rate coefficients for the NeH^+ ion formation by reaction (1) was measured in [7] and [8] by different methods. These values found for the lowest energy of products are, correspondingly: $1.1 \cdot 10^{-9} cm^3mol^{-1}s^{-1}$ and $2.3 \cdot 10^{-9} cm^3mol^{-1}s^{-1}$.

The situation with formation of the ArH^+ ions is very much different. The ionization potential of argon atom is very close to that for H_2 molecule, and the crossing occurs close to the equilibrium distance of H_2 molecule and in the nearest vicinity of the zero-point H_2 energy. Therefore the ground state of ArH^+ can be realized rather easily even at low potential energy of interactive particles, with vibrational state of H_2 close to the ground state. Formation of ArH^+ ions is possible through reactions (1) and (2) with high probabilities. The rate coefficients measured for these reactions in [9] are $0.62 \cdot 10^{-9}$ $cm^3mol^{-1}s^{-1}$ and $2.3 \cdot 10^{-9}$ $cm^3mol^{-1}s^{-1}$, accordingly (much more results of measurements are shown in Tables 2 and 3).

For Kr the crossing of potential curves occurs near the exit out of the potential minimum. Because of this, the reaction $Kr^+ + H_2$ leads to appearance of the unstable products [6] and as a result, the effective rate coefficient of reaction (1) decreases to the value $\sim 1.5 \cdot 10^{-10}$ $cm^3mol^{-1}s^{-1}$ [9]. As for reaction (2), its rate constant is rather high, according to measurements by authors of that paper, i.e., $2.9 \cdot 10^{-9} \cdot cm^3mol^{-1}s^{-1}$.

In the case of Xe, the data are very limited. According to [9] reactions (1) and (7) result in formation of XeH^+ ions with the rate constants $0.6 \cdot 10^{-9}$ $cm^3mol^{-1}s^{-1}$ and $1.0 \cdot 10^{-9}$ $cm^3mol^{-1}s^{-1}$, correspondingly.

Table 2 shows the rate coefficients of the most important reactions between hydrogen molecules and molecular ions on the one hand, and ions and atoms of a rear gas, on the other hand, when low temperature plasma is produced in a rare gas – hydrogen mixture. It is seen that there is a qualitative agreement with conclusion that follows from theoretical consideration [6]. Namely, the lowest probability for hydride ions to be produced takes place for helium-hydrogen plasma (because of very big different between ionization potential values). Much higher reaction rates do realize in the neon-hydrogen and xenon-hydrogen mixtures. In both cases, as for helium-hydrogen mixture, practically only one reaction (1) leads to a positive result, i.e., production of molecular ions of rare gas hydrides. In contrast that for krypton-hydrogen mixture both reactions give the desired products, still asymmetry is very high between both brunches, ~ one order in magnitude. And only for argon – hydrogen mixture the hydride molecular ions are formed by both reactions, (1) and (2), with rate coefficients which are not too much different.

Reactions in a argon-hydrogen mixture plasma

In the $Ar+H_2$ mixture the hydride ion production can be realized by several reactions known for discharges in a rare gas – hydrogen mixture, if the temperatures of ions and neutrals (Ar atoms and H_2 molecules) is below 1 eV (such range of ion temperature is frequently realized in discharges used for wall conditioning in fusion devices). The ArH^+ ions are formed as a result of exoteric reactions of argon atoms with H_2^+ ions in all available (at given conditions) vibrational states, and also by reaction of Ar^+ ions in ground ($^2P_{3/2}$) and excited ($^2P_{1/2}$) states with hydrogen molecules, as well as in reaction with H_3^+ molecular ions, which are known to be frequently the most abundant ion component in a low temperature hydrogen plasma. Under term "low temperature plasma" we imply everywhere below in the text the plasma with approximately room temperature of ion and atom components, with the electron temperature several orders in magnitude higher.

In Table 3 the rate coefficients of different reactions for argon-hydrogen mixture are collected. It is seen that the most investigated is reaction Ar^+ with H_2 (D_2), and there is a quite big spread of published data. We did not include in Tables the results of measurements with D_2 and HD molecules and also results for high energy of reacting particles, these data can be found in majority of references indicated in Tables.

It is seen from this Table that in average the observed data for reaction $Ar^++H_2 \rightarrow H_2^++Ar$ are below those for reaction $H_2^++Ar \rightarrow ArH^++H$. Roughly one can take the ratio of some "average" rate coefficients $k(Ar^++H_2)/k(H_2^++Ar)$ close to ½. This value is in quite good agreement with results of calculations by authors of [10] who used the charge induced dipole theory developed in [31]. Namely, according to [10], this ratio equals: $k(Ar^++H_2)/k(H_2^++Ar) \cong k(Ar^++D_2)/k(D_2^++Ar) \cong 0.7$ for reactions in H_2-Ar and D_2-Ar mixture. However, the energy dependence of theoretical and experimental cross sections of reactions (2) and (4) are very different, as graphs of Fig. 3 demonstrate, i.e., the experimental cross section values decrease with energy much faster than theory predicts ($\sim E^{-1/2}$ [31]). At the same time, the measured rate coefficient for reaction (1) depends weakly, e.g., [14, 16; 23; 28], or does not depend at all [32] from the energy of colliding particles. Therefore, for further analysis of reactions that occur in the Ar-H_2 mixture we will use some "average" values of rate coefficients, which are shown in Table 2 as the bold figures.

Discussion

According to the list of reactios in Table 3, three reactions lead to formation of argon hydride ions (1, 2, and 7) and only one (3) results in direct putting these ions out of "play". Besides, reaction (4) is also negative because it deactivates the Ar+ ions and thereby brings to decrease an efficiency of ArH^+ ions production. Reaction (5) partly "returns" Ar+ ions into operation but the rate coefficient of this reaction is too small to take it into account.

With taking these comments into consideration, the balance equation for the hydride ions (ArH^+) in low temperature hydrogen plasma is:

$$\partial n(ArH^+)/\partial t = k_1 \cdot n(Ar^+) \cdot n(H_2) + k_2 \cdot n(H_2^+) \cdot n(Ar) + k_7 \cdot n(H_3^+) \cdot n(Ar) - k_3 \cdot n(ArH^+) \cdot n(H_2) - k_8 n_e \cdot n(ArH^+) - n(ArH^+)/\tau(ArH^+). \quad (1)$$

For the mixture with identical initially concentration of both components, Ar50% + $H_2$50%, the approximate equality $n(H_2) \cong n(Ar)$ has to fulfill during all the discharge time as the relative concentration of every ion components satisfies the inequalities: $n(Ar^+)/n(H_2) << 1$, $n(H^+)/n(H_2) << 1$, $n(ArH^+)/n(H_2) << 1$. Besides, at the stationary state of discharge the left part of this equation is zero, therefore, after division by the density of hydrogen molecules (equals to density of argon atoms) one gets the following equation for such discharge:

$$k_1 \cdot n(Ar^+) + k_2 \cdot n(H_2^+) + k_7 \cdot n(H_3^+) - k_3 \cdot n(ArH^+) - n_e \cdot k_8 [n(ArH^+)/n(H_2)] = [n(ArH^+)/n(H_2)]/\tau(ArH^+), \quad (2)$$

or

$$10^{-9}\{1.2 \cdot n(Ar^+) + 2 \cdot n(H_2^+) + 0.2 \cdot n(H_3^+) - 0.5 \cdot n(ArH^+) - n_e \cdot 100[n(ArH^+)/n(H_2)]\} = [n(ArH^+)/n(H_2)]/\tau(ArH^+). \quad (3)$$

It is seen from comparison of coefficients for terms corresponding to different plasma components that the recombination rate coefficient of hydride ions strongly influences the charged particle balance and therefore is very important for the left side of (2) to be positive. As an example, let us consider the particular case, which relates to the experimental conditions described in [4], namely, when $n(H_2) \approx n(Ar) \approx 1/2 \cdot [4 \cdot 10^{12} cm^{-3}]$, $n(Ar^+) \approx n(H_2^+) \approx n(H_3^+) \approx 1 \cdot 10^{10} cm^{-3}$, $T_e = 5 eV$. After substitution of these numbers the equation (3) becomes:

$$10\{1.2 + 2 + 0.2 - 0.5 - 1.5\} = 10^{-2}/\tau(ArH^+),$$

and from this equality we see that for the given combination of rate coefficients the degree of ionization near 1% is close to the critical value, i.e., for better realization of the conditions that would provide the accumulation of ArH^+ ions in the discharge, the degree of ionization of the Ar-H_2 mixture has to be below 1%.

Two indispensable conditions are necessary to provide the production and accumulation of rare-gas hydride ions correspond to the state when reactions (1)-(7) do correctly describe the "chemistry" of low temperature Ar-H_2 plasma. These are: (i) the long enough life time of hydride ions, what means that they are to have rather high dissociation energy, and (ii) the life time of neutral hydride molecules is short, i.e., their dissociation energy is small. The data presented in Table 4 demonstrate that these conditions are really satisfied: $\Delta_{dis}(ArH) << \Delta_{dis}(ArH^+)$.

Under conditions of the above cited example, the ions will gain ~15 eV of energy due to acceleration by the sheath potential. When hitting the surface, the heavy Ar^+ and ArH^+ ions will give much larger portion of this energy to absorbed impurity molecules compare to value that the light H_2^+ ions of the same energy can give, as it follows from the kinematic ratio: $E = E_0 \cdot \{4M_1M_2/(M_1+M_2)^2\}$, where M_1 and M_2 are masses of ion and impurity molecules and E_0 – is the ion energy and E – the energy which the particle on the surface will get after collision with ion. If the surface is coated by a carbon film, the C atom will get $0.7E_0$ energy due to collision with ArH^+ ion and only ~$0.2E_0$ due to collision with H_2^+ ion. The ion energy E_0=15eV, is not enough for effective sputtering of desorbed molecules, but is sufficient to break the bonds of absorbed molecules. Thus, we can suppose that the effect of increasing efficiency of conditioning observed in [4] is based on the following mechanism. The heavy ArH^+ ions after acceleration by the sheath potential hit the adsorbed impurity-containing molecules and break some intermolecular bonds. At this process they become neutral and quickly dissociate to Ar and H atoms (see Table 4). The free argon atoms go back into plasma, but the free hydrogen atoms occupy the released bonds and form new molecules, part of which are volatile and thus can be pumped out. Argon ions, Ar^+, if their energy is not enough for physical sputtering of impurity molecules, do also break bonds of contaminants and thus facilitate formation of volatile molecules by those H atoms which are produced in the plasma by dissociation of H_2^+ ions and hit surface as single particles. Without heavy Ar^+ and ArH^+ ions, in pure hydrogen plasma with identical ion flux density to the contaminated surface, similar process will have significantly lower efficiency.

Conclusion

All abovementioned data allow to state that in the low temperature plasma produced by a discharge in the Ar-H_2 mixture the formation of ArH^+ ions will occur as a result of three reactions with two of them having rather high rate coefficients, in comparison with only one reaction of a quite small rate coefficient leading to disappearance of these ions. The process of hydride ions production is more effective in the Ar-H_2 mixture compare to mixture of hydrogen with other rare gases because no one rare gas has so ways of hydride ions formation in conditions that can be realized during conditioning procedure in fusion devices, as argon. The realization of some reactions in mixture of hydrogen with other rare gases is either impossible or has small rate coefficients. Namely an addition of argon can provide the best properties of the working mixture when there is a need to clean the vessel walls or inner components of plasma diagnostics in fusion devices. The presence in plasma of heavy ions, which can get the energy corresponding to the sheath potential, highly increase the probability of sputtering and desorption of impurities from the surfaces subjected to plasma impact during conditioning procedure. Besides, the liberation of hydrogen atom due to fast disintegration of hydride molecule on the surface being conditioned, would facilitate the generation of volatile molecules containing atoms of light impurities which can be pumped out.

We suppose that just such process has resulted in the increase of desorption rate of impurity-containing molecules in the HL-1 tokamak [4] when the rare gas – hydrogen mixture was used as a working gas.

Important that the use of noble gases in the course of conditioning procedure is compatible with limitation on requirements to the vacuum in fusion devices, e.g., full exclusion of using oxygen.

References

1. G.Federici, C.H.Skinner, J.N.Brooks et al. Plasma-material interactions in current tokamaks and their implications for next step fusion reactors. – Nucl. Fusion, 41 (2001) 1968.
2. V.Voitsenya, A.E.Costley, V.Bandourko et al. Diagnostic first mirrors for burning plasma experiments (invited), - Rev. Sci. Instr., 72 (2001) 475.

3. B.Landkammer, A. von Keudell, W.Jacob. J.Nucl.Mater. **264** (1999) 48.
4. Lianghua Yao, Shonqi Sun and all. Experimental investigation of AC discharge cleaning with mixed gas in a HL-1 torus. J. Nucl. Mater. 176&177 (1990) 645.
5. G.R.McKee, M.Murakami, J.A.Boedo et al. Physics of Plasmas, 7 (2000) 1870-1878.
6. P. J. Kuntz and A. C. Roach. Ion-Molecule Reactions of the Rare Gases with Hydrogen. – J. Chem. Scos. Faraday Trans. 268 (1972) 259.
7. T.F.Moran, L.Friedman. Neon-hydrogen ion-molecule reactions. – J. of Chemical Physics, 39 (1963) 2491.
8. R.D.Smith, D.L.Smith, H.Futrell. Ion-molecule reactions in H_2/rare-gas systems by ion cyclotron resonance. I. Reactions with He and Ne. – Int. J. Mass Spectrom. Ion. Phys. 19 (1976) 369.
9. K.R.Rian, I.G.Graham. Ionic collision processes in mixtures of hydrogen and rare gases. – J. Chem. Phys. 59 (1973) 4260.
10. M.T.Bowers and D.D.Elleman. Kinetic analysis of the concurrent ion-molecule reactions in mixtures of argon and nitrogen with H_2, D_2 and HD utilizing ion-ejection-ion-cyclotron-resonance techniques. – J. Chem. Phys. 51 (1969) 4606.
11. V. Aquilanti, A.Galli, A.Giardini-Guidoni, G.G.Volpi. – Ion-Molecule reactions in hydrogen-rare-gas-mixtures. – J. Chem. Phys. 43 (1985) 1965.
12. D.Hyatt, K Lacmann. Chemical reaction kinematics. – Z. Naturforsch. 23a (1968) 2080.
13. C.F.Giese, W.B.Maier. Ion-molecule reactions studies with mass analysis of primary ion beam. – J. Chem. Phys. 35 (1961) 1913.
14. R.D.Smith, D.L.Smith, H.Futrell. Ion-molecule reactions in H_2/rare-gas systems by ion cyclotron resonance. II. Reactions in systems H_2 with Ar, Kr and Xe. – Int. J. Mass Spectrom. Ion. Phys. 19 (1976) 395.
15. P.F.Fennelly, J.D.Payzant, R.S.Hemsworth, D.K.Bohme. Determination of the activation energy for the reaction $Kr^+(^2P_{3/2}) + H_2(D_2) \rightarrow KrH^+(KrD^+) + H(D)^*$. – J. Chem. Phys. 60 (1974) 5115.
16. P.R.Kemper, P.V.Neilson, D.Parent, M.T.Bowers. Temperature dependence of the reaction of Kr^+ with H_2, D_2, and HD: An unusual isotope effect. – J. Chem. Phys. 68 (1978) 322.
17. N.G.Adams, D.Smith, E.Alge. Reactions of the 2P 3/2 and 2P ½ doublet ground states of Kr+ and Xe+ at 300 K. – J Phys. B: Molec. Phys. 13 (1980) 3235.
18. F.C.Fehsenfeld, E.E.Ferguson, A.L.Schmeltekopf. Thermal-energy ion-neutral reaction Rates. VI. Some Ar^+ charge-transfer reactions. – J. Chem. Phys. 45 (1966) 404.
19. H.Villinger, J.H.Futrell, F.Homorka, N.Duric, W.Lindinger. The proton transfer from ArH^+ to various neutrals. – J. Chem. Phys. 76 (1982) 3529.
20. R.D.Smith, J.H.Futrell. A tandem ICR study of internal energy effects in the D_3^++Ar and $ArD^+ + H_2(D_2)$. – Int. J. Mass Spectrom. Ion. Phys. 20 (1976) 33.
21. A.B.Rakshit, P.Warneck. A drift chamber study of the reaction $ArH^+ + H_2 \rightarrow H_3^+ + Ar$. – J. Chem. Phys. 74 (1981) 2853.
22. R.L.Mills, P.Ray. Substantial change in the characteristics of a microwave plasma due to combining argon and hydrogen. – New J. Phys. 4 (2202) 22.1-22.17.

23. N.G.Adams, D.K.Bohme, D.B.Dunkin, F.C.Fehsenfeld. Temperature dependences of the rate coefficients for the reactions of Ar^+ with O_2, H_2, and D_2. – J. Chem. Phys. 52 (1970) 1951.
24. N.G.Adams, D.K.Bohme, E.E.Ferguson. Reactions of He_2^+, Ne_2^+, Ar_2^+ and rare-gas hydride ions with hydrogen at 200K. – J. Chem. Phys. 52 (1970) 5101.
25. D.P.Stevenson, D.O.Shissler. Reaction of gaseous molecule ions with gaseous molecules. IV. Experimental methods and results. – J. Chem. Phys. 29 (1958) 282.
26. I.Dotan, W.Lindinger. Energy Dependences of the reactions of Ar+ with H2, N2, CO,)2, CO2, N2) and COS. – J. Chem. Phys. 29 (1958) 294.
27. R.J.Shul, R.Passarella, B.L.Upschulte, R.G.Keesee, A.W.Castleman, Jr. Thermal energy reactions involving Ar+ monomer and dimmer with N2, H2, Xe, and Kr. – J. Chem. Phys. 86 (1987) 4446.
28. K.M.Ervin, P.B.Armentrout. Translational energy dependence of $Ar^+ + XY \rightarrow ArX^+ + Y$ ($XY=H_2$, D_2, HD) from thermal to 30 eV. – J. Chem. Phys. 83 (1985) 166.
29. E.A.Gisiason, G.Parlant. Capture cross sections on adiabatic vibronic potential curves – The reaction of $Ar+(^2P_j)+H_2$. – J. Chem. Phys. 94 (1991) 6598.
30. K.Tanaka, J.Durup, T.Kato, I.Koyano. State selected ion-molecule reactions by TESICO technique. II. Separation of te reactat spin-orbit states in the reaction $Ar^+(^2P_{3/2}, {}^2P_{1/2}) + H_2(D_2) \rightarrow ArH^+(ArD^+) + H(D)$. – J. Chem. Phys. 74 (1981) 5561.
31. G.Gioumousis, D.P.Stevenson. Reactions of gaseous molecule ions with gaseous molecules. V. Theory. – J. Chem. Phys. 29 (1958) 294.
32. R.P.Clow, J.H.Futrell. Ion-cyclotron resonance study of the kinetic energy dependence of ion-molecule reaction rates. I. Methane, hydrogen and rare gas-hydrogen systems. – Int. J. Mass Spectrom. Ion. Phys. 4 (1970) 165.
33. T.F.Moran, L.Friedman. Application of the Platt electrostatic model to diatomic hydride ions. – J. Chem. Phys. 40 (1964) 860.

Table 1. Increase of partial pressure for indicated mass numbers of impurity-containing molecules [4]

Mixture	Ratios of partial pressure values with and without gas addition				
	M=15	M=16	M=17	M=18	M=28
H_2 + Ne	1.9	1.4	1.9	1.3	1.6
H_2 + Xe	2.8	2.6	1.5	1.8	2.6
H_2 + Kr	2.6	4.8	7.7	3.1	3.1

Table 2. Rate coefficients for most important reactions in the low temperature plasma of a discharge in a rare gas – hydrogen mixture.

Reaction	k at ~ room temperature, 10^{-9} $cm^3 molecule^{-1} s^{-1}$				
	He	Ne	Ar	Kr	Xe
$H_2^+ + X \rightarrow XH^+ + H$	0.12 [8] 0.16 [13] 0.1 [32]	1.1 [7] 2.3 [8]	2.3 [9] 1.24 [10] 2.0 [12]* 2.2 [13]* 1.8 [14]*	2.9 [9] 2.3 [14]	2.4 [14] 2.1 [14]*
$X^+ + H_2 \rightarrow XH^+ + H$	< 0.002 [8] <0.0035 [11]	< 0.002 [8] <0.008 [11]	0.62 [9] 0.68 [10] 1.6 [11] 1.6 [12]* 1.7 [13]* 0.98 [14]* 1.1 [18] 0.95 [28]	0.15 [9] 0.6 [11] 0.17 [14] 0.2 [15] 0.17 [16] 0.28 [17]	<0.02 [11]
$XH^+ + H_2 \rightarrow H_3^+ + X$	1.4 [9]	0.9 [9]	0.3 [9]		

*estimated from the cross section for $Ar^+ + D_2 \rightarrow ArD^+ + D$ and $D_2^+ + Ar \rightarrow ArD^+ + D$ using the isotope effect for similar reactions of H and D.

Table 3. Rate coefficients for reactions in the low temperature plasma of a discharge in the argon – hydrogen mixture.

№ №	Reaction	k at ~ room temperature, 10^{-9} $cm^3 molecule^{-1} s^{-1}$
1	$Ar^+ + H_2 \rightarrow ArH^+ + H$	0.62 [9]; 0.68 [10]; 1.6 [11]; 1.6 [12]*; 1.7 [13]*; 0.98 [14]*; 1.1 [18]; 0.54 [21]; 1.7 [25]; 1.0 [26]; 0.82 [27]; 0.95 [28]; 1.04 [29]; 2.0 [30]; 1.3* [32] **1.2**
2	$H_2^+ + Ar \rightarrow ArH^+ + H$	2.3 [9]; 1.24 [10]; 2.0 [12]*; 2.2 [13]*; 1.8 [14]*; 2.2 [32]* **2.0**
3	$ArH^+ + H_2 \rightarrow H_3^+ + Ar$	0.5 [24]; 0.32 [9]; 0.8 [19]; 0.34 [20]; 0.35 [21]; **0.5**
4	$Ar^+ + H_2 \rightarrow H_2^+ + Ar$	0.27 [9]; 0.1 [30]; **0.15**
5	$H_2^+ + Ar \rightarrow Ar^+ + H_2$	~0.27 [14]; ≤0.1 [14]*; 0.27 [22]; **0.25**
6	$H_2^+ + H_2 \rightarrow H_3^+ + H$	2.05 [13]; 2.4 [9]; 2.0 [25]* **2.2**
7	$H_3^+ + Ar \rightarrow ArH^+ + H_2$	0.37 [10]; 0.06 [22]; 0.5 [23]; **0.2**
8	$e + ArH^+ \rightarrow Ar + H$	~**100** [22]
9	$e + Ar^+ \rightarrow Ar$	

Table 4. Measured and calculated dissociation energies of rare gas hydride ions and molecules.

Excluding NeH^+ [7], all other data are from [33].

Hydrides	Dissociation energies, Δ_{dis}, eV	
	Experimental	Calculated
NeH+	2.15	
NeH		0.26
ArH+	≥ 2.65; ≥ 2.14	3.03
ArH		0.17
KrH+	$3.42 \leq \Delta_{dis} \leq 4.09$	3.46
KrH		0.12
XeH+	$1.2 \leq \Delta_{dis} \leq 3.19$	2.66
XeH		0.15

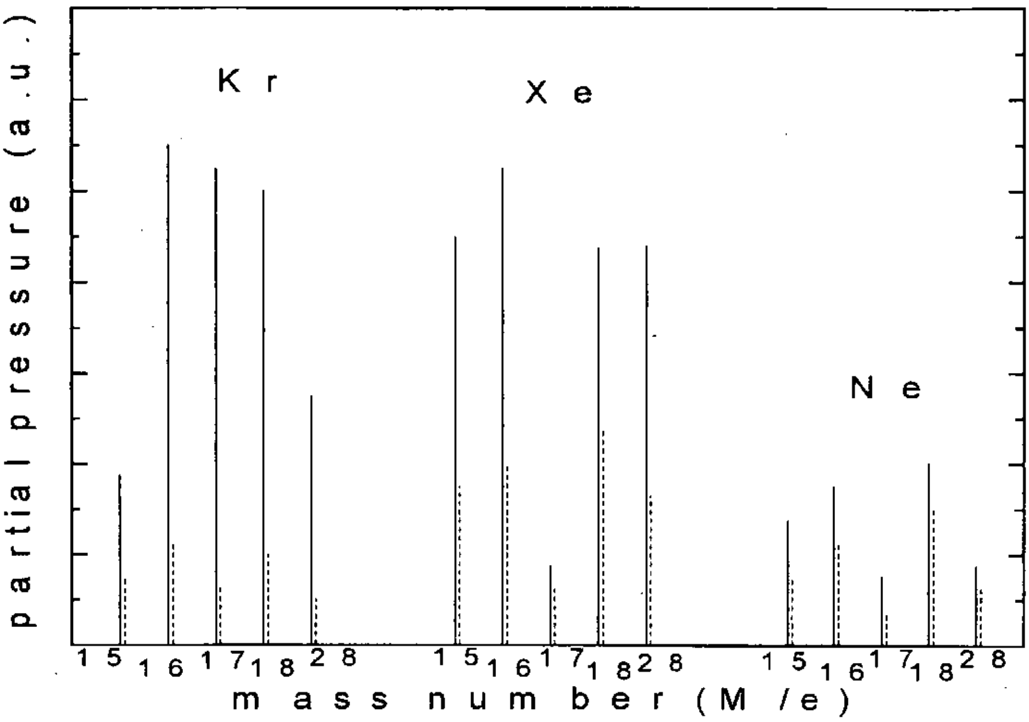

Fig. 1.Change of the partial pressure with pure H_2 and mixed gas (50 Hz) discharge cleaning. Dashed lines for pure hydrogen, solid lines for mixtures: H_2+Kr, H_2+Xe, and H_2+Ne. [4]

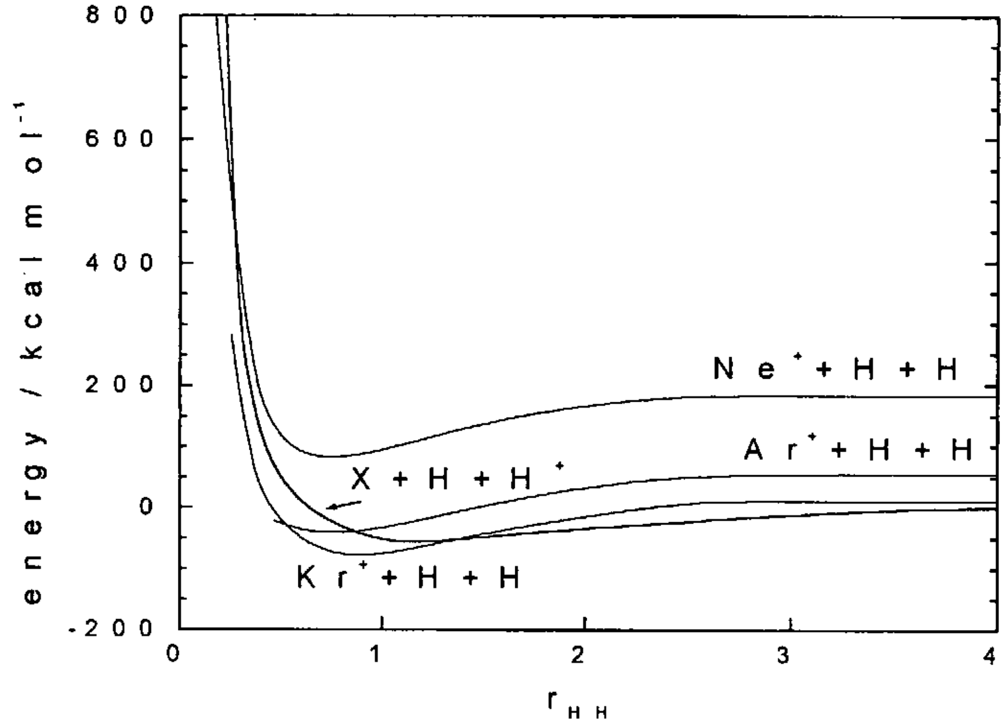

Fig. 2. Potential curves in the entrance valley. In shape these represent the potential curves of H_2^+ (heavy line) and H_2 (light line), unperturbed by remote rare gas atom. The ionization potential of X does, however, contribute to the vertical separation between the two reactant states. The H-H distance is in Å. [6]

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