

SEARCH FOR "COLD-FUSION" IN SOME Me-D SYSTEMS AT HIGH PRESSURES OF GASEOUS DEUTERIUM*

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(Received September 19, 1989)

Summary

Metallic palladium and nickel were treated with gaseous deuterium at 298 K to pressures of 3.1 GPa and 1.0 GPa respectively. The high concentrated deuterides did not exhibit, at long time equilibrium as well as in dynamic conditions, evidence of neutron emission nor evolution of heat due to possible "cold fusion". The volume concentrations of deuterium definitely exceeded those achieved by electrolytic charging. Electrical resistance measurements of palladium deuteride up to 3.1 GPa of gaseous deuterium indicated a further uptake of deuterium above the estimated stoichiometry of octahedral vacancies. A partial filling up of tetrahedral vacancies probably takes place. Electrolytic charging in high pressures of gaseous deuterium did not improve the negative observations above. Thus the observations of Fleischmann and Pons are not confirmed at higher volume concentrations of deuterium in the palladium and nickel lattice as well in equilibrium as in dynamic conditions (phase transitions, high pressure electrolysis).

1. Introduction

The recently published information about "cold fusion" in electrolytically prepared palladium deuteride [1] presents an attractive challenge for Me-D systems.

However, the electrochemical preparation used [1] has three disadvantages.

(1) The thermodynamically reversible range is rather limited and uninteresting for "cold fusion" purposes, but in the range of large overpotentials the activity of the electrode surface is hardly reproducible and stable. Thus results obtained at different places cannot be compared in an objective way and station-

*Results of this paper were presented on July 20 on the high pressure conference (AIRAPT) in Padeborn (F.R.G.).

arity with respect to current–potential conditions mostly does not coincide with stationarity with respect to the deuterium content in the bulk metallic phase. In other words the effective chemical potential of deuterium remains in most cases a hardly controlled variable.

(2) Energetic effects are occurring in an open system with many consecutive processes due to the input of electrical energy. Therefore quantitative results are to be treated with great care, as considerable errors can easily be introduced.

(3) The highest deuterium contents, that is concentrations close to stoichiometry with respect to the octahedral vacancies in the palladium lattice, are difficult to achieve by electrolysis.

In the situation where on one hand the optimistic results of Fleischmann and Pons [1] initiated unrealistic hopes and on the other hand their interpretation can hardly be accepted, it seemed reasonable to search for “cold fusion” by a completely different technique.

As compared with electrochemistry, the preparation of metallic deuterides by a high pressure technique offers the following advantages.

(1) We can work in conditions of thermodynamic equilibrium between gaseous deuterium and the metallic bulk phase. Therefore all results can be easily reproduced, independent of the place and equipment.

(2) We can achieve much higher concentrations of deuterium in the metals which cannot be reached by electrolysis.

(3) All experiments can be carried out in stationary conditions with practically unlimited times.

(4) All experiments are carried out in a closed system. Therefore possible energetic effects can be investigated in uniquely reproducible conditions, without any additional input of energy from outside.

Owing to our long tradition using Me–H/D systems in high pressure conditions [2–5], such investigations could easily be carried out without additional development of new high pressure devices. Hereby we looked for two possible demonstrations of eventual “cold fusion”.

(1) A possible emission of neutrons.

(2) A possible evolution of heat.

Contrary to the electrochemical method we performed our search for “cold fusion” under the following conditions.

(1) In deuterium concentrations close to $D/Me = 1$ or probably even higher values, the systems Pd–D and Ni–D were investigated.

(2) For long stationary equilibrium conditions (between gaseous deuterium and bulk metal), ranging from about 5 months to at least some hours.

(3) At controlled dynamic changes of the metallic lattice during deuteride formation and decomposition. This was carried out for nickel deuteride.

(4) During pressure changes of the palladium deuteride in the range 10–20 GPa in a diamond anvil device.

(5) During cathodic deposition of additional deuterium on a palladium surface in high pressure electrolysis.

The last experiment can be treated as a combination of traditional electro-

chemistry and a high pressure technique and it should be considered as an example of extreme intensive charging conditions.

2. Experimental details

The high pressure devices used were described previously [3–5], being cylinder–piston combinations with the precautions necessary to avoid any contact between gaseous deuterium and steel elements. The more simple device was loaded with pure gaseous deuterium, starting with a commercially available gas bottle pressure of about 10 MPa and achieving higher pressures using a gas compressor and finally in the working volume by a suitable piston movement. Here the upper pressure of about 1.5 GPa was limited by the mechanical properties of the beryllium bronze elements, being in direct contact with gaseous deuterium. Higher pressures were achieved in two-stage equipment where the working volume with gaseous deuterium was separated from the steel elements by a piston and an organic pressure transmitting liquid. Here the upper limit was determined by the mechanical properties of the steel elements used, being about 3 GPa.

The temperature of the pressure vessels was kept at a constant value controlled by a Pt thermometer and regulated by an electric heater surrounding the outside supporting ring of the pressure vessel. The pressure was measured either by the force of the hydraulic press (being previously standardized to pressure measurements by a manganine gauge) or *in situ* by a manganine resistance. Pressure changes of the gaseous deuterium could be achieved by changing the displacement of the mobile piston. Possible heat effects inside the samples could be monitored using a copper–constantan thermocouple, whereby one junction was placed inside the metallic sample in the high pressure volume and the second junction was, outside the pressure vessel (ambient pressure), kept in a mixture of liquid and solid water. The temperature difference between both junctions was continuously registered graphically.

The neutron emission measurements were carried out using a scintillation probe, the silver activation detector and the CR-39 nuclear track detector.

The scintillation probe consisted of an NE-102 A plastic scintillator and PM tube. This probe was connected to the pulse counter via an amplitude discriminator. Because of the relatively large dimensions of the scintillator (150 mm in diameter and 150 mm in height) this probe was able to count pulses from neutron recoil protons (reaction $D + D \rightarrow n + {}^3\text{He}$) as well as the γ -rays from a reaction $n(\text{slow}) + p \rightarrow D + \gamma$ (2.5 Mev). The overall efficiency was about 2.5% for neutrons and about 0.5% for γ -rays.

The silver activation detector consisted of a GM counter coated with a thin silver foil and a thick paraffin layer in order to slow down the fast neutrons from the DD reactions. The neutron registration efficiency of this detector was about 10^{-6} .

The plastic CR-39 nuclear track detector registered the neutron recoil protons which are included in this compound. Before the experiments the detector

was calibrated using an Am-Be neutron source as well as using a “plasma focus” discharge. The neutron registration efficiency determined by these methods amounted to 2×10^{-3} .

3. Results and discussion

Points (1) and (2) of the program formulated in the introduction, that is experiments with high loaded deuterides over long time observations, were carried out with palladium and nickel samples.

In the first experiment, a cylindrical palladium sample of 1.1 cm diameter and 5.63 cm length (corresponding to 67.618 g palladium or 5.63 cm³ of this metal) was charged with gaseous deuterium starting from 3 MPa and finishing at 0.8 GPa. This was performed over a time period of about 3 days, increasing the deuterium pressure stepwise. Such a procedure was chosen in order to ensure homogeneous distribution of the deuterium even at the highest pressure. A rapid increase in pressure could cause a non-homogeneous concentration in the bulk due to a strong concentration dependence of the deuterium diffusion in palladium deuteride [6]. The creation of a highly concentrated deuteride layer near the surface would correspond to a diffusion barrier inhibiting the quick penetration of deuterium into the bulk. After reaching a pressure of about 0.8–1.0 GPa gaseous deuterium, the palladium sample was kept under stationary conditions for more than 5 months. *No indication of temperature changes—due to evolution of heat—nor an emission of neutrons which would exceed the background were noticed.* Owing to the absorption of the high pressure device only 36% of the total neutron emission should be detected outside the pressure vessel. The temperature of the high pressure vessel was kept at 298 K but several times an increase to about 400 K and later coolings were performed in order to introduce some dynamics into the system considered. This procedure didn't give any indication of traces of “cold fusion”. Let us remark that our sample is a factor of five larger than the critical size mentioned by Fleischmann and Pons [1] as being dangerous for a laboratory treatment. Concerning the volume concentration of deuterium we can give here some numbers. Figure 1 presents the atomic ratio D/Pd as a function of the deuterium pressure at 298 K being in equilibrium with metallic palladium.

At 0.8 GPa of gaseous deuterium nearly 94% of the octohedral interstices of the f.c.c. palladium lattice are occupied by deuterium particles. This is surely a higher concentration than that achieved by electrolysis. Full stoichiometry with respect to the occupation of these interstitials is to be expected, according to Fig. 1 at pressures higher than 2.2 GPa of gaseous deuterium. For comparison the corresponding concentration of hydrogen particles in the palladium lattice is given. As can be seen, lower hydrogen pressures are required to achieve the same volume concentration as compared with deuterium. This is a common isotope effect in Me-H/D systems, caused by the difference in the zero energies of both gases. Both curves on Fig. 1 were calculated from formulae, given by Wicke and Nernst [7].

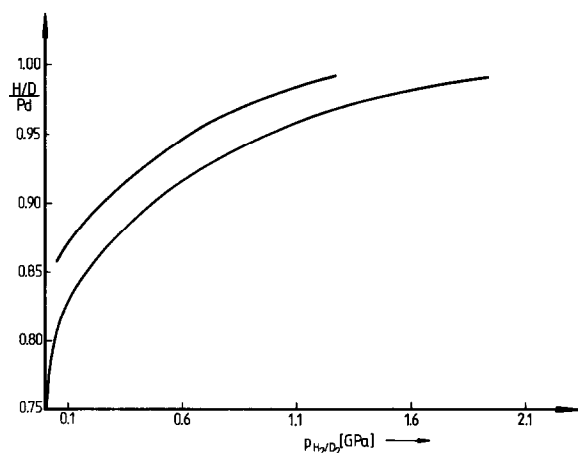


Fig. 1. Atomic ratio H/Pd (upper curve) and D/Pd (lower curve) as a function of pressure of gaseous hydrogen (lower curve) or deuterium (upper curve) at equilibrium conditions between gaseous and metallic phases at 298 K calculated from eqns. (1) and (2).

$$\ln f_{\text{H}_2} = \frac{-(100.4 - 90.1n)(\text{kJ mol}^{-1})}{RT} + \frac{106.4(\text{J mol}^{-1}\text{K}^{-1})}{R} + \frac{2 \ln n}{(1-n)} \quad (1)$$

$$\ln f_{\text{D}_2} = \frac{-(95.6 - 90.1n)(\text{kJ mol}^{-1})}{RT} + \frac{106.4(\text{J mol}^{-1}\text{K}^{-1})}{R} + \frac{2 \ln n}{(1-n)} \quad (2)$$

where f_{H_2} and f_{D_2} are the fugacities of gaseous hydrogen and deuterium, n denotes the atomic ratio, H/D/Pd and RT have the conventional meaning. Wicke and Nernst [7] use pressures instead of fugacities. Equation (1) was compared [6] with direct experiments [8] giving good agreement. The number “1” in the last terms on the right-hand sides of eqns. (1) and (2) denotes the maximal occupation of light particles in the palladium lattice that is the complete occupation of the octahedral interstitials. To complete our thermodynamic considerations, Fig. 2 presents the dependence between pressure and fugacity for both gases [9].

For instance, at 2 GPa gaseous pressure, the fugacity is more than four orders of magnitude higher. This simple thermodynamic fact was overlooked by Fleischmann and Pons [1] in their discussion of the deuterium pressures corresponding to the electrode potential, forgetting that both authors did not distinguish reversible and irreversible (overpotential) electrode potentials. Only the first exhibit a thermodynamic significance. The second only have an importance for kinetic discussions of the electrode reactions involved. The large difference between pressure and fugacity at high pressures can be simply treated, as caused by the covolume of the particles, what finally leads to a continuous transition of the chemical potential dependence on pressure from logarithmic (for dilute gases) to a linear dependence (for an incompressible condensed phase).

For achieving even higher concentrations of deuterium in the palladium lattice, we started a second experiment, with a palladium wire of about 50 cm

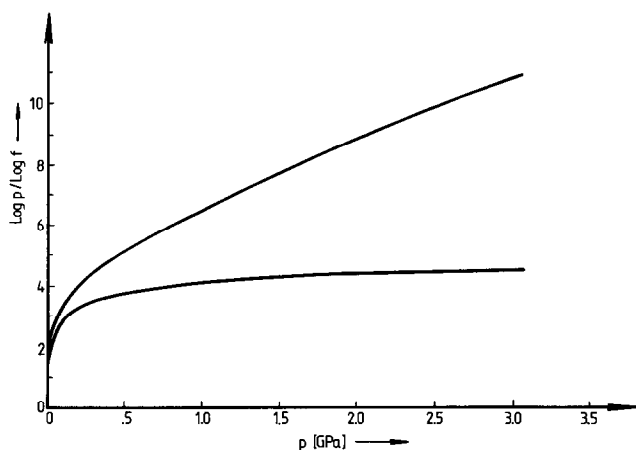


Fig. 2. Logarithm of pressure (lower curve) and logarithm of fugacity (upper curve) as a function of pressure of gaseous hydrogen or deuterium at 298 K (based on ref. 9).

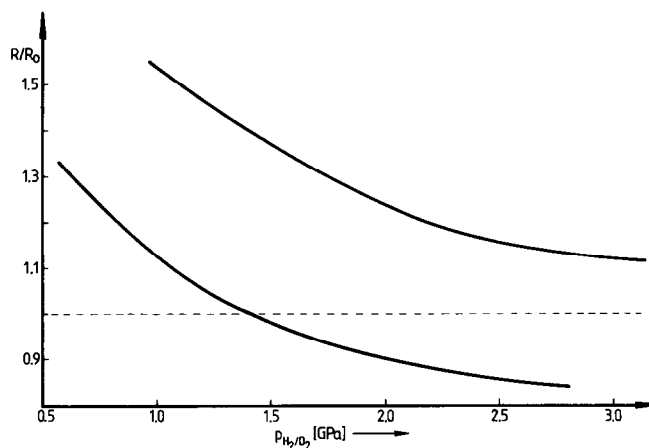


Fig. 3. Stationary relative electrical resistance of palladium (R_0 , resistance of pure palladium; R , resistance at the pressure of gaseous hydrogen) (lower curve) and deuterium (upper curve) at 298 K.

length and 1 mm in diameter (volume of palladium about 0.4 cm^3 , mass of palladium about 4.7 g). The electrical resistance of this wire was measured at non-stationary and stationary conditions as a function of time and the pressure of gaseous deuterium at 298 K in the pressure range 1.0–3.1 GPa. Figure 3 presents the values of stationary relative resistances of the above-mentioned wire sample as a function of deuterium pressure. R_0 is the electrical resistance of the same sample at 298 K in hydrogen-free conditions.

We notice a continuous decrease in the relative resistance from about 1.53 at 1 GPa to about 1.11 at 3.1 GPa of gaseous deuterium. For comparison, the relative electrical resistance of palladium hydride (the lower curve) is given [10–12]. The

large isotope effect is pointed out, leading to much higher electrical resistances in the deuteride as compared with palladium hydride. In the last phase at about 1.4 GPa of gaseous hydrogen the electrical resistance coincides with the initial (hydrogenless conditions) value, whereby in palladium deuteride even at the highest pressure (3.1 GPa) the value of the electrical resistance is still much higher than for the initial (hydrogenless) sample. The simplest presentation of the relative electrical resistance of palladium deuteride can be given as a function of the logarithm of the deuterium fugacity (in the gas phase). This is shown in Fig. 4.

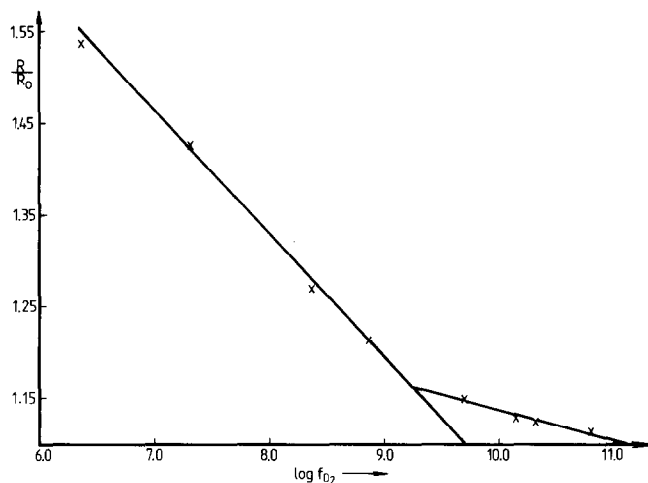


Fig. 4. Logarithm of the stationary relative electrical resistance of PdD as a function of logarithm of fugacity of gaseous deuterium at 298 K.

We see that, with a certain approximation, two linear regions can be distinguished whereby at higher pressures a much lower slope is noticed. One would expect that at the highest pressures only the pure hydrostatic effect is registered. Figure 5 proves that this is not the case.

In this figure we present the pure hydrostatic course whereby the pressure coefficient for pure palladium was taken over [9]. This coefficient is lower for hydrogen-charged samples than the value taken over for Fig. 5. It is clear that even in the pressure range 2.4–3.1 GPa of gaseous deuterium the experimental decrease in the electrical resistance is much higher than the expected influence of the hydrostatic pressure. As compared with Fig. 1, one can conclude that even after the estimated complete filling up of the octahedral vacancies a further taking up of deuterium particles takes place, the available tetrahedral vacancies (two for each palladium atom) probably start to become occupied in a continuous way. An additional argument for the further up-take of deuterium at pressure, estimated to be above the stoichiometric concentration, is the time course of the electrical resistance. Figure 6 presents such an example for a deuterium pressure of 2.56 GPa at 298 K.

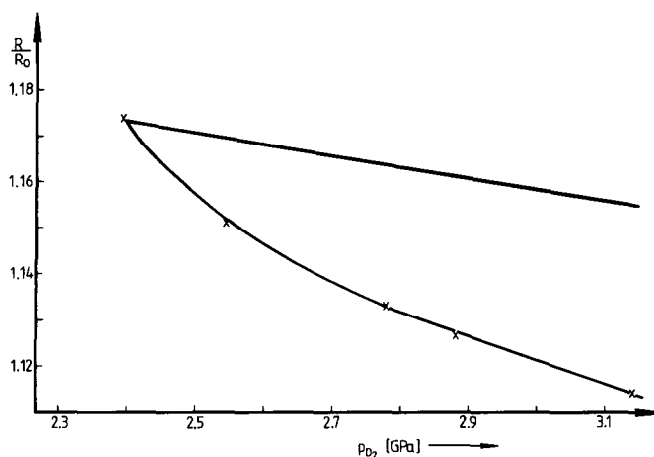


Fig. 5. Stationary relative electrical resistance of palladium as a function of pressure of gaseous deuterium (in the highest pressure range!) (lower curve) compared with pure hydrostatic changes in the electrical resistance (upper curve).

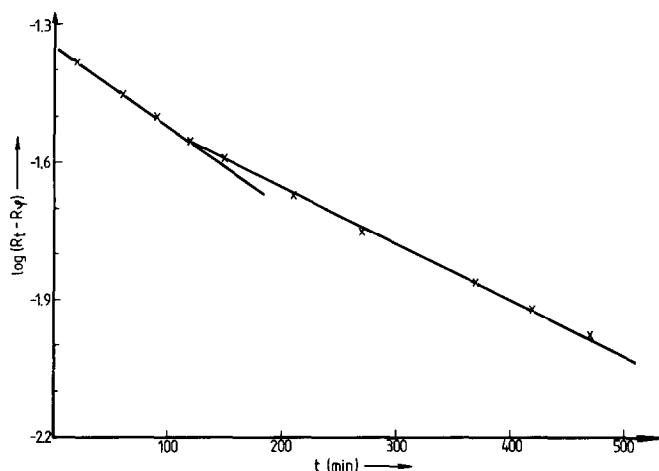


Fig. 6. $\log(R_t - R_\phi)$ as a function of time for a palladium wire ($r = 5 \times 10^{-2}$ cm) at 298 K and pressure of gaseous deuterium equals 2.56 GPa (R_t , resistance at time t ; R_ϕ , stationary resistance).

The linear course of the logarithm of $(R_t - R)$ is an indication of bulk diffusion as the rate-determining step [6]. The calculated Fick's diffusion coefficient equals $2.1 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, *i.e.* one order of magnitude lower than that determined at the same temperature for palladium deuteride at 1.0 GPa of gaseous deuterium [6]; this difference may be caused by a higher deuterium concentration in the bulk phase as well as by the insufficient surface activity of the sample used.

Even such a concentrated palladium deuteride sample did not show any evidence of neutron emission, especially under dynamic conditions, *i.e.* during changes in deuterium pressure. It has to be remarked that only 7% of the total

neutron emission could be detected owing to the estimated absorption of the metallic elements by the high pressure device. There is no doubt that the last experiment was carried out at a deuterium concentration higher than in any experiment under electrochemical conditions of formation.

In order to prove whether the intense lattice dynamics during deuteride formation and decomposition can induce "cold fusion", the system Pd-D₂ was not very suitable. At room temperature the formation pressure of palladium hydride and deuteride is of the order of 10⁻³ MPa [7], but only giving atomic ratios H/D/Pd of 0.6–0.7. The approach to stoichiometry requires pressures six orders of magnitude higher, as indicated above (see Fig. 1). Thus working with high pressures of gaseous deuterium we always move inside the deuteride phase of palladium with continuously changing compositions, as shown in Fig. 1. For discontinuous, large changes in deuterium content inside the metallic lattice in the high pressure region, the system Ni-D₂ is a good candidate. The formation pressure of this phase was found to be about 0.75 GPa of gaseous deuterium [13] whereby the decomposition equals 0.4 GPa. Both values are higher than that characteristic of nickel hydride [2–4]. During the formation or decomposition processes the concentration of deuterium in the f.c.c. lattice of nickel changes abruptly between 1 and about 0.02 for D/Ni, whereby the accompanying volume change is in the range of about 20% of the volume of pure nickel. Thus intense dynamics are occurring here. For our experiments tablets of carbonyl nickel powder were used, containing about 5 g of nickel. Temperature changes due to the pressure changes of deuterium as well as due to the formation and decomposition reactions were clearly detected by the copper-constantan thermopower changes. However, additional changes in the long-term experiments due to eventual "cold fusion" were not found. The nickel sample was held at high pressure conditions for about 2 months. During that time several cycles of decomposition and formation of nickel deuteride were carried out. Simultaneously, the counting numbers of the neutron scintillator were registered, at least 10 min before any dynamics took place, then the same registration time was taken during the formation and decomposition processes. No differences outside the average error range of the mean values were found. Thus we can state that even such intense lattice dynamics in the highly concentrated deuterium nickel lattice samples did not give any evidence of neutron emission. The same conclusion is valid with respect to the temperature changes. This is obvious, since neutron emission detection should normally precede any detectable temperature changes.

We were also able to perform electrolytic charging of a palladium cathode at high pressures of gaseous deuterium in our apparatus. In this respect we have some experience with reversible electrode potential measurements at hydrogen pressures up to 0.8 GPa [14]. The upper limit of pressure was determined by the freezing of the dilute electrolyte solution used.

For high pressure electrolysis we used the piston-cylinder device with deuterium gas (without any further pressure-transmitting medium). A short schema of the arrangement is shown in Fig. 7.

The anode consists of a Pd_{0.75}Ag_{0.25} thin-walled vessel (1), the cathode consisted of a spiral of (0.5 mm, radius; 35 cm, length) palladium wire (2). The high

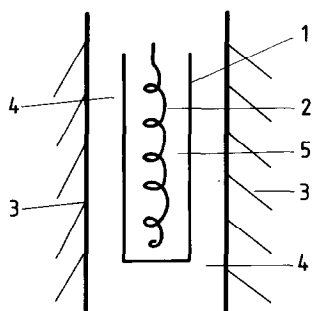


Fig. 7. Schema of the electrolytic high pressure device: 1, $\text{Pd}_{0.75}\text{Ag}_{0.24}$ anode; 2, palladium cathode; 3, high pressure device; 4, deuterium gas; 5, electrolyte solution.

pressure vessel (3) was supporting the gaseous deuterium volume (4) and the solution of lithium deuterioxide in heavy water (5). Both electrodes were isolated from the metallic elements of the high pressure vessel. Cathodic charging, at stationary deuterium pressures of 0.4 and 0.6 GPa, with current densities up to 10 mA cm^{-2} did not give any evidence of neutron emission. Only preliminary measurements were carried out, as this new high pressure electrolysis requires a more detailed elaboration. Before additional electrolytic charging, the initial D/Pd values in the cathode already corresponded to numbers of 0.89 and 0.91 (see Fig. 1). Making the palladium wire a cathode or an anode (*i.e.* equivalent to an increase or decrease in the deuterium concentration as compared with the equilibrium value of the deuterium pressure maintained) meant that no change with respect to eventual neutron emission was noticed. Thus, so far, the combination of high pressure with electrochemistry did not give any evidence of traces of “cold fusion” connected with neutron emission.

What remained to be proved is the composition of the deuterium gas and that evolved from the metallic samples after the release of pressure. From the results described above no revelations are to be expected. The analysis mentioned will be carried out after we have finished our current observations.

4. Conclusions

(1) Long-term experiments (up to 5 months) with highly concentrated palladium and nickel deuterides did not give any indication of neutron emission nor any detectable heat evolution. Experiments were carried out both under conditions of changes in concentration with time (continuous as well as discontinuous) as well as in thermodynamic equilibrium between gaseous deuterium and bulk deuteride phases.

(2) Palladium takes up deuterium under conditions exceeding probably the full stoichiometry with respect to octahedral interstitials of the f.c.c. lattice. It seems reasonable to assume that a partial filling of the tetrahedral interstitials occurs.

(3) It seems obvious that, even at a higher volume concentration of deuterium in palladium and nickel lattices, than can possibly be achieved by electrolysis, “cold fusion” seems rather doubtful.

(4) High pressure electrolysis did not improve the above negative results.

(5) Our results confirm previous statements about misinterpretation of electrolysis effects by Fleischmann and Pons [15].

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Appendix A

After this paper was ready for publication a preprint of I. F. Silvera and F. Moshary, *Cold fusion: search in deuterated palladium at temperatures from 4.3 to 400 K and pressures to 105 kbar*, came to our knowledge. More than six orders of magnitude smaller (than applied in our paper) palladium samples were used in their investigation but the temperature and pressure ranges in a DAC device were higher than described above. No evidence of cold fusion was found as in our measurements. Let us remark that similar negative results are reported in our recent DAC X-ray investigation of the equation of state of PdD_{0.75} and PdD_{0.6} at even higher pressures [16].