Polish J. Chem., **75**, 1051–1058 (2001)

Diffusion Coefficients of Deuterium in Palladium Deuteride during Ab- and Desorption in High Pressures of Gaseous Deuterium at 298 K

by B. Baranowski and S.M. Filipek

Institute of Physical Chemistry, Polish Academy of Sciences,
Kasprzaka 44/52, 01-224 Warszawa, Poland

(Received March 16th, 2001)

Exerting pressure jumps of several kbar in gaseous deuterium in the range of 5–28 kbar, surrounding a palladium deuteride wire, the diffusion coefficients of deuterium in the solid phase were evaluated by following the time course of the electrical resistance. Absorption of deuterium is characterized by a smaller diffusion coefficient than its desorption. Both represent a decreasing function with the inrease of deuterium pressure. The difference of the ab- and desorption kinetics is explained by the influence of the elastic energy on the energetics of the occupation of metallic interstitials by deuterium particles. Comparisons with previous measurements are given.

Key words: diffusion, deuterides, high pressure, mechanical stresses, relaxation, volume of activation

The majority of diffusion data of Pd–H and Pd–D systems concerns the α- and diluted β-phases [1–3]. At room temperature the concentration range of the β (hydride) phases in Pd–H,D systems extends from 0.6 –1 in atomic ratios of H,D to Pd. The work in these pure phase β-regions requires, in terms of thermodynamic equilibrium between the gaseous (H_2,D_2) phases and the solid hydride or deuteride phases, high pressures of hydrogen or deuterium. As example the Pd–H system approaches the 1:1 stoichiometry at hydrogen pressure about 10 kbar at 298 K [4,5]. Higher deuterium pressures are required to reach a similar stoichiometry in the Pd–D system [6].

As determination method of the diffusion coefficients in metal–hydrogen systems in high gaseous pressures the time relaxation of the electrical resistance is a simple procedure. This method was applied in two previous papers in Pd–H [7] and Pd–H,D systems [8]. In [7] the hydrogen pressure range covered 40 bar to about 23 kbar at 298 K and in [8] the H_2 and D_2 pressures were limited to 10 kbar, but the temperature covered 208–338 K.

As compared to these results [7,8], the purpose of this paper is two-fold: 1) The extension of deuterium pressure up to 28 kbar. 2) The evaluation of diffusion coefficients both in ab- and desorption of deuterium and the correlation of the data obtained with other characteristics of the Pd–D system.

EXPERIMENTAL

A Pd wire (produced by Godfellow Metals) of 1 mm diameter and 45 cm length was exposed to gaseous deuterium at 298 K in consecutive pressure jumps in both directions in the pressure range 5–28 kbar. The high pressure device used was a two-step vessel, described in details previously [5,9–11]. Pressure was determined by a manganine gauge, kept in the liquid part of the device used. Temperature was kept at 298 K by a controlled heating system with fluctuations below 0.1 degree. The large heat capacity of the high pressure vessel was here an advantage. The electrical resistance of the Pd wire was computer registrated in time steps between 1–15 minutes by the four pole technique. The evaluation of the diffusion coefficients was carried out in the same way as described in [7,8], that is basing on the solution of Fick's diffusion equation for the appropriate boundary and initial conditions. Furtheron a proportionality between the average electrical resistance of the wire had to be assumed. In this way, of course, only the average diffusion coefficient in the deuterium concentration covered by the pressure jump considered, is evaluated. It is obvious that smaller pressure jumps would give more specified values of the diffusion coefficients in respect to its concentration dependence. But on the other hand, smaller pressure jumps reduce the resistance differences involved, causing finally a larger error of the calculations. Basing on the fact, that in small concentration ranges the electrical resistance of the wire is proportional to the deuterium concentration and that the solution of Fick's equation reduces to one exponential term for long times [8], the diffusion coefficient can by calculated from:

$$D = \frac{a^2}{5.77} \frac{d\ln(R_t - R_\infty)}{dt} \qquad (1)$$

which is identical with (7) from [8]. In (1) R_t and R_∞ denote the resistances of the wire at time t and $t = \infty$ respectively, "a" is the radius of the wire. The linearity of $\log(R_t - R_\infty)$ with time is the criterion for the possible neglection of further terms in the exact solution of Fick's law. Pressure changes were realized by changing the position of a mobile piston.

RESULTS AND DISCUSSION

Diffusion coefficients were evaluated from relaxation measurements carried out between 8.5 and 27.6 kbar of gaseous deuterium at 298.15 K. Fig. 1 presents two examples of the $\ln(R_t - R_\infty)$ time dependences for one ab- and one desorption process, whereby the slopes, according to (1), served for the calculation of the corresponding diffusion coefficients. As it is clearly shown in Fig.1, for short times not only the last term of the solution of Fick's equation series [8] contributes to the time course of $\ln(R_t - R_\infty)$. After dying out of the successive expansion terms, we are finally left with only one first order relaxation term, which enables the calculation of the diffusion coefficient by (1).

The mean pressures for curves I and II of Fig. 1 are practically the same (23.1 kbar), but the corresponding diffusion coefficients for the ab- and desorption processes are clearly different: The increase of deuterium concentration during absorption is a slower process than the inverse change of deuterium concentration (desorption), which is characterized by about 50% higher diffusion coefficient. This tendency is repeated in similar concentration changes at other deuterium pressures. All results obtained are presented on Fig. 2.

First of all let us remark that the diffusion coefficients are decreasing functions of the deuterium pressure. This is an obvious course if the elementary jumps of the deu-

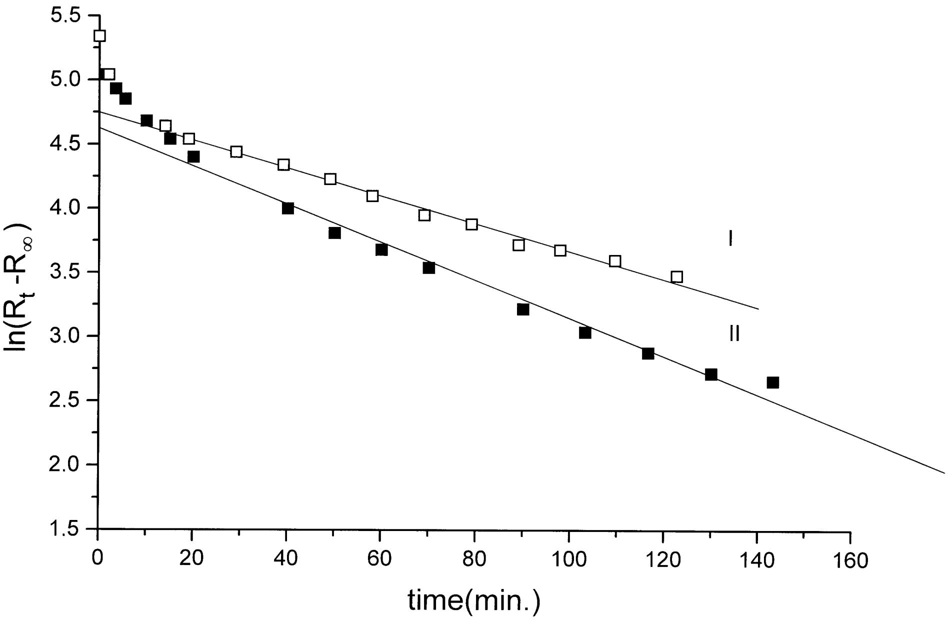

Figure 1. $\ln(R_t - R_\infty)$ as a function of time for II (24.3 → 21.9 kbar) and I (22.1 → 24.3 kbar) pressure jumps. The calculated diffusion coefficients are: I – (p_{mean} = 23.1 kbar) 7.6×10^{-8} cm^2/sec; II – (p_{mean} = 23.2 kbar) 1.1×10^{-7} cm^2/sec.

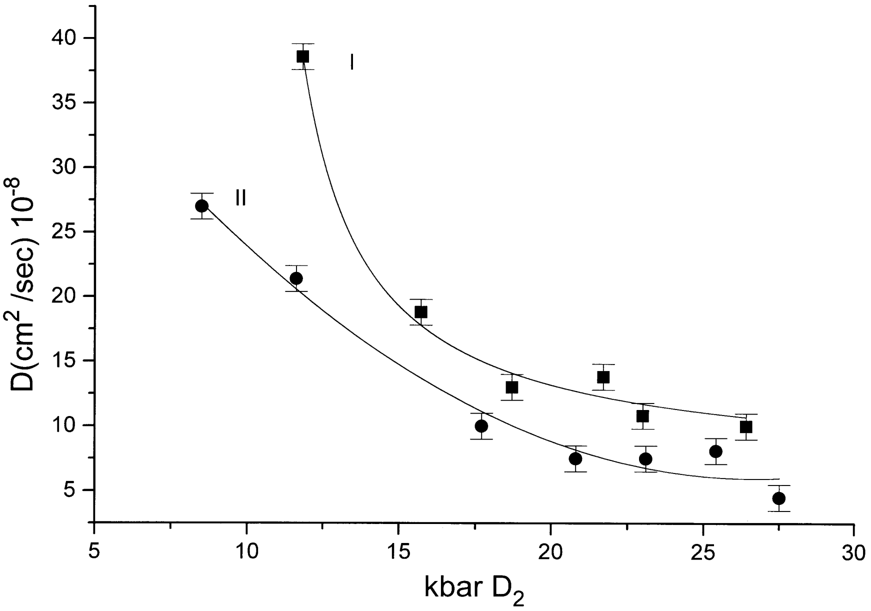

Figure 2. Diffusion coefficients (cm^2/sec) as a function of deuterium pressure (kbar). I – values for the desorption (decreasing pressure). II – values for the absorption (increasing pressure).

terium particles are to be realized over empty interstitial places. As the concentration of these interstitials is decreasing with the increasing pressure of deuterium, the concentration dependence of the diffusion coefficient observed seems reasonable. In this respect our results differ from recently published [12], where a hardly to separate combination of surface and bulk processes was investigated. The evaluated diffusion coefficients varied by four orders of magnitude: from 10^{-9} cm^2/sec for atomic ratio H/Pd 0.1 to 10^{-5} for stoichiometric palladium hydride. These results are doubtful not only, because a hardly to follow calculation procedure was applied, but also due to a not discussed scatter of the numerical results. Some authors claimed even to see in these scattering results an evidence for a third γ- phase in the Pd–H system. Previous results from our group [7,8] confirm the decreasing tendency of the diffusion coefficients in Pd–H and Pd–D systems with the increasing pressure of the gaseous component, what corresponds to the increase of the H,D concentration in the palladium lattice. With previous published data, the results presented on Fig. 2 can be directly compared with [8] at 10 kbar of D_2 only (the upper pressure in [8]). From Fig. 2 of [8] we extrapolate for Fick's diffusion coefficient at 298 K the value 3.2×10^{-7} cm^2/sec, which agrees quite well with the mean value from both curves for the same pressure, taken from Fig. 2 of this paper. A comparison with paper [7] cannot be carried out in a direct way, as in [7] the diffusion coefficients were measured for palladium hydrides only. Let us mention two values of Fick's diffusion coefficients from Tab. 1 of [7]: At 11 kbar of H_2 the diffusion coefficient equals 7.5×10^{-8} cm^2/sec and at the highest pressure measured, that is nearly 23 kbar, it equals 2.3×10^{-8} cm^2/sec. From Fig. 2 of this paper at similar deuterium pressures the mean values (approximate arithmetic mean value from the ab- and desorption processes) are about 3×10^{-7} cm^2/sec for 11 kbar and 8×10^{-8} for 23 kbar. For both pressures the diffusion coefficients of the deuterides are between 3–4 times larger than the corresponding values for the hydrides at the same pressures.

Can a similar behavior, as presented in Fig. 2, be expected in diffusion of other binary systems in the solid state? What is in this respect a special feature of the metal–hydrogen systems? Well, let us first of all underline that the system considered in this paper represents a phase, in which the components involved exhibit mobilities differing by many orders of magnitude: Self-diffusion coefficient of palladium at room temperature is about 40 orders of magnitude smaller than the diffusion coefficient of deuterium, discussed above. Thus, a practical immobile metallic lattice is elastically expanded by small, as compared to the size of metallic particles, mobile interstitials. The absorption process is accompanied by an input of elastic energy by the invading particles. In certain sense, it is an uphill migration for the penetraning mobile interstitials, what results in an effective retardation of the absorption process. In other words, some elastic energy is stored in the metallic matrix. The desorption process, on the other hand, will be accompanied by the relaxation of this elastic energy, what – in contrast to the absorption – will lead to an acceleration of the individual jumps of the hydrogen particles involved. In other words, the diffusion coefficient not influenced by the eleastic energy input should be expressed by the mean value of the diffusion coefficients determined during the ab- and desorption processes.

A similar behavior in respect to diffusion coefficients evaluated by ab- and desorption procedures, as presented in Fig. 2, was recently found in PdPt alloy system [13] (see Fig. 1 in [13]). The differences between this paper and [13] concern a) The phase character: The system considered in this paper treats continuous concentration changes in a β-phase, whereby in [13] a low concentrated α-phase was considered. b) The evaluation methods: In this paper – a relaxation method, valid after a certain time of the ab- and desorption processes was applied, whereby in [13] the time-lag method, valid for the time interval before the stationary period of the penetration process through the membrane is the basis of calculation. c) The pressure range: In this paper a high pressure range, both in respect to pure hydrostatic aspect as well as in respect to the deuterium activity is applied, whereby in [13] low pressures, in both aspects mentioned, were present. In fact the difference between ab- and desorption break – through times was observed earlier (see p.1197 in [14]). The mean values of the diffusion coefficients from Fig. 2, that are the so called Fick's diffusion coefficients were transformed to the so called Einstein diffusion coefficients D' defined by

$$D' = D/\gamma \tag{2}$$

where γ denotes the thermodynamic factor, given by

$$\gamma = 1/2\ \ (d\ \ln(a_{D2})/(d\ \ln(n)) \tag{3}$$

where a_{D2} is the fugacity of gaseous deuterium taken from [15] and extrapolated to higher pressure and n is the atomic ratio D/Pd calculated from Wicke's formula [16]

$$\ln a_{D2} = -((95.6 - 90.1\ n)\ (KJ/mol)/(RT) + (106.4\ J/mol\ K\ )/R + 2\ \ln(n/(1 - n)) \tag{4}$$

In terms of (4) the thermodynamic factor equals

$$\gamma = (90.1\ KJ/mol)/(2RT)\ n + n/(1 - n) + 1 \tag{5}$$

A further diffusion coefficient possible to calculate from D′(2) is D″ defined by

$$D'' = D'/(1 - n) \tag{6}$$

The difference (1 – n) is proportional to the empty octahedral interstitials in the palladium lattice, if 1 is the maximal concentration in terms of n. It was evaluated for the given activity (pressure) of gaseous deuterium by (4).

Which linear correlations are possible, when numerical data from Fig. 2 are taken into account and Wicke's relation (4) is considered as suitable functional dependence between fugacity of gaseous deuterium and its concentration in the metallic matrix?

Well, first of all let us notice that the mean diffusion coefficient D_m, evaluated from Fig. 2, as the algebraic mean value from the ab- and desorption curves, nicely correlates with the atomic ratio's D/Pd calculated from (4). This is shown in Fig. 3. Similar linear relationships are established for $D'$and D'', calculated from D_m and equations (2) and (6), shown in Figs. 4 and 5. A clear decrease of all diffusion coefficients (D_m, $D'$and D'') as linear functions of n is demonstrated in Figs. 3–5. Forgetting a fundamental physical explanation, Wicke's relation (4) seems very efficient for formulation of simple linear dependencies between the diffusion coefficients determined and the concentration of the lattice deuterium particles calculated. Whereby let us remark that the linearity of D_m in respect to n (Fig. 3) does not automatically imply a similar linearity in respect to D' and D'' as (3) and (5) and (6) demonstrate. From pure numerical point of view the linearity discussed follows from the small variety range of the parameter n. As shown in Figs. 3–5, it changes in the range from about 0.965 to 0.998, from the lowest 10 kbar to the highest 28 kbar of gaseous deuterium. Therefore, in terms of (2) to (6) one should be rather careful with a deeper explanation of the linearities observed.

On the other hand, a decrease of the diffusion coefficient with the increase of hydrostatic pressure has to be expected, as the volumes of activation of hydrogen and deuterium in diffusion metallic palladium exhibit positive values [8,17]. In [8] the volumes of activation as a function of temperature (see Fig. 9 in [8]) were evaluated from the slope of the curves D'' as a function of hydrostatic pressure, whereby the numerical values varied between 3 and 0.5 cm^3/mole (see Fig. 9 in [8]) More realistic is the value calculated from the difference of Fick's diffusion coefficients measured at

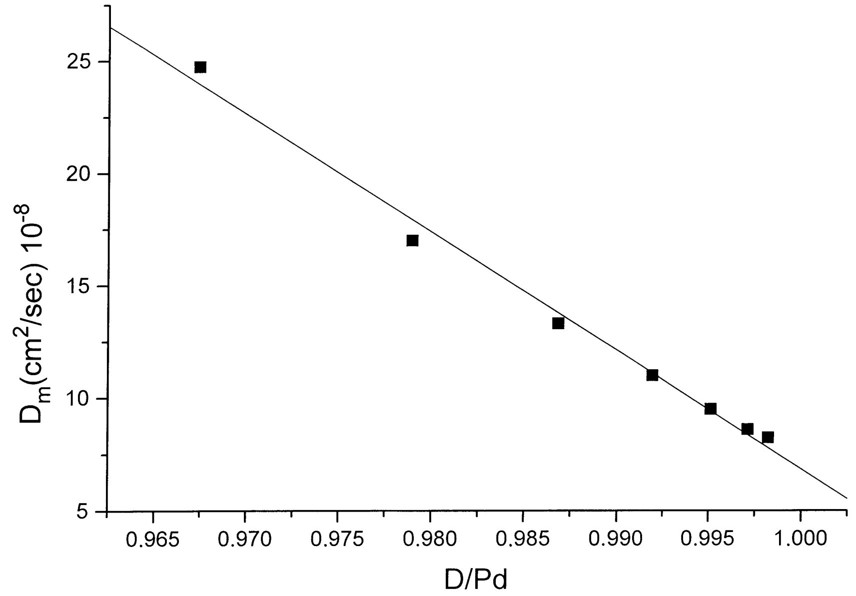

Figure 3. Mean diffusion coefficients [$D_m = 1/2\ (D_{ab} + D_{des})$], where D_{ab} and D_{des} denote the diffusion coefficients I and II from Fig. 2 for a given pressure.

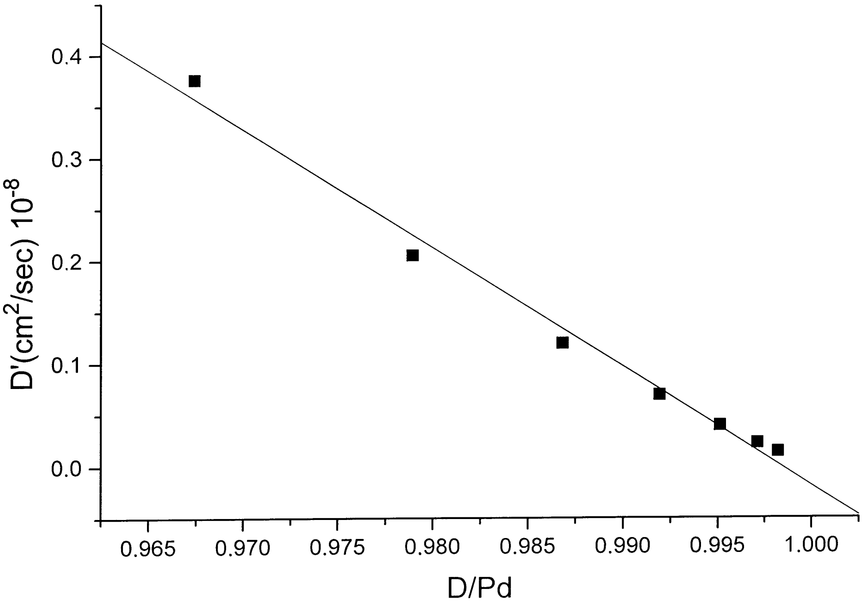

Figure 4. Diffusion coefficients D′, calculated from (2) and values of D_m, taken from Fig. 3 as a function of D/Pd = n, calculated from (4).

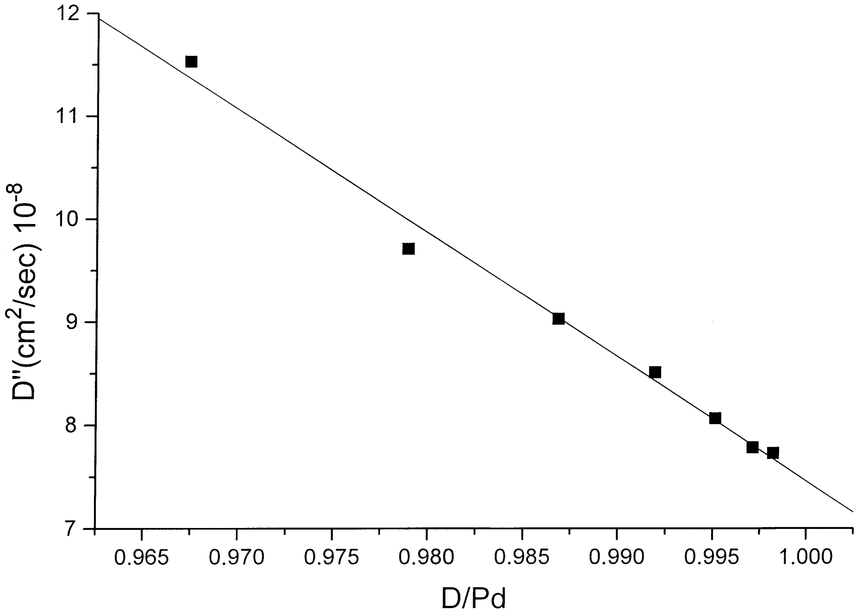

Figure 5. Diffusion coefficients D″, calculated from (6), as a function of D/Pd = n, calculated from (4).

the same hydrogen fugacity but different hydrostatic pressures [17], due an addition of gaseous helium. Thus, the influence of an inert hydrostatic pressure was directly extracted. This value [17] equals about 1 cm^3/mole, being comparable with the partial molar volume of hydrogen in the Pd–H system [18]. Such activation volume confirms the simple interstitial jump mechanism of hydrogen particle between two empty octahedral places. For such a mechanism the difference of volumes between the initial state of a particle in the Pd lattice and its intermediate state, in the course of the jump to the next stable position, should be comparable with the partial volume of the moving particle. Let us remark that the activation volumes in [8] and [17] are so far the only numerical values of this quantity in Me–H systems, as neither in [2] nor in [3] this quantity was even not mentioned.

In our case plotting $\ln D''$ as a function of hydrostatic pressure, similar to Fig. 7 in [8], does not lead to a straight line. A rough estimate gives an activation volume of about 3 cm^2 /mole, thus, comparable with the highest value in [8]. On the other hand, taking the value of 1 cm^3/mole from [17], we calculate that an increase of hydrostatic pressure of 20 kbar, what corresponds to the maximal hydrostatic pressure changes in this paper, should lead to a reduction of the diffusion coefficient comparable with values presented in Fig. 5. Therefore, before any more sophisticated discussion of Figs. 2–5 in respect to deuterium pressure (concentration of deuterium particles in the palladium lattice) can be undertaken, the contribution of the volume of activation should be clearly evaluated. For such a purpose diffusion measurements in inert high pressure environment, like in [17], seem unavoidable.

REFERENCES

1. Lewis F.A., The Palladium Hydrogen System, Academic Press, London-N.Y., 1967.
2. Völkl J. and Alefeld G., in ”Hydrogen in Metals I”, eds. by G. Alefeld and J. Völkl, Topics in Applied Physics, **28** (Springer, Berlin-Heidelberg 1978), p. 321.
3. Wipf H., Diffusion of Hydrogen in Metals, Topics in Applied Physics, **73**, Wipf H. (Ed.), (Springer Berlin-Heidelberg 1997), p. 51.
4. Tkacz M. and Baranowski B., *Roczn. Chem.*, **50**, 2159 (1976).
5. Baranowski B., in “Hydrogen in Metals II”, eds. by G. Alefeld and J. Völkl, Topics in Applied Physics, **28** (Springer, Berlin-Heidelberg 1978), p. 157.
6. Wicke E. and Brodowsky H., in “Hydrogen in Metals II”, eds. by Alefeld G. and Völkl J., Topics in Applied Physics, **28,** (Springer Berlin-Heidelberg 1978), p.73.
7. Kuballa M. and Baranowski B., *Ber. Bunsenges.*, **78**, 335 (1974).
8. Majorowski S. and Baranowski B., *J. Phys. Chem. Solids*, **43**, 111 (1982).
9. Baranowski B. and Bujnowski W., *Roczn. Chem.,* **44**, 2271 (1970).
10. Baranowski B., *Plat. Met. Rev.*, **16**, 10 (1972).
11. Baranowski B., *Ber. Bunsenges. Phys. Chem.*, **76,** 714 (1972).
12. Mengoli G., Fabrisio M., Manduchi C. and Zamoni G., *J. Electroanal. Chem.*, **350**, 57 (1993).
13. Dudek D. and Baranowski B., *Z. Phys. Chem.*, **206**, 21 (1998).
14. Dudek D. and Baranowski B., *Polish J. Chem.*, **69**, 1196 (1995).
15. de Graaf V., Thesis, Amsterdam (1960).
16. Wicke E. and Nernst G., *Ber. Bunsenges*, **68**, 224 (1964).
17. Baranowski B. and Majorowski S., *J. Less-Comm. Met.*, **98**, L27 (1994).
18. Baranowski B., Majchrzak S. and Flanagan T.B., *J. Phys. F,* **1,** 258 (1971).