

**Calorimetric Enthalpies in the β -phase regions
of Pd black-H(D) Systems**

Y.Sakamoto, M.Imoto, K.Takai and T.Yanaru

Department of Materials Science and Engineering, Nagasaki University,
Nagasaki 852, Japan

Abstract

The enthalpies for the reaction of gaseous hydrogen and deuterium with palladium black in β -phase region have been measured in the temperature range 323 K to 194.5 K and pressures up to about 7.6 MPa of $H_2(D_2)$ using a differential heat flow low temperature calorimeter. The calorimetrically determined enthalpies, $\Delta H_{H(D)}$, for solution in the β -phase regions of $0.7 < H/Pd < 0.9$ and $0.65 < D/Pd < 0.83$ for Pd black-H(D) systems become less exothermic almost in a linear fashion with increasing H(D) content, independently of temperature. The variation in $\Delta H_{H(D)}$ values with H(D) content are in agreement with that calculated from van't Hoff plots of the relative chemical potentials of hydrogen and deuterium. Enthalpies of almost the same magnitude are obtained from the desorption data. At the same H(D) content, the ΔH_H values for Pd black-H system are a slightly more exothermic than the ΔH_D values for the Pd black-D systems. The corresponding entropy, $\Delta S_{H(D)}$, on absorption calculated from the calorimetrically determined $\Delta H_{H(D)}$ and the relative chemical potentials have a tendency to decrease gradually with increase of H(D) content independently of temperature, however there is no marked difference in the magnitude of the $\Delta S_{H(D)}$ values between the two systems.

1. Introduction

The excess heat generation in "cold fusion" reactions [1-3] during electrolysis of $D_2O/LiOD$ solution at room temperature by Pd cathode, although observed with poor reproducibility, seems to be closely related to highly deuterated Pd, $D/Pd > 0.83$ [4-7], where the electrical resistance of the deuterated Pd electrodes should still be high, even though the resistance passes through the maximum near $D/Pd = 0.75$ [8,9]. Many experimentally unknown factors exist, for instance the electrical quantities introduced into the electrolysis up to the onset of the heat generation, the action of the Li ions contained in the electrolyte on the electrode surface, and the variations in electrolysis current density and electrode overpotential etc. during the electrolysis.

Material Science Studies

If the key factor for the excess heat generation is a "high deuterium content" in Pd, the observation of any heat generations by a gas phase method is rather free from unnecessary complications compared to the electrochemical method mentioned above. Calorimetric enthalpies obtained by gas phase method, together with p-c isotherm measurements, should also reflect the dynamic conditions as the electrolysis method, because the dynamic conditions are related to the hydriding or dehydriding processes.

In previous measurements [10] of the calorimetric enthalpies for the reaction of gaseous hydrogen and deuterium with bulk Pd as a function of H/Pd and D/Pd contents up to about 0.865 and 0.85, respectively, in the temperature range 298 K to 194.5 K using a differential heat flow low temperature calorimeter, it has been found that the calorimetrically determined enthalpies, $\Delta H_{H(D)}$, for solution in the β -phase regions of both systems becomes less exothermic almost in a linear fashion with increasing H(D) content, independently of temperature. The $\Delta H_{H(D)}$ values are in agreement with the values determined from van't Hoff plots of the chemical potential of dissolved hydrogen and deuterium in Pd measured by Wicke and Nernst [11]. At the same H(D) content, the ΔH_H values for Pd-H system are a slightly more exothermic than the ΔH_D values for the Pd-D system. Enthalpies of almost the same magnitude are obtained from the desorption data. These results are also in agreement with the previously reported values by Flanagan et al. [12], although the enthalpies for absorption of hydrogen determined by Tkacz and Baranowski [13] using a high pressure device in the range of H/Pd=0.87 to 0.995 show a large exothermicity with increase of hydrogen content.

The present study was to obtain calorimetric information about the enthalpies of reaction of gaseous hydrogen and deuterium with Pd black at high H(D) contents at temperatures between 323 K and 194.5 K by a combination of twin-cell, differential heat flow calorimetry and p-c isotherm measurements.

Frieske and Wicke [14] have shown that the assumption that p-c isotherm, $p(r)$, and magnetic susceptibility, $\chi(r)$, measured on Pd black are valid for bulk Pd generally leads to misinterpretations. The characteristic differences between bulk Pd and Pd black are as follows : Pd black has 1) reduced hysteresis loops, and 2) displacements of the $p(r)$ and the $\chi(r)$ isotherms towards higher r values, and 3) smaller susceptibility at $r \rightarrow 0$ compared with bulk Pd. These differences can be attributed to the special features of the dispersed state of Pd black with high surface area and strong lattice distortions. However, the values obtained for the critical temperature, $T_c=290 \pm 3$ °C and pressure, $p_c=19.5 \pm 0.2$ atm agree with the results for bulk Pd within the experimental errors [14]. Therefore, it is also interesting to examine whether there is a difference in calorimetric enthalpies or not between Pd black-H(D) and bulk Pd-H(D) systems.

Arata and Zhang [15,16] have reported that in their cold fusion experiments using a double structure cathode vessel filled with Pd black (0.1 mol), an excess energy higher

Material Science Studies

than 200 MJ was obtained with an average rate of 50-100 kJhr⁻¹, although in this case the chemical reaction energy between Pd and deuterium is only 4 kJ.

2. Experimental details

The Pd black used in this study was powder less than about 45 μm of Wako Pure Chemical Industries Ltd. The purity is > 98.1 %, the remainder is moisture. The twin-cell differential heat flow calorimeter used in this study is the Setaram low-temperature calorimeter (model BT 2.15 II). The two identical hydriding cells, i.e., the reaction (sample) vessel and reference vessels of the calorimeter are connected to a Sieverts p-c isotherm measurement apparatus, where a filter gasket was inserted between the connecting tube and both the vessels in order to avoid suction effect disturbances of powder samples on evacuating.

About 6 gr. of Pd black was used as a sample in the reaction vessel by mixing Cu foils with about 50-60 μm thickness and about 2 mm x 2 mm. An amount of Cu, whose volume was the same as that of the (Pd black + Cu foils) in the reaction vessel, was placed in the reference vessel in order to improve the heat conduction. In order to obtain an highly active state for the p-c isotherm measurements and calorimetry, the vessels were completely outgassed at about 4×10^{-6} Pa and at 573 K, and then the samples were exposed to hydrogen gas of about $p_{\text{H}_2}=0.1$ to 3 MPa for 10 min. Subsequently, the vessels were slowly cooled down to ice water, and dehydriding was then accomplished by re-heating at the same temperature. This hydriding-dehydriding treatment was repeated more than ten times.

In addition to the calorimetry at 298 and 323 K, low temperature calorimetry at 273 K, 237 K (Pd black-H), 233K (Pd black-D) and 194.5 K was carried out, respectively by controlling temperatures with a Setaram CS-32 controller under cooling with a liquid nitrogen flow. The variation in the temperature was ± 0.01 to ± 0.02 K at all the measurement temperatures.

For the high pressure experiments, it is in general difficult to obtain precise p-c isotherm data even for Pd-H(D) systems, because of the small variations in the high pressures due to the gas valve-handling operations and small variations in temperature of the measuring system, leading to significant errors in hydrogen moles absorbed or desorbed. In this study in order to avoid the difficulty of obtaining H(D)/Pd values at higher pressures, it was assumed that high pressure solubilities coincide with the values obtained by extrapolating from low to high pressure isotherms using a relation of $\log f_{\text{H}_2(\text{D}_2)} = -A(T) + B(T) \cdot \text{H(D)}/\text{Pd}$ [10,11], where $f_{\text{H}_2(\text{D}_2)}$ is the fugacity of gases, A(T) and B(T) are temperature-dependent constants; by measuring the initial and final equilibrium pressures during the absorption and desorption processes, the H(D)/Pd values were calculated according to the relations. Furthermore, the low temperature calorimetric

Material Science Studies

measurements with higher $p_{H_2(D_2)}$ pressures at low temperature are generally difficult [1], because when the reaction valve for $H_2(D_2)$ absorption (introduction) was opened, an instantaneous heat flux was produced from the reference vessel towards the sample vessel before the occurrence of heat flux due to the heat of solution. Conversely, on opening the valve for $H_2(D_2)$ gas desorption (removal), an heat flux in the opposite direction is instantly produced. The origin of the instantaneous heat flux generation on opening the reaction valve for absorption or desorption is unknown, however, it may be associated with the differences in heat conductivity and/or in specific heat between the sample vessel containing Pd and Cu foil samples and the reference vessel containing only Cu foils, i.e., with the difference in heat transfer effects between both the vessels from the gas reservoir which is not at the calorimeter temperature. Therefore, these phenomena lead more or less to the errors in enthalpy values derived from the integration of the heat flux vs. time curves.

3. Results and discussion

Figures 1 and 2 show the calorimetrically determined enthalpies for hydride and deuteride formations at different temperatures for Pd-H and Pd-D systems, respectively, together with calculated enthalpies from van't Hoff plots of relative chemical potentials shown in upper part of the same figures.

It can be seen that the calorimetrically determined enthalpies for hydrogen and deuterium absorptions in the β -phase region become less exothermic almost linearly with increasing H and D contents, independently of temperature, and that the linearly decreasing tendencies for both systems are in agreement with the calculated values from van't Hoff plots. The dependence of the present calorimetric enthalpies on H and D concentrations in the range $0.70 < H/Pd < 0.90$ and $0.60 < D/Pd < 0.83$ is expressed as :

$$|\Delta H_H| \text{ (kJ(molH)}^{-1}) = 48.06 - 42.39 \cdot H/Pd$$

and

$$|\Delta H_D| \text{ (kJ(molD)}^{-1}) = 44.99 - 41.89 \cdot D/Pd$$

At the same H(D) content, the enthalpies for Pd-H system are a little more exothermic, about 3 kJ(molH)^{-1} than that for Pd-D system. Enthalpies of almost the same magnitude are obtained from desorption data. Compared to the previously determined enthalpies for bulk Pd-H(D) systems [10], there is no marked difference in the magnitude of $\Delta H_{H(D)}$ values within the experimental errors between the bulk Pd and Pd black samples.

Figures 3 and 4 show the corresponding entropies calculated from the relation of $\Delta S_{H(D)} = \Delta H_{H(D)}/T - R \ln p_{H_2(D_2)}^{1/2}$ for Pd-H and Pd-D systems, respectively, together with values determined from van't Hoff plots. There are scatter in the entropy values, however, it can be seen that the entropies for H and D absorptions have a tendency to decrease gradually with H(D) content independently of temperature. At the same H(D)

Material Science Studies

content, the entropies for absorption in Pd-H system are a little larger than that for Pd-D system.

References

1. M.Fleishman and S.Pons, *J.Electroanal.Chem.*, 261 (1989) 301. Erratum, 263 (1989) 187.
2. M.Fleishman, S.Pons, M.W.Anderson, L.J.Li and M.Hawkins, *J.Electroanal.Chem.*, 287 (1990) 293.
3. "Frontiers of Cold Fusion, Proc. of ICCF 3, Nagoya 1992", Frontiers Science Series No. 4, ed. H.Ikegami, Universal Academy Press Inc., Tokyo (1993).
4. M.C.H.Mckubre, S.Crouch-Baker, A.M.Riley, S.I.Smedley and F.L.Tanzella, ref.[3], p. 5.
5. E.Storms, ref.[3], p. 21.
6. K.Kunimatsu, N.Hasegawa, A.Kubota, N.Imai, M.Ishikawa, H.Akita and Y.Tsuchida, ref.[3], p. 31.
7. N.Hasegawa, K.Kunimatsu, T.Ohi and T.Terasawa, ref.[3], p. 377.
8. B.Baranowski and R.Wisniewski, *Phys.stat.sol.*, 35 (1969) 593.
9. J.C.Barton, F.A.Lewis and I.Woodward, *Trans.Faraday Soc.*, 59 (1963) 1201.
10. Y.Sakamoto, M.Imoto, K.Takai, T.Yanaru and K.Ohshima, *J.Phys : Condensed Matter*, 8 (1996) 3229.
11. E.Wicke and G.H.Nernst, *Ber.Bunsenges.Phys.Chem.*, 68 (1964) 224.
12. T.B.Flanagan, W.Luo and J.D.Clewley, *J.Less-Common Met.*, 172-174(1991)42.
13. M.Tkacz and B.Baranowski, *Roczniki Chemii Ann.Soc.Chim.Polonorum*, 50 (1976) 2159.
14. H.Frieske and E.Wicke, *Ber.Bunsenges.Phys.Chem.*, 77 (1973) 48.
15. Y.Arata and Y.C.Zhang, *Proc. Japan Acad.*, 70B (1994) 106.
16. Y.Arata and Y.C.Zhang, *Proc. Japan Acad.*, 71B (1995) 98.

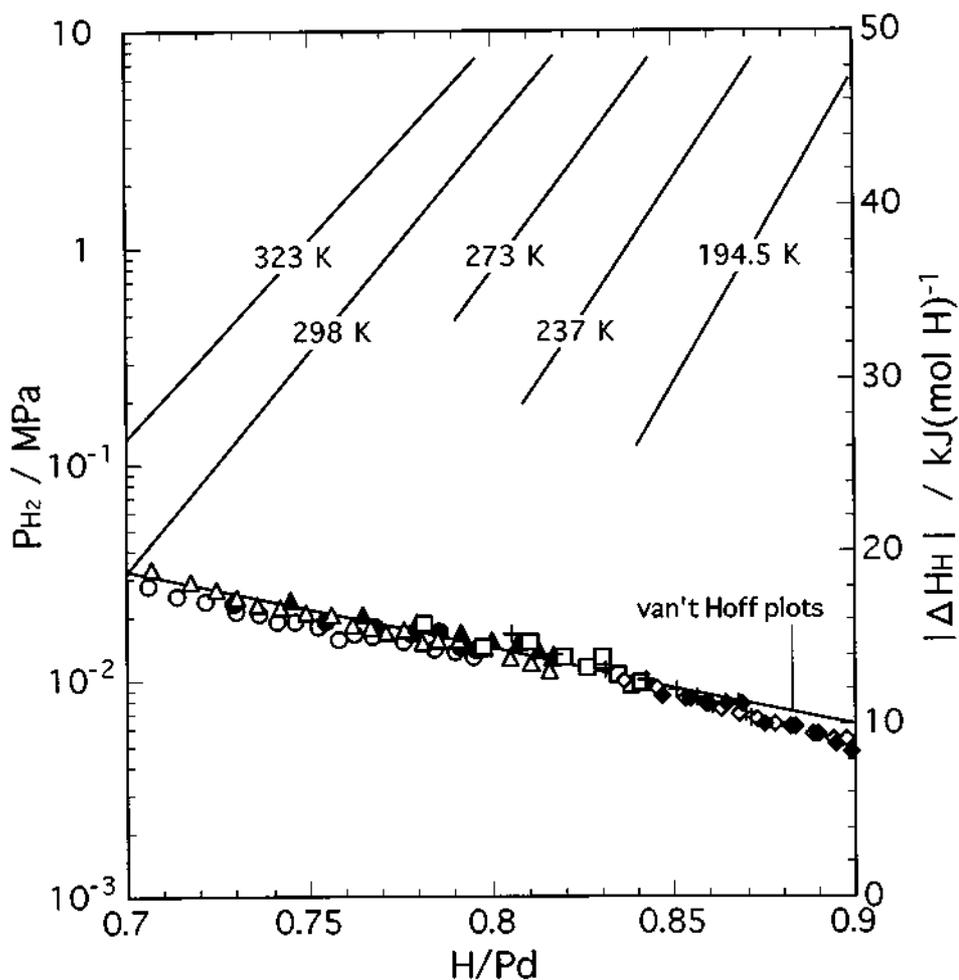


Fig. 1 Calorimetrically determined enthalpies for hydride formation at different temperatures in Pd-H system, together with calculated enthalpies from van't Hoff plots. \circ, \bullet , 323 K, $\triangle, \blacktriangle$, 298 K, \square , 273 K, $+$, 237 K, \diamond, \blacklozenge , 194.5 K (open symbols = absorption, closed symbols = desorption). The p_{H_2} -H/Pd isotherms at each temperature [10,11] are shown in the upper part.

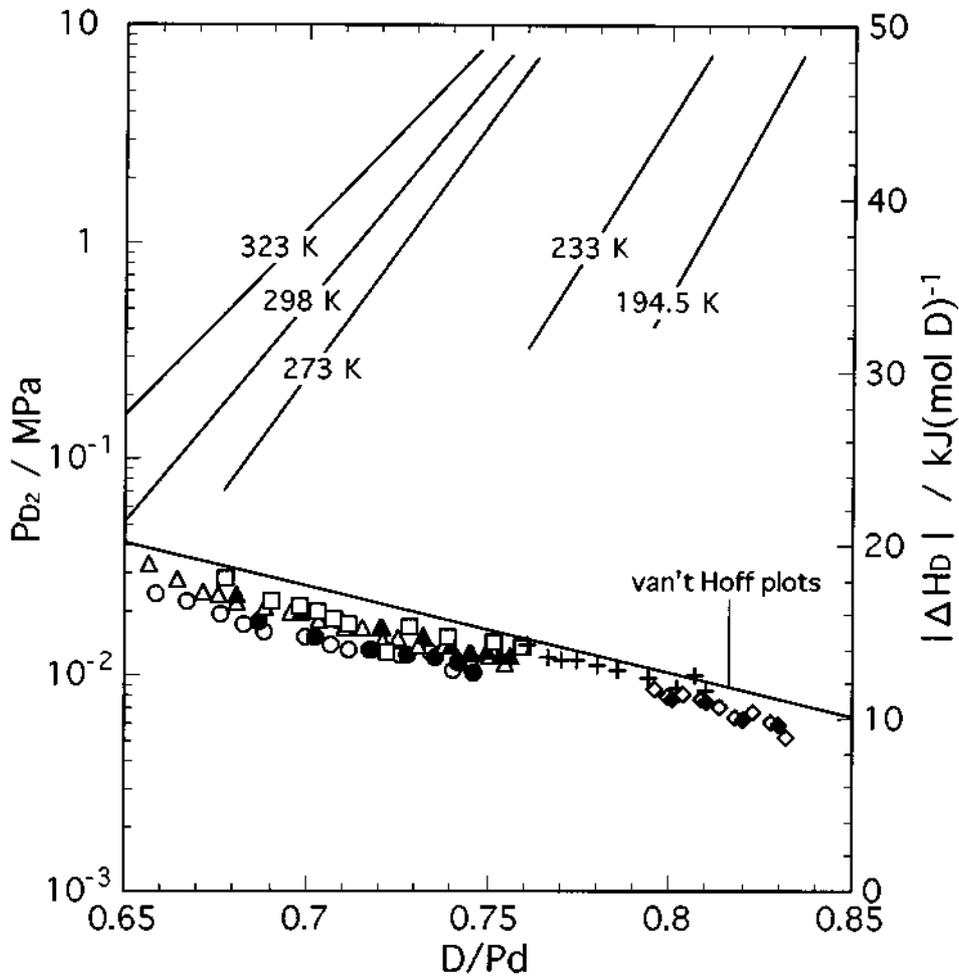


Fig. 2 Calorimetrically determined enthalpies for deuteride formation at different temperatures in Pd-D system, together with calculated enthalpies from van't Hoff plots. \circ, \bullet , 323 K, $\triangle, \blacktriangle$, 298 K, \square , 273 K, $+$, 237 K, \diamond, \blacklozenge , 194.5 K (open symbols = absorption, closed symbols = desorption). The p_{D_2} -D/Pd isotherms at each temperature [10,11] are shown in the upper part.

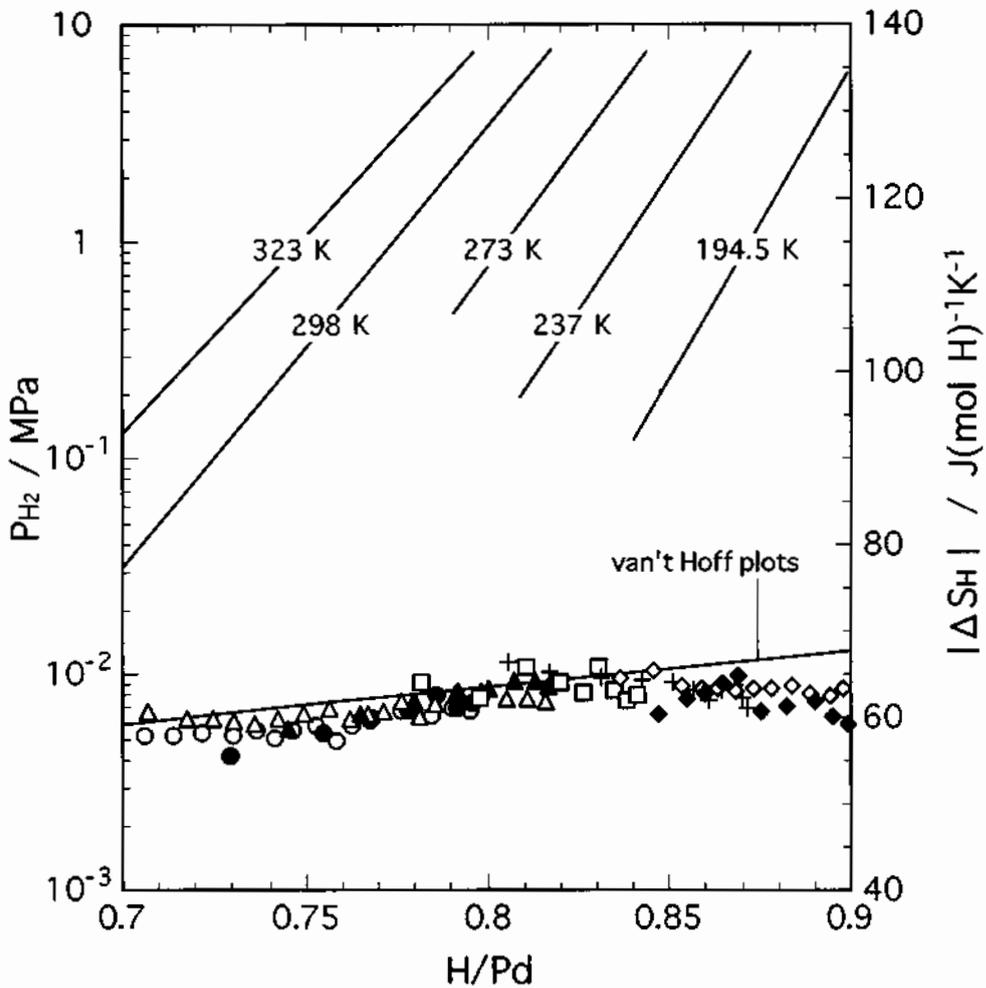


Fig. 3 Relative partial molar entropies for hydride formation at different temperatures in Pd-H system, together with calculated entropies from van't Hoff plots. \circ, \bullet , 323 K, $\triangle, \blacktriangle$, 298 K, \square , 273 K, $+$, 237 K, \diamond, \blacklozenge , 194.5 K (open symbols=absorption, closed symbols=desorption). The p_{H_2} -H/Pd isotherms at each temperature [10,11] are shown in the upper part.

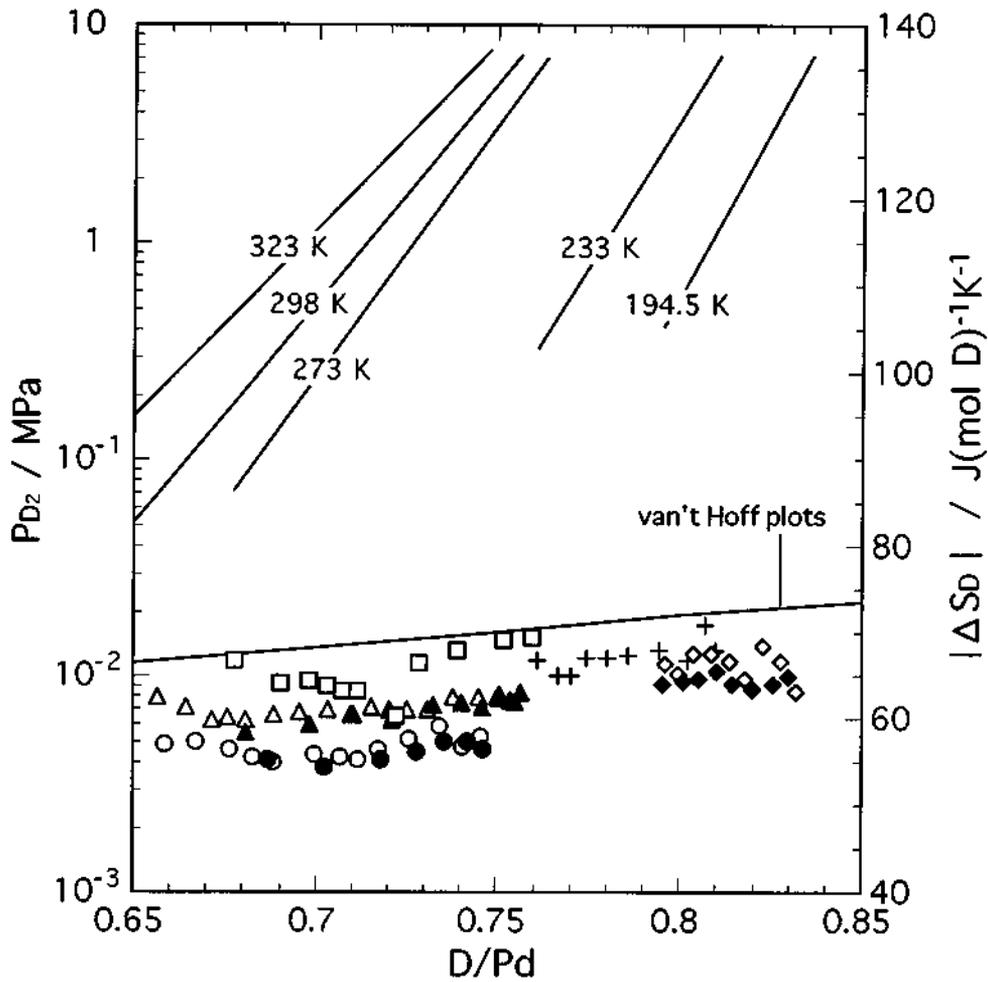


Fig. 4 Relative partial molar entropies for deuteride formation at different temperatures in Pd-D system, together with calculated entropies from van't Hoff plots. \circ, \bullet , 323 K, $\triangle, \blacktriangle$, 298 K, \square , 273 K, $+$, 233 K, \diamond, \blacklozenge , 194.5 K (open symbols=absorption, closed symbols=desorption). The p_{D_2} -D/Pd isotherms at each temperature [10,11] are shown in the upper part.