Solubility Isotherms of Tritium in Palladium at Low Equilibrium Pressures

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The solubility of tritium at low pressures in bulk palladium was analysed again. The gasvolumetric method used, working with only 2 cm³ stp tritium gas, is described. The Sieverts constants obtained obey the following relationship: $\ln K_s = -832/T + 6.243$.

1. Introduction

The phenomenon of hydrogen absorption by metals, discovered about 100 years ago, nowadays demands some interest for technological reasons (hydrogen storage, fuel cells, hydrogen embrittlement of construction materials).

The palladium/hydrogen system claims for an exceptional position among the metal hydrides of the protonic type: because of its relative simplicity the Pd/H_2-system serves as a model revealing some discernible thermodynamic features, that govern the behaviour of those systems.

From measurements of Nernst [1] and Frieske [2] the systems Pd/H_2 and Pd/D_2 are well known, whereas the Pd/T_2-system is widely unknown; from separation factor measurements with traces of tritium [3] in the hydrogen-rich β-phase of the Pd-hydride one can calculate the β-PdT_n isotherms [4]. Direct measurements on the PdT_n-system ($n = T/Pd$) at low tritium pressures were performed by Favreau et al. [5] (temperature region 200 to 400 °C); the results of this research, however, are not in agreement with what can be extrapolated from the PdH_n- and PdD_n-systems, assuming a normal run of the isotope effect.

For this reason and since, because of the known tritium permeation and separation problems (nuclear power plants), the palladium-tritium system may become of particular interest, the solubility of ^3H in Pd at low pressures (1.3 to 50 mbar) and temperatures (25 to 70 °C) was analysed again [6]. For this purpose an apparatus was constructed permitting the exact determination of absorption- and desorption-isotherms with only about 2 cm³ stp of tritium gas.

2. Apparatus and Procedure

The experimental arrangement shown in Fig. 1 is based on a gasvolumetric method. The equipment may be subdivided into three parts: the measuring part, the compensating part und the high vacuum part.

The measuring part consists of a capillary system, thermostated in an air bath, a tritium storage and an absorption vessel. The high purity tritium was stored as uranium-tritid UT_n; T_2-gas, when needed, was generated by thermal decomposition. The absorption vessel was filled with finely divided Cu-powder, working as a catalyst [1] for the transfer of tritium gas into the bulk palladium* embedded in the Cu-powder. The sample was thermostated (±0.1 K) by well stirred silicon oil filled in a double shell basin. The measuring part is separated from the compensating part of the apparatus by the membrane of a differential manometer, working on the capacity of a tuned tank.

The compensating part of the arrangement consists of a thermostated glass jar (volume of 4 liters) as buffer volume connected with silicon oil and mercury manometers. For compensating the tritium pressure in the measuring part there is a further connection to an air inlet needle valve; the compensating part therefore acts as an artificial atmosphere and after equilibration of the tritium absorption/desorption the differential manometer was used as a suppressed zero instrument only.

Measuring and compensating parts could be evacuated and controlled separately by aid of a customary combination of rotary valve pump, mercury vapour pump and penning vacuum gauges (high vacuum part).

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* The Pd-sample (plates of thickness 120 μm and size 20 × 23 mm) was ground with emery-paper, cleaned in acetone and wound on a glass rod.

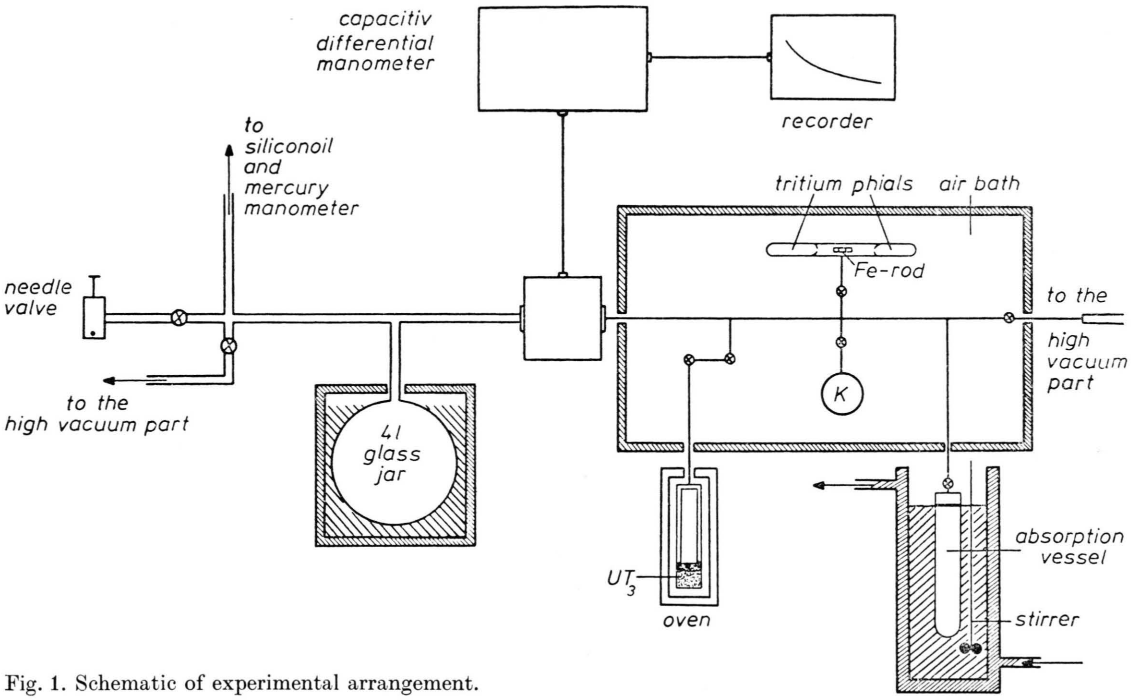

Fig. 1. Schematic of experimental arrangement.

Before starting the measurements, the Cu-powder and the Pd-plate within the reaction vessel were carefully reduced with light hydrogen* (five hours at 1 bar hydrogen pressure and 475 K). The reduction procedure was followed by about ten hours of evacuating; the reduction/evacuation cycle was repeated three times. By this way the oxide layers on Pd and Cu were completely removed.

The solubility of tritium in Pd was measured at constant gas phase volume with varying quantities of tritium and at different temperatures. The particular volumes of the gas phase separated by the stop cocks were calibrated by the aid of a reference volume (K in Fig. 1) of approximately 25 cm³. The tritium gas (2.08 cm³ stp) was furnished from Amersham-Buchler with isotopic composition of more than 98% tritium and less than 2% hydrogen.

3. Evaluation and Results

In Fig. 2 the measured equilibrium pressures are put together as $\sqrt{p_{T_2}}$/n-isotherms. The single values represent mostly "descending n"-measurements (see the direction of the arrow in Fig. 2); in some

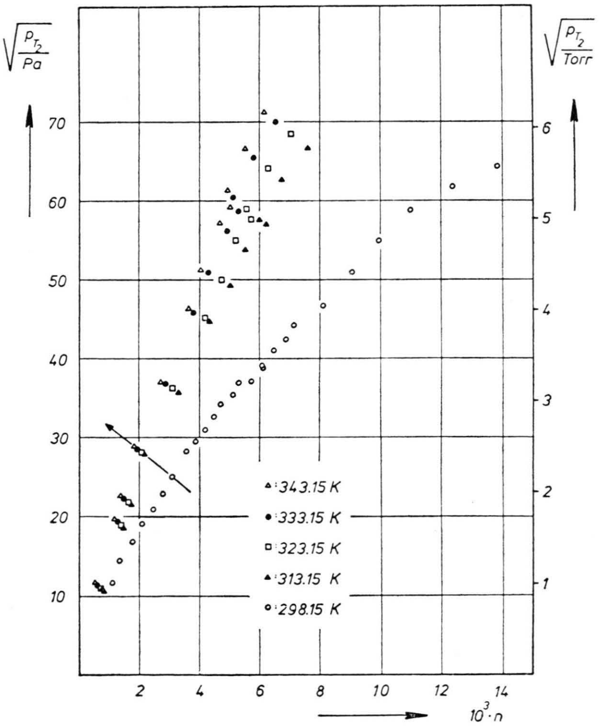

Fig. 2. PdT_n α-phase isotherms.

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* Electrolytically produced hydrogen, purified by diffusion [7] through Palladium.

cases measurements in the opposite direction (decreasing temperature) were performed. At low pressures no hysteresis could be observed; this is in agreement with former experiments [1] in the α-phase (in some distance to the two-phase region) of the PdH_n-system.

In the case of thermodynamic equilibrium the isotherms are implicitely described by:

$$\tfrac{1}{2}\,\mu^0_{T_2} + \tfrac{1}{2}\,RT \ln p_{T_2} = \mu^0_T + RT \ln \frac{n}{1-n} + \Delta\mu_{T^+}(n, T) + \Delta\mu_{e^-}(n) \qquad (1)$$

with $\mu^0_{T_2}$ und μ^0_T the standard potentials in the gas and solid phase and $RT \ln(n/1-n)$ the configurational term of ideal statistical distribution of the dissolved tritium within the Pd-lattice. Deviations from the ideal dissolution are respected by an excess potential $\Delta\mu_T$, firstly discussed for the PdH_n-system by Wagner [8] and split into two terms by Brodowsky [9]:

$$\Delta\mu_T(n, T) = \Delta\mu_{T^+}(n, T) + \Delta\mu_{e^-}(n)\,. \qquad (2)$$

By Eq. (2) the dissociation of tritium into tritons and electrons is taken into consideration; more precisely, the attractive interaction between tritons due to lattice distortions [9] and the effect of Fermi-energy shifts due to band filling by the added electrons [8] are accounted for. The excess potential $\Delta\mu_T(n, T)$ contains the observable deviations from Sieverts [10] law

$$\sqrt{p_{T_2}} = K_S\, n\,, \qquad (3)$$

with

$$K_S = \exp\{-(\tfrac{1}{2}\,\mu^0_{T_2} - \mu^0_T)/RT\}\,. \qquad (4)$$

From Eqs. (1) and (4) one obtains

$$\ln\left\{\frac{p_{T_2}}{n^2}\,(1-n)^2\right\} = 2 \ln K_S + \frac{2\Delta\mu_{T^+}(n, T)}{RT} + \frac{2\Delta\mu_{e^-}(n)}{RT}\,. \qquad (5)$$

As is well known from measurements with H_2 and D_2 [1] the excess potentials $\Delta\mu_{T^+}(n, T)$ as well as $\Delta\mu_{e^-}(n)$ show proportionality with n for small hydrogen contents. The plot of the left hand side of Eq. (5) over n therefore yields straight lines (Fig. 3, referred to 1 Pa hydrogen pressure) intersecting the ordinate at $2 \ln K_S$.

The enthalpy and entropy of desorption follow from the temperature dependence of the Sieverts constant after

$$2 \ln K_S(T) = -\frac{\Delta H^0_{T_2}}{RT} + \frac{\Delta S^0_{T_2}}{R} \qquad (6)$$

(see Fig. 4, referred to 1 Pa hydrogen pressure) with $\Delta H^0_{T_2}$ and $\Delta S^0_{T_2}$ the standard desorption enthalpy and entropy for the tritium. From the entropy of desorption the entropy of the dissolved tritium can be evaluated:

$$S^0_T = \tfrac{1}{2}\,S^0_{T_2} - \tfrac{1}{2}\,\Delta S^0_{T_2}\,, \qquad (7)$$

whereby the entropy of the gaseous tritium is 153.4 J/K mole T_2 [11]. The value for S^0_T comprehends essentially the oscillation of the tritons in the octahedral steady positions; a small portion traced back to elastic and electronic (opposite signs) contributions may be neglected. Assuming local modes for the dissolved tritons, the frequency for the tritons may be estimated with Planck-Einstein functions.

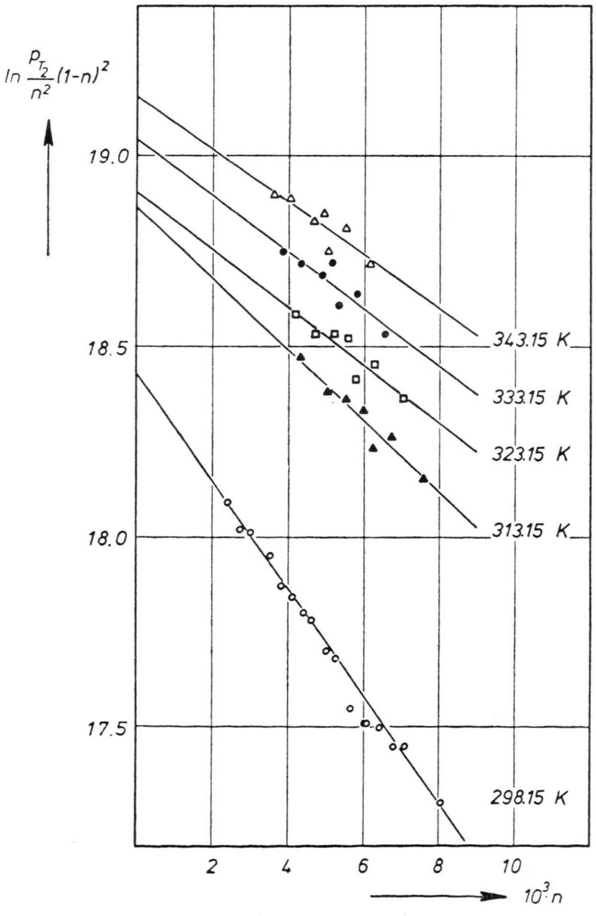

Fig. 3. Straight lines $\ln\left\{\frac{p_{T_2}}{n^2}\,(1-n)^2\right\}$ vs · n.

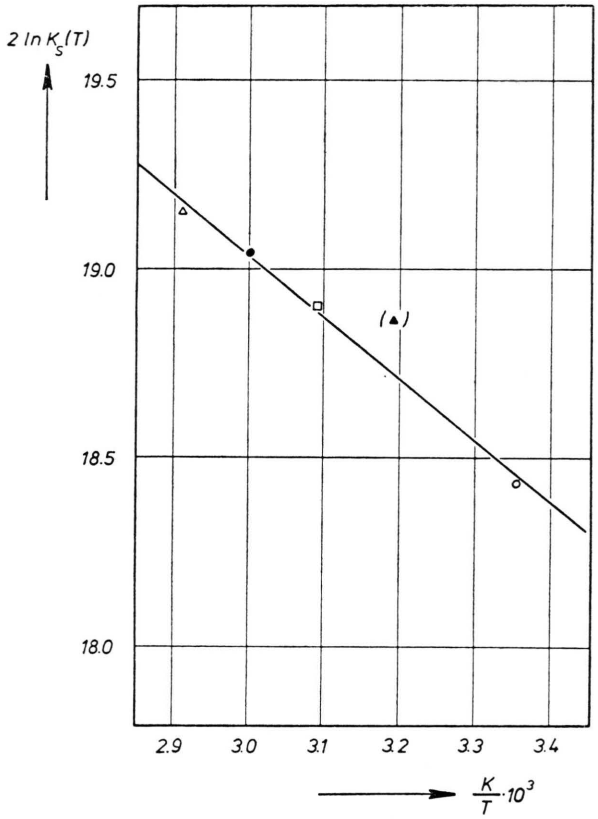

Fig. 4. α-PdT_n Van't Hoff plot.

In the following table the thermodynamic data for the Pd/T-system are compared with those for the systems Pd/D and Pd/H.

The values for H and D in Pd are taken from Wicke and Nernst [1] indexed (i) and Brodowsky and Poeschel [12] indexed (ii). The Sieverts constants for normal temperature are related to 1 bar hydrogen pressure.

Because of the contamination of the tritium with about 2% of light hydrogen the measured p, n equilibrium values were corrected in a first order approximation, taking into account the equilibrium distribution of the isotopes between the solid phase and the gas [3]. The Figs. 2–4 as well as the table represent results involving these corrections. Neglecting the hydrogen impurity the Sieverts constant e.g. would turn out with a value 8% higher than that given in the Table 1.

4. Discussion

As can be seen from the table, the solubility of the hydrogen isotopes — expressed as $1/K_S$, cf. Eq. (3) — is lowered going from H, D to T. This phenomenon (inverse isotope effect) is well understood: because of the flat potential well around the dissolved hydrogen isotopes in their octahedral steady state positions, compared with the steep ones of the diatomic molecules, the difference between the zero point vibration energies in the gaseous and dissolved states diminishes with increasing isotope mass; the desorption enthalpy therefore is lowered in the same direction.

Table 1. Thermodynamic data of α-phase Pd-hydrides.

		H	D	T
K_S (298)	(i)	12.67	24.61	31.57
	(ii)	12.36	23.92	
ΔH^0_{XX}	(i)	19340	15780	13830
[J/mole XX]	(ii)	18840	15715	
ΔS^0_{XX}	(i)	107.1	106.2	103.8
[J/K mole XX]	(ii)	105.0	105.5	
S^0_X	(i)	11.75	19.35	24.75
[J/K gat]	(ii)	12.80	19.70	
ν_X	(i)	$12.9 \cdot 10^{12}$	$8.8 \cdot 10^{12}$	$6.9 \cdot 10^{12}$
[s^{-1}]	(ii)	$12.3 \cdot 10^{12}$	$8.8 \cdot 10^{12}$	

From the normal run of the partial desorption entropy local vibration frequencies are derived that approximately obey the relation $\nu_X \sim 1/\sqrt{m_X}$ with m_X the isotopic mass ($\nu_H/\nu_D \approx 1.43$; $\nu_H/\nu_T \approx 1.82$). The nearly constant values for $\nu_X \sqrt{m_X}$ (about $5.1 \cdot 10^{-14}\ N^{1/2}\ cm^{-1/2}$) indicate likewise constant and harmonic potential wells for the three isotopes in Pd. After Brodowsky [9] the excess potential $\Delta\mu_X^{+}$ (Eq. (2)) pays regard to the lattice distortions caused by the hydrogen uptake; this leads to lattice-induced attractive forces between the dissolved hydrogen atoms and to an exothermic formation of XX-pairs in neighbour octahedral positions of the Pd-matrix. Because of the higher zero point vibration energy of the light hydrogen compared with deuterium, the formation of HH-pairs is favoured (ε_{HH}: -2810 [9] to -3175 [13] J/mole HH; ε_{DD}: -2730 [9] to -3100 [13] J/mole DD). For the same reason the pair formation tendency should be lowest in the case of dissolved tritium.

As mentioned above, the measurements were carried out with tritium gas containing about 2% of light hydrogen; with this T_2/HT-mixture an atomic fraction of about 0.05 of light hydrogen in the solid state was adjusted, due to an equilibrium separation factor of about 2.7 at normal temperature [3]. As far as the Sieverts constant is concerned the first order correction mentioned in Chapt. 3, taking into account the isotopic impurity, works in a satisfactory manner. The deviations from Sieverts law, however, are influenced by the presence of the light hydrogen in a more complicated "mixed phase behaviour"; the contamination of the solid phase with about 5% H weighted with a stronger lattice distortion than in case of T may dominate the non-idealities of the system. We therefore renounce any evaluation of the run of $\Delta\mu_T^+$ with tritium content and temperature or even the pair interaction energy $\varepsilon_{\mathrm{TT}}$.

5. Conclusions

It is demonstrated that the tritium solubility in the Sieverts law region is relatively easy to determine. On the other hand, it must be noted that the isotopic purity of the tritium gas is too poor to get correct information about the non-idealities of metal-tritide systems.

Especially for the purpose of verifying the triton excess potential by the pair interaction model [9] approved for the palladium-hydrogen system, tritium of higher purity is needed. Because of sometimes surprising isotope effects with metal hydrides [3, 14] not yet cleared up in detail, it seems desirable to supplement the research in that field by systematic measurements with tritium.

Acknowledgements

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