272
3/4/82
JB

I-1265

(1)

Ni. 251

DECEMBER 1981

PPPL-1862
UC-20c,f

25

MASTER

MEASUREMENTS OF H_2, D_2 SOLUBILITIES IN Zr-Al

BY

R.J. KNIZE, J.L. CECCHI, AND
H.F. DYLLA

PLASMA PHYSICS LABORATORY

PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY

This work was supported by the U.S. Department of Energy Contract No. DE-AC02-76-CHO 3073. Reproduction, translation, publication, use and disposal, in whole or in part, by or for the United States government is permitted.

Measurement of H_2, D_2 Solubilities in Zr-Al

R.J. Knize, J.L. Cecchi, and H.F. Dylla

Plasma Physics Laboratory
Princeton University
Princeton, New Jersey 08544

PPPL--1862
DE82 010[illegible]27

ABSTRACT

We have measured solubility constants for hydrogen and deuterium in the Zr-Al alloy to be: $K_H = \exp(11.1(5) - 16900(600)/T)$ (Torr/[Torr-l/g]^2) and $K_D = \exp(12.2(8) - 16800(600)/T)$ (Torr/[Torr-l/g]^2) respectively, where is defined implicitly by $P = Kq^2$ with P the equilibrium pressure (in Torr) and q the bulk concentration (in Torr-ℓ/g). These values, in conjunction with a model for the solubility, predict that the constant for tritium, $K_T \sim 4\ K_H$. Consequently, the regeneration of tritium will be faster by a factor of four over that for hydrogen at the same temperature, or the tritium regeneration temperature can be reduced ~ 50°K compared to hydrogen for the same regeneration time.

I. INTRODUCTION

To attain the most favorable operating regimes for the Tokamak Fusion Test Reactor (TFTR), it is essential that both impurities and hydrogenic recycling be controlled.[1] This will be facilitated by a Zr-Al non-evaporable bulk getter system which pumps hydrogen isotopes reversibly and impurities (C,N,O) irreversibly.[2] The getter utilizes the alloy ST 101® (84% Zr - 16% Al)[3] in the form of a powder press bonded to a constantan heating substrate. The pump is activated (following an air exposure) by heating to 700°C for 45 minutes to diffuse surface impurities (C,N,O) into the bulk. During normal operation a temperature of 200° - 400°C is maintained, which provides adequate hydrogenic and (steady state) impurity diffusion.

When the hydrogenic concentration approaches the embrittlement limit of 20 Torr-l/g, or the tritium concentration exceeds the allowable in-vessel limit, the hydrogenic species are desorbed by heating the getter to 600° - 700°C. Knowledge of the hydrogenic solubilities is important to this phase of operation in determining the bulk hydrogenic concentration (in conjunction with equilibrium pressure measurements) as well as the kinetics of the desorption.[4]

In Sec. 2 we present measurements of hydrogen and deuterium solubilities in Zr-Al for a range of temperatures (750°-1050°K). The observed isotopic difference in the solubilities is ascribed to atom-lattice vibration effects based upon a model discussed in Sec. 3. This model is used in Sec. 4 to predict the tritium solubility and the associated differences in desorption rates. Our results are summarized in Sec. 5.

II. MEASURED HYDROGEN AND DEUTERIUM SOLUBILITIES

The solubility of a hydrogenic species in a metal has been defined in a variety of ways.[5] Our measurements will be expressed as the constant of proportionality K between the equilibrium pressure P and the square of the hydrogenic concentration in the metal q:

$$P = Kq^2. \qquad (1)$$

Implicit in Eq. (1) is the fact that hydrogenic molecules dissociate following surface adsorption. The factor K is a function of temperature T and is equal to the ratio k_o/k_i where k_o is the rate of desorption and k_i the rate of adsorption for the reaction.

$$H_2 + 2\,(\mathrm{ZrAl}) \underset{k_o}{\overset{k_i}{\rightleftarrows}} 2\,(\mathrm{ZrAl\text{-}H})\ . \qquad (2)$$

The relationship between the equilibrium hydrogen and deuterium pressure and the concentration was measured using the apparatus shown schematically in Fig. 1. All measurements were performed on the same getter module which was of standard size with a Zr-Al mass of 120 g. The getter temperature was measured with three thermocouples and an IRCON-300 Infrared Radiation Thermometer. These measurements showed that the temperature was uniform throughout the getter with a drop of ~ 15°C at the extreme ends. Figure 2 shows the observed relationship between the hydrogen pressure and q for a variety of temperatures. As shown in the figure, the data can be fit to Eq. (1) from which K is determined. The results of repeated sets of measurements are summarized in Fig. 3 and 4 for hydrogen and deuterium, respectively, over the temperature range 750° - 1050°K.

The constants which are derived from the pressure/concentration data can be expressed in Arrehnius/forms: $K_H = \exp(11.5(1) - 16900(600)/T)$ (Torr/[Torr-l/g]^2) for hydrogen and $K_D = \exp(12.2(8) - 16800(600)/T)$ (Torr/[Torr-l/g]^2) for deuterium. Previous measurements,[6] which have been made for hydrogen, are in good agreement with our results.

III. SOLUBILITY MODEL

From the measured values of K the thermodynamic properties of the reaction in Eq. (2) can be determined.[7] The free energy change ΔG is related to the enthalpy change ΔH and entropy change ΔS by the equation:

$$\Delta G = \Delta H - T\Delta S. \tag{3}$$

ΔG, in turn, can be expressed in terms of the constant K as

$$\Delta G = -RT \ell n\ K, \tag{4}$$

where R is the universal gas constant. Combining the value of K_H with Eqs. (3) and (4), we calculate an enthalpy change of $\Delta H = -16$ kcal/mole and an entropy change $\Delta S = 7.4$ e.u. The signs of these thermodynamic functions reflect the fact that the getter is an exothermic absorber with an increasing entropy with absorption. In comparing these numbers to measurements for pure elements[8] such as Zr or Ti, there is a notable difference. ΔH for Zr-Al is nearly equal to the measured values for Zr and Ti but the entropy change is only half as large. This smaller value of ΔS for the alloy results in a relatively large K, and consequently, regeneration of the getter can be effected in a short time.

Using the statistical mechanical model of McLellan,[8,9] we can express the ratio of K_i for hydrogenic isotope i to K_H as

$$\ell n\,(K_i/K_H) = \frac{5}{2}\,\ell n\,M_i + \ell n\,\left\{\frac{1-\exp\,(-\theta/T)}{1-\exp\,(-\theta/\sqrt{M_i}\,T)}\right\}$$

$$+\,6\,\left[\left\{\frac{\theta'/T}{\exp(\theta'/T)-1} - \frac{\theta'/\sqrt{M_i}T}{\exp(\theta'/\sqrt{M_i}T)-1}\right\}\right.$$

$$\left. -\,\ell n\,\left\{\frac{1-\exp\,(-\theta'/T)}{1-\exp\,(-\theta'/\sqrt{M_i}T)}\right\}\right] \qquad (5)$$

where M_i is the mass of isotope i, θ is the vibration temperature of a free hydrogen molecule (θ = 6140°K) and θ' is the vibration temperature of a hydrogen atom in the lattice. From the experimental data for K_H and K_D we calculate that θ' = 3700 ± 400°K. This vibration temperature can be used to estimate the pre-exponential factor D_o in the diffusivity ($D = D_o \exp\,[-E/RT]$) by the Zener approximation:[10]

$$D_o \approx a^2 \nu\ , \qquad (6)$$

where a is the lattice spacing and ν is the vibration frequency. Our estimate of $D_o \approx 0.1$ cm^2 s^{-1} is in good agreement with the measured value.[11]

IV. TRITIUM SOLUBILITY

Using the model of Sec. III and the hydrogen vibrational temperature in the Zr-Al lattice determined from the H and D experiments we calculate that for tritium, $K_T \approx 4\ K_H$. The salient consequence of this calculation is that the regeneration time for tritium will be less than that for hydrogen at the same regeneration temperature. The regeneration time τ is given by[12]

$$\tau = \alpha^{-1} \left(\frac{1}{q_f} - \frac{1}{q_i}\right) \tag{7}$$

where q_f and q_i are the final and initial hydrogenic concentrations, respectively, and α = SK/M with S being the back-up pumping speed and M the getter mass. Thus the tritium regeneration time would be 1/4 of that for hydrogen.

Equivalently, for a fixed regeneration time, the required temperature will be less for tritium as compared to hydrogen. For example, if a particular hydrogen regeneration scenario required a 873°K temperature, the corresponding temperature for tritium would be ~ 813°K. This would ameliorate the problem of the thermal load on the TFTR vacuum vessel during regeneration.

V. SUMMARY

We have measured the solublity constants for hydrogen and deuterium (K_H and K_D) in Zr-Al over the temperature range of 750° - 1050°K. Our value for K_H agrees with previous measurements. The result for K_D is ~ $3K_H$. Using the model of McLellan we derive a hydrogen/Zr-Al vibrational temperature θ' = 3700 ± 400°K. The diffusivity pre-exponential factor inferred from θ' agrees with other measurements. The calculated value for tritium is $K_T \sim 4K_H$ which predicts shorter regeneration times or lower regeneration temperatures for tritium as compared with hydrogen.

ACKNOWLEDGMENTS

We wish to thank E. Pinelli, T. Provost, and F. Egan for their excellent technical support. This work was supported by the Department of Energy Contract Number DE-AC02-76-CHO-3073.

REFERENCES

1. J.L. Cecchi, J. Nucl. Mater. 93 & 94, 28, (1980).

2 B. Ferrario, and L. Rosai, Proc. 7th Intern. Congr. & 3rd Intern. Conf. Solid Surfaces (International Atomic Energy Agency, Vienna, 1977) 359.

3. The Zr/Al getter is manufactured by SAES Getters, S.P.A., Milan, Italy.

4. R.J. Knize, J.L. Cecchi, and H.F. Dylla, J. Nucl. Matter. to be published.

5. See, for example: Scientific Foundations of Vacuum Technique, S. Dushman, and J.M. Lafferty, Eds. (Wiley, New York, 1962) 517 and W.G. Perkins, J. Vac. Sci. Technol. 10, 543 (1973).

6. L. Rosai, B. Ferrario, and P. della Porta, J. Vac Sci. Technol. 15, 746 (1978).

7. B.H. Mahan, University Chemistry, (Addison-Wesley, Reading, Mass., 1965), 301.

8. R.B. McLellan, and C.G. Harkins, Materials Science and Engineering, 18, 5 (1975).

9. R.B. McLellan in Phase Stability in Metals and Alloys, P.S. Rudman, J. Stringer, and R.I. Jaffee, eds., (McGraw Hill, New York, 1966) 393.

10. C. Wert and C. Zener, Phys. Rev., 76, 1169 (1949).

11. R.J. Knize and J.L. Cecchi, to be published.

12. J.L. Cecchi, S.A. Cohen, and J.J. Sredniawski, J. Vac. Sci. and Technol. 17, 294 (1980).

FIGURE CAPTIONS

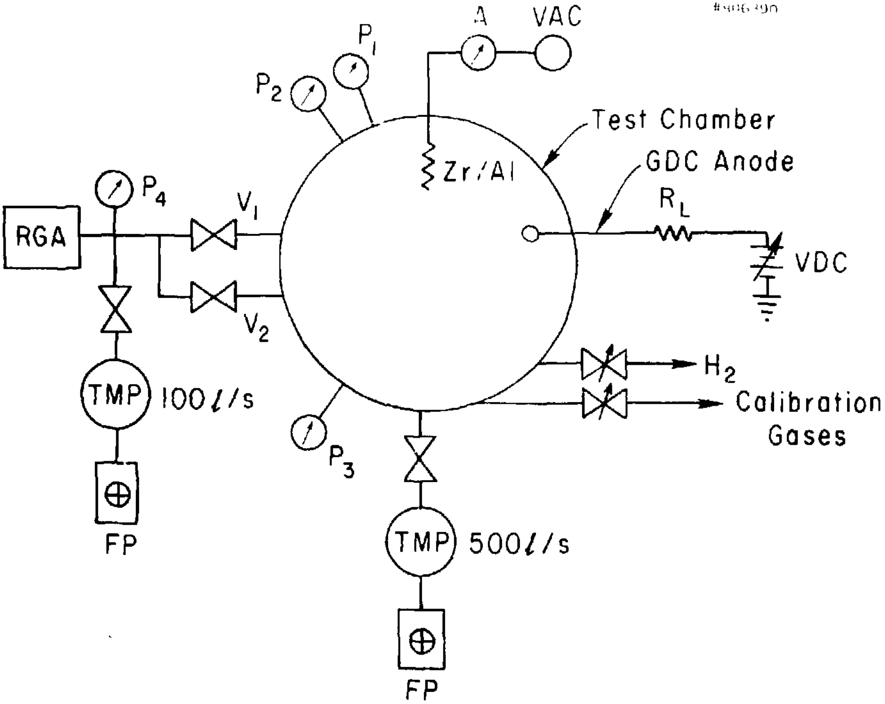
Fig. 1 Schematic diagram of the apparatus. The 107 liter test chamber contains a Zr-Al getter module and can also be pumped by a nominal 500 l/sec turbomolecular pump whose measured H_2 speed is 300 l/sec. H_2 influx rates are controlled by a piezoelectric valve (Veeco type PV-10) and monitored by measurement of the pressure differential across a molecular flow orifice (MKS type FE 1.0). Total pressure measurements are made using (1) a nude Bayard-Alpert gauge, (2) a nude triode gauge, and (3) a capacitance manometer (MKS type 310). Partial pressure measurements are made with a quadrupole residual gas analyzer (RGA).

Fig. 2 Equilibrium pressure P as a function the hydrogen loading q and alloy temperature T. The data follows Sievert's expression $P = Kq^2$.

Fig. 3 Hydrogen equilibrium constant K_H as a function of alloy temperature T.

Fig. 4 Deuterium equilibrium constant K_D as a function of alloy temperature T.

#806390



A
VAC
P_1
P_2
Test Chamber
Zr/Al
GDC Anode
R_L
VDC
P_4
RGA
V_1
V_2
H_2
Calibration Gases
TMP
100 ℓ/s
FP
P_3
TMP
500 ℓ/s
FP

Fig. 1

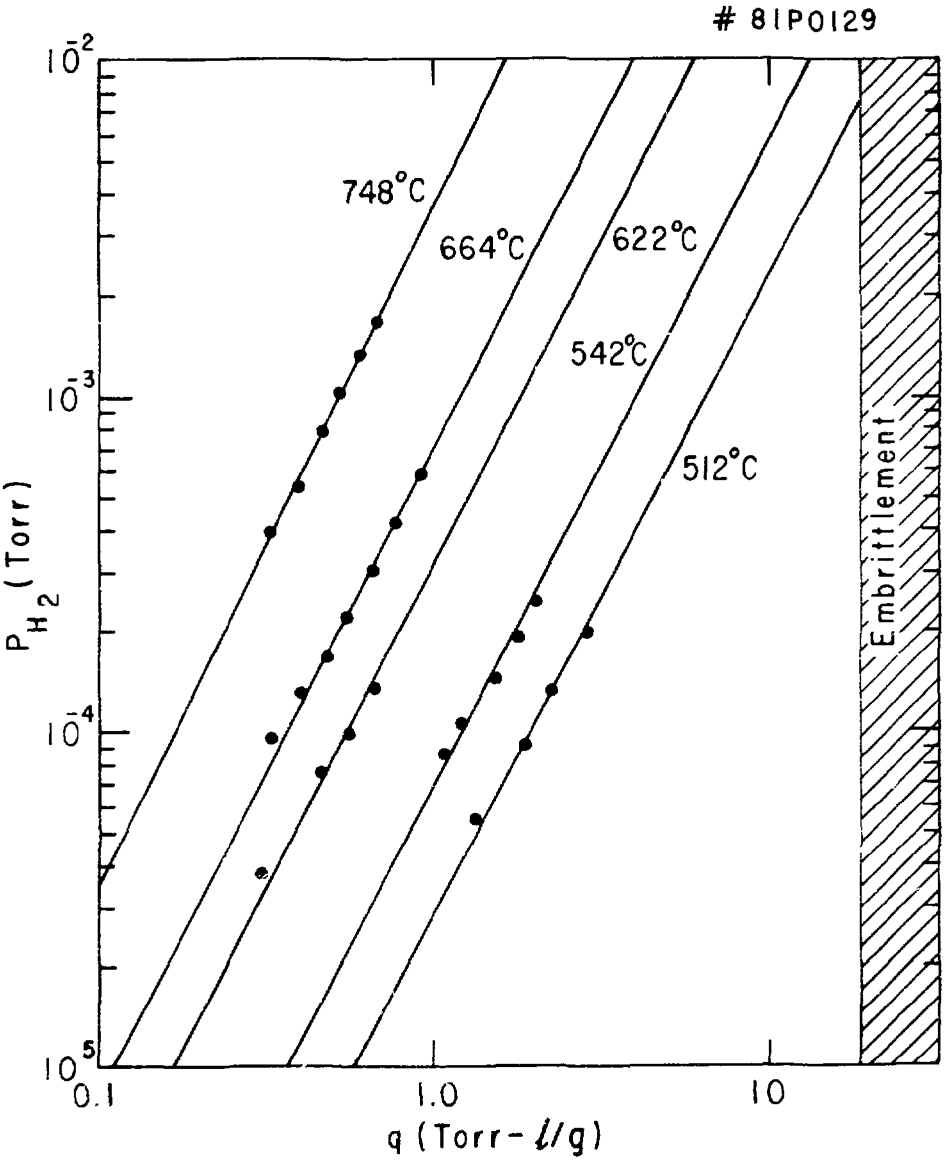

81P0129
10^{-2}
10^{-3}
10^{-4}
10^{5}
P_{H_2} (Torr)
748°C
664°C
622°C
542°C
512°C
Embrittlement
0.1
1.0
10
q (Torr-ℓ/g)

Fig. 2

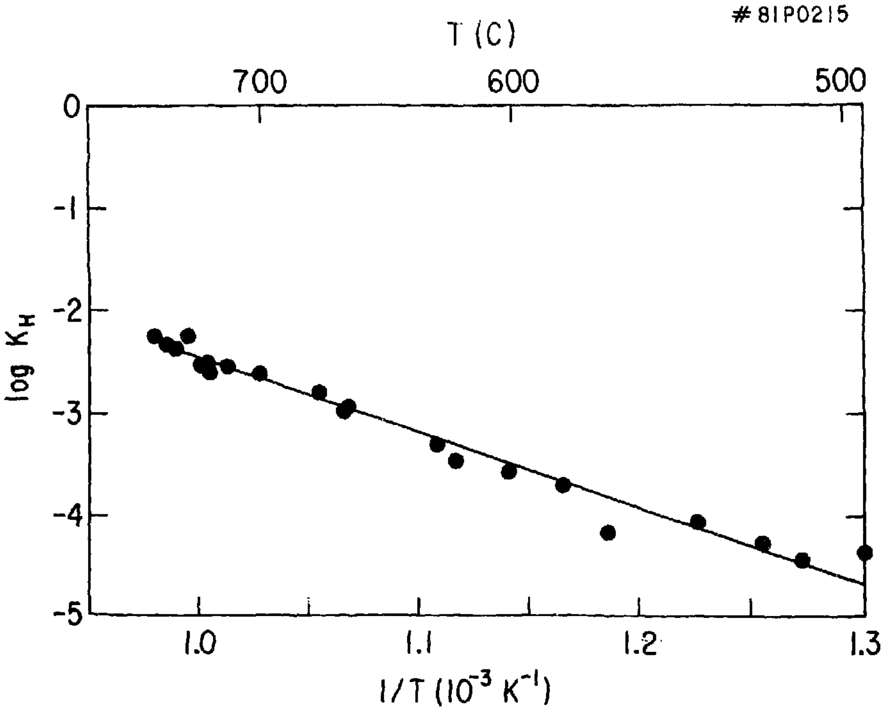


Fig. 3

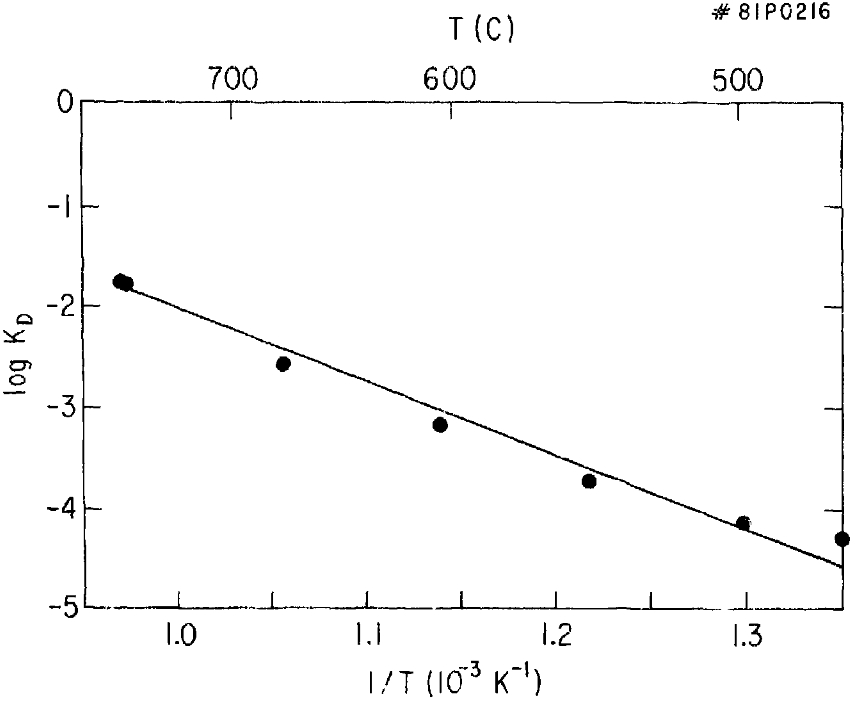


Fig. 4