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Empirical Correlation of Equilibrium Separation Factors in the Pd−H_2/D_2 System with Temperature and Composition

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The range of available data on separation factors (α) in the palladium−hydrogen/deuterium system has been extended in this study using a thermal conductivity detector. The thermal conductivity detector employed a matched pair of glass-coated bead thermistors to measure the gas-phase composition of hydrogen isotope mixtures. Separation factors (α) were measured in the β-phase, over the temperature (T) and hydrogen mole fraction (x_H) ranges $T = 175$ K to 389 K and $x_H = 0.195$ to 0.785, respectively. These data were correlated with temperature (T) and hydrogen mole fraction in the palladium (x_H) by $\alpha = \exp[-0.27 + B(x_H)(1000/T)^{0.75}]$ and $B(x_H) = 0.5155 - 0.0569x_H - 0.12x_H^2$, where $B(x_H)$ is an empirical function relating the dependence of the separation factor on composition.

Introduction

The separation factor α is a quantitative measurement of the thermodynamic isotope effect as described by Andreev et al. (1996). It is defined as the ratio of heavy to light isotope mole fractions in the gas phase divided by that ratio in the solid phase. In the present context, this definition becomes

$$\alpha \equiv \frac{y_D/x_D}{y_H/x_H} \tag{1}$$

where y_i are mole fractions in the gas phase and x_i are mole fractions in the solid phase.

Several investigators (Andreev et al., 1978; Botter et al., 1965; Fukada et al., 1995; Glückauf and Kitt, 1957; Ortiz, 1998; Thomas and Smith, 1958; Wicke and Nernst, 1964) have measured separation factors in the palladium−hydrogen/deuterium system. Wicke and Brodowsky (1978) also presented a thermodynamic solid solution model. This thermodynamic model helps provide a better understanding of why separation occurs, and is presented here as an introduction.

According to Wagner (1944), the chemical potential of hydrogen in an ideal solid solution may be written as

$$\mu_H = \mu_H^\circ + RT \ln\left(\frac{n}{1-n}\right) \tag{2}$$

where n is the atomic ratio (H/Pd) of hydrogen in the solid phase and μ_H° is the standard chemical potential. For equilibrium between the solid and gas phases, the chemical potential of the hydrogen atom in the palladium must equal one hydrogen in the gas

$$\mu_H = \frac{1}{2}\mu_{H_2} = \frac{1}{2}\mu_{H_2}^\circ + \frac{1}{2}RT \ln(p_{H_2}) \tag{3}$$

where p_{H_2} is the pressure of hydrogen in the gas phase. Introducing Sievert's constant

$$K_H = \exp\left(\frac{\mu_H^\circ - \frac{1}{2}\mu_{H_2}^\circ}{RT}\right) \tag{4}$$

and combining eqs 2−4 yields

$$\ln\sqrt{p_{H_2}} = \ln\left(K_H\frac{n}{1-n}\right) \tag{5}$$

The temperature dependence on Sievert's constant is determined using

$$K_H = \exp\left(-\frac{\Delta H^\circ}{2RT} + \frac{\Delta S^\circ}{2R}\right) \tag{6}$$

where ΔH° is the molar standard enthalpy and ΔS° is the molar standard entropy of desorption. Applying eq 5 for both H and D at the same value of n yields

$$\ln\left(\frac{p_{D_2}^\circ}{p_{H_2}^\circ}\right) = 2\ln\left(\frac{K_D}{K_H}\right) \tag{7}$$

where the pressure superscripts indicate constant n. The separation factor (eq 1) can be rewritten using partial pressures as

$$\alpha = \frac{(2p_{D_2} + p_{HD})/(2p_{H_2} + p_{HD})}{x_D/x_H} \tag{8}$$

Replacing p_{HD} by means of the exchange equilibrium

$$\frac{1}{2}H_2 + \frac{1}{2}D_2 \leftrightarrow \text{HD:}\quad K_{HD} = \frac{p_{HD}}{\sqrt{p_{D_2}p_{H_2}}} \tag{9}$$

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and using $K \approx 2$ (true values around 1.8) gives

$$\alpha = \frac{(p_{D_2} + \sqrt{p_{H_2}p_{D_2}})/(p_{H_2} + \sqrt{p_{H_2}p_{D_2}})}{x_D/x_H} = \frac{\sqrt{p_{D_2}/p_{H_2}}}{x_D/x_H} = \sqrt{p^\circ_{D_2}/p^\circ_{H_2}} = \frac{K_D}{K_H} \quad (10)$$

Using the temperature dependence of Sievert's constant (eq 6) gives

$$\ln \alpha = \frac{\Delta H^\circ_H - \Delta H^\circ_D}{2RT} + \frac{\Delta S^\circ_D - \Delta S^\circ_H}{2R} = \frac{A}{T} + B \quad (11)$$

where A and B are constants.

However, in the β region of the palladium–hydrogen phase diagram, hydrogen exists not as a dissolved species but as a combined species (Santandrea and Behrens, 1986). Furthermore, proportionality laws such as Sievert's and Henry's laws are strictly valid only as the solute approaches infinite dilution (Denbigh, 1981). Therefore, this model (eq 11) may not be valid in the β phase. Andreev et al. (1996) allude to this by mentioning that "a variety of forms" have been proposed for relating the mole fractions of isotopes in the solid phase to their partial pressures in the gas phase. Fukada et al. (1995) also noted "appreciable discrepancies" exist in the literature on the temperature–separation factor correlation. Nonetheless, Wicke and Brodowsky (1978) reported that the elastic contribution to nonideal behavior related to the attractive interactions between H and D atoms in the lattice results in a functional form of the dependence of separation factor on temperature similar to that of eq 11.

This study was undertaken to extend the range of data on palladium–hydrogen/deuterium separation factors and reduce uncertainties. These measurements were conducted using a thermal conductivity detector to measure gas compositions over a packed bed of palladium powder. The thermal conductivity technique was chosen in order to avoid taking gas samples out of the system for analysis. The thermal conductivity detector has the additional advantages of being relatively inexpensive and capable of measuring a mole fraction difference as small as 0.002. We believe this accuracy has provided measured separation factors with uncertainties of about ±2%.

Apparatus

A bed of compacted palladium powder weighing 50.55 g was used in this study to achieve isotopic separation. The palladium had a specific surface area of 1.0 m^2/g and the void volume of the bed was 6.91 cm^3. The bed was placed inside a Despatch 936 E environmental chamber and connected by high-pressure tubing to the thermal conductivity detector and the metal bellows pump, as illustrated in Figure 1.

The reference side of the thermal conductivity detector was filled with hydrogen (99.9985%) from Air Products and Chemicals Corp. The test side was filled with isotope mixtures prepared by Scott Specialty Gases to nominal mole percents of 20%, 40%, 60%, and 80% H_2. All quoted isotope percentages in this paper are mole percentages. Gas introduced into the test side was circulated using a Senior Flexonics MB 601 metal bellows pump in order to bring the reaction to equilibrium quickly (generally equilibrium was reached within 3 min). A Julabo F33-HD oil bath controlled gas temperatures to within ±0.03 °C. Bed temperature was measured within ±0.5 °C using an Omega type K thermocouple fed through the door of the environmental chamber. Gas pressure was measured using a Heise 901B transducer within 0.05%.

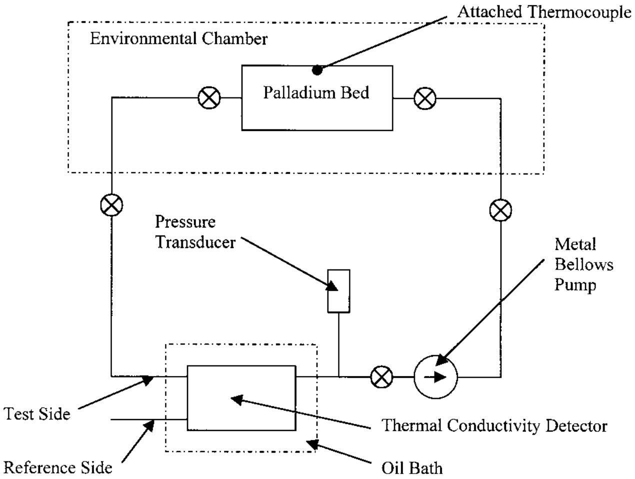

Figure 1. Schematic of experimental apparatus.

The bridge circuit for the thermal conductivity detector used in this study is discussed in detail by Ortiz (1998) and follows the example of Yabsley and Dunlop (1975). All measurements of bridge balance resistance were made with the valves on either side of the palladium bed closed to ensure a static system. Having a static system is necessary, since gas flow will change the heat-transfer rate from the thermistors and thereby alter the temperature (resistance required to balance the bridge).

Procedure

A calibration curve relating balance resistance and protium mole fraction was generated using gas mixtures of protium and deuterium with the following mole fractions of protium: 0.000, 0.195, 0.397, 0.591, 0.785, and 0.9999. This calibration curve was used to confirm the gas composition and the stability of the setup prior to data collection. The bed temperature was then set, and the gas was circulated in the counterclockwise direction, as shown by the arrow inside the pump symbol in Figure 1. Circulation times were between 1 and 3 min; after each circulation cycle the bridge was balanced and the value of the balance resistance was recorded in order to verify equilibrium.

Results and Discussion

In this study separation factors were measured for four different gas mixtures purchased from Scott Specialty Gases: 19.5%, 39.7%, 59.1%, and 78.5% total H. These data are presented in Figure 2 and tabulated in Tables 1–4. The correlation (eq 12) fits the data of this study within ±5%.

The curve fits shown in Figure 2 are applications of the following generalized correlation:

$$\alpha = \exp\left[-0.27 + B(x_H)\left(\frac{1000}{T}\right)^{0.75}\right] \quad (12)$$

where

$$B(x_H) = 0.5155 - 0.0569x_H - 0.12x_H^2$$

Figure 3 shows a comparison of the correlation (eq 12) with results from the literature. In general, agreement is within 12% between the present correlation and literature

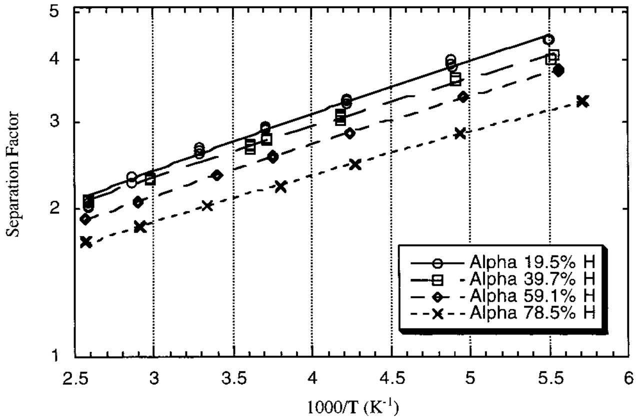

Figure 2. Separation factor vs temperature at four values of gas mixture. The data for various gas mixtures is represented by the symbols shown on the figure and the lines represent eq 12.

Table 1. Separation Factors for 19.5 mole % H_2 in the Solid (x_H)

1000/T (K^{-1})	separation factor	uncertainty (%)
2.589	2.008	4.3
2.589	2.026	4.3
2.589	2.045	4.4
2.861	2.256	4.5
2.862	2.310	4.6
2.862	2.318	4.6
3.288	2.573	4.8
3.285	2.612	4.8
3.286	2.652	4.8
3.704	2.897	5.1
3.703	2.910	5.1
3.703	2.934	5.1
4.224	3.261	5.4
4.222	3.306	5.4
4.220	3.337	5.4
4.889	3.876	5.9
4.886	3.918	6.0
4.884	4.005	6.0
5.502	4.395	6.4
5.496	4.396	6.4

Table 2. Separation Factors for 39.7 mole % H_2 in the Solid (x_H)

1000/T (K^{-1})	separation factor	uncertainty (%)
2.588	2.066	2.0
2.590	2.083	2.0
2.591	2.079	2.0
2.592	2.066	2.0
2.979	2.288	2.0
2.978	2.292	2.0
2.977	2.300	2.0
3.612	2.640	2.1
3.604	2.674	2.2
3.609	2.674	2.2
3.613	2.684	2.2
3.713	2.745	2.2
3.711	2.756	2.2
3.711	2.761	2.2
4.185	3.020	2.3
4.187	3.063	2.3
4.183	3.069	2.3
4.183	3.094	2.3
4.913	3.618	2.5
4.913	3.627	2.5
4.908	3.668	2.5
5.539	4.082	2.7
5.517	4.010	2.6

Table 3. Separation Factors for 59.1 mole % H_2 in the Solid (x_H)

1000/T (K^{-1})	separation factor	uncertainty (%)
2.569	1.895	1.3
2.568	1.904	1.3
2.569	1.906	1.3
2.898	2.048	1.3
2.898	2.063	1.3
2.897	2.068	1.3
3.402	2.327	1.3
3.401	2.338	1.3
3.400	2.528	1.3
3.752	2.544	1.3
3.750	2.550	1.3
3.752	2.828	1.3
4.242	2.839	1.4
4.242	2.842	1.4
4.244	3.353	1.4
4.962	3.367	1.5
4.962	3.381	1.5
4.964	3.774	1.5
5.563	3.802	1.5
5.566	3.082	1.5
5.566	3.841	1.5

Table 4. Separation Factors for 78.5 mole % H_2 in the Solid (x_H)

1000/T (K^{-1})	separation factor	uncertainty (%)
2.572	1.700	1.3
2.573	1.715	1.3
2.574	1.719	1.3
2.915	1.831	1.3
2.913	1.837	1.3
2.912	1.844	1.3
3.339	2.202	1.2
3.339	2.024	1.2
3.338	2.029	1.2
3.804	2.211	1.2
3.804	2.219	1.2
3.803	2.227	1.2
4.276	2.451	1.2
4.274	2.459	1.2
4.280	2.459	1.2
4.939	2.822	1.2
4.942	2.845	1.2
4.942	2.855	1.2
5.713	3.279	1.2
5.713	3.294	1.2
5.722	3.306	1.2

data. The results of Andreev et al. (1978) (98% H) and Botter et al. (1965) (~100% H) at 0 °C differ from those of eq 12 by +12% and +10%, respectively. The results of Andreev et al. (2% H) and eq 12 differ by −11% at 0 °C.

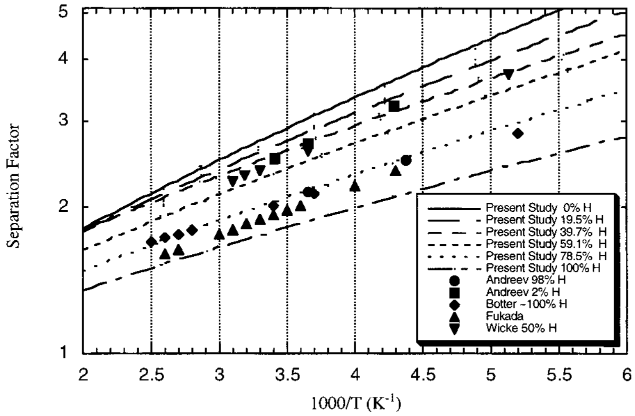

Figure 3. A comparison of eq 12 with data from the literature is shown. The data are represented by the symbols shown on the figure and the lines represent eq 12.

The results of Wicke and Nernst (1964) (50% H) differ from those of eq 12 by +5% at 0 °C. For 95% H, the results of eq 12 differ from the results of Fukada et al. by +5% at 0 °C. This agreement is felt to be good and thus allows eq 12 to be used for calculating separation factors for all gas compositions with confidence over the temperature range 175 K to 398 K.

Conclusions

The correlation developed in this study (eq 12) fits the data of this study within ±5% and the data referenced in the literature within ±12%. This is good agreement and thus allows eq 12 to be used in calculating separation factors for the $Pd-H_2/D_2$ system in the β phase with confidence over the temperature range 175 K to 398 K. To the knowledge of the authors this is the first published correlation where both temperature and gas composition are provided in a single correlation. Further work is required to determine isotopic effects on the separation factor for $Pd-H_2/T_2$ (protium/tritium) and $Pd-D_2/T_2$ (deuterium/tritium) systems.

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Nomenclature

Roman Symbols

A = separation factor−temperature correlation constant
B = separation factor−temperature correlation constant
D = atomic deuterium
D_2 = molecular deuterium
H = atomic hydrogen; total protium in supply gas mixture
H_2 = molecular hydrogen
K = Sievert's law constant
n = atomic ratio (H/Pd)
p = partial pressure
R = gas constant
T = temperature
x = mole fraction in the solid phase
y = mole fraction in the gas phase

Greek Symbols

α = separation factor; solution region of the palladium−hydrogen phase diagram
β = hydride region of the palladium−hydrogen phase diagram
ΔH = enthalpy of solution
ΔS = entropy of solution

Subscripts

D = deuterium
H = hydrogen
i = component i

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