SAND2011-2827C

# Thermodynamic and Kinetic Characterization of H-D exchange in Pd and Pd Alloys

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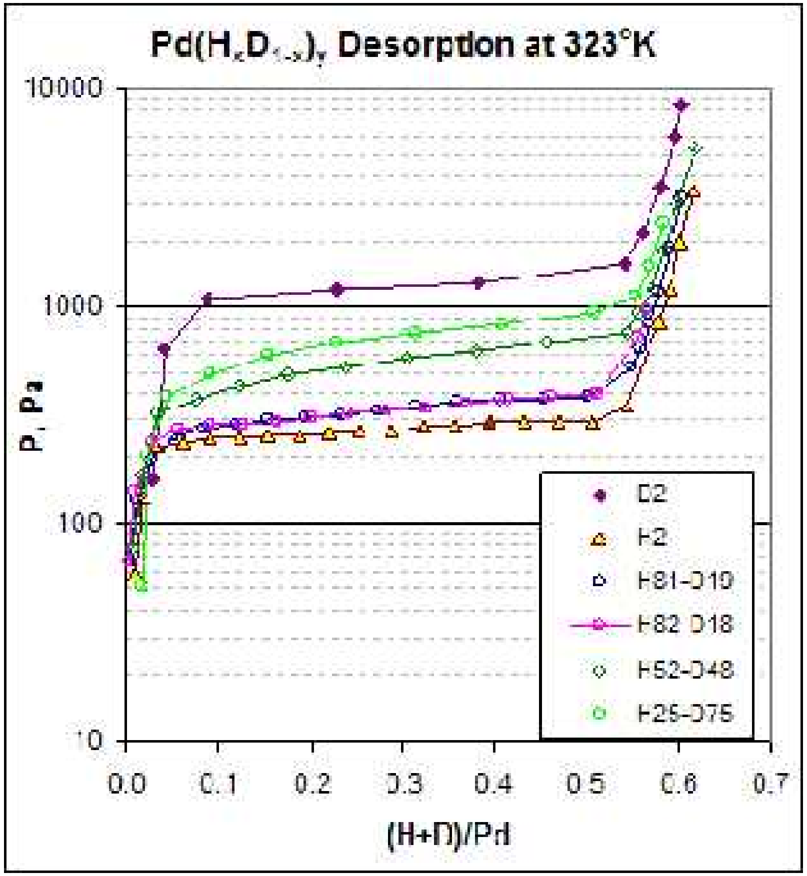

**MRS Sprint Meeting SF**
**Apr. 28, 2011**

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# Research interests in H-Pd

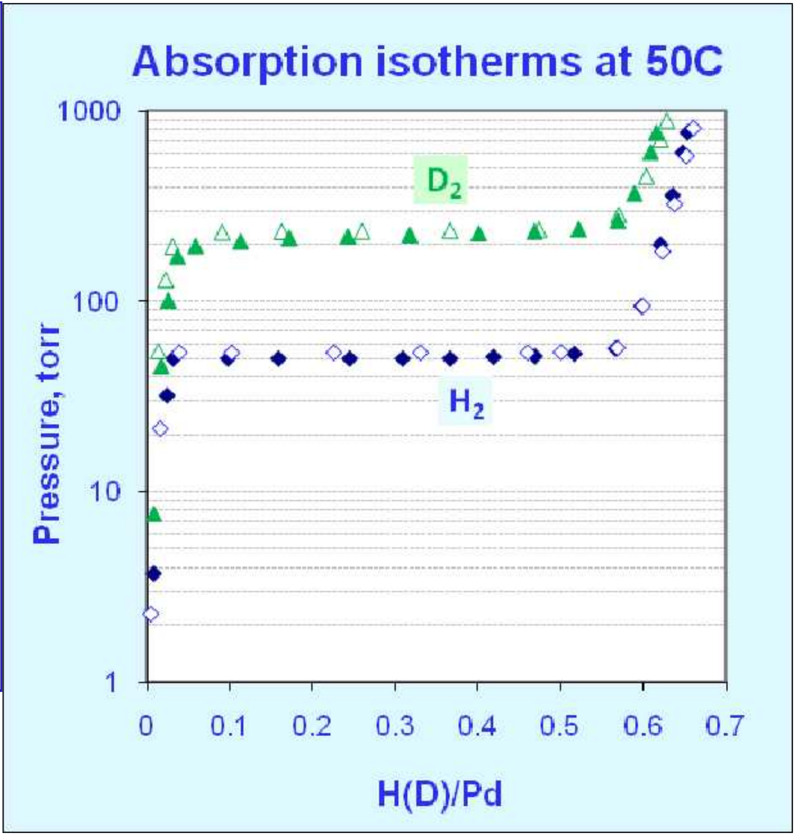
**A century-long research interest in H(D)-Pd, due to:**

- $H_2$ storage
- $H_2$ dissociation catalysis
- $H_2$ purification
- Isotope effect
- Isotope exchange

# Isotope effect in H-D-Pd

- Large isotope effects in Pd => isotope exchange/separation
- Effect of H-D in Pd:

  Equilibrium pressure of D is higher than H, i.e. Affinity of H for Pd is greater than D for Pd



# Isotope exchange equilibrium

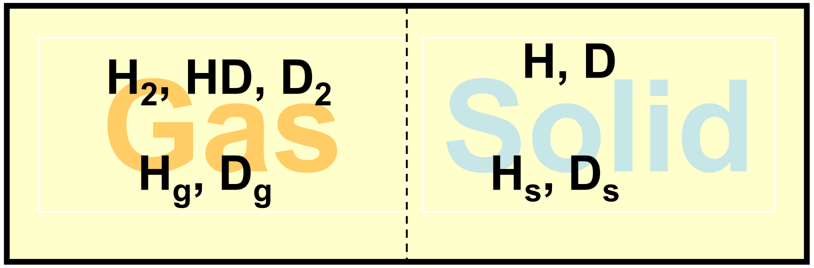
**2-step Isotope exchange:**

$$D_2 + Pd_mH = HD + Pd_mD$$
$$HD + Pd_mH = H_2 + Pd_mD$$

## Possible species:

**In gas: $H_2$, HD, $D_2$**

**In solid (Pd): H, D**



Gas

$H_2$, HD, $D_2$

$H_g$, $D_g$

Solid

H, D

$H_s$, $D_s$

$$H_2 + D_2 \Leftrightarrow 2HD$$

**Equilibrium Constant**

$$K_{HD} = P_{HD}^2/(P_{H2} * P_{D2})$$

H and D distribution in gas and solid:

Separation Factor $\alpha$

$$\alpha = (D_g/H_g)/(D_s/H_s)$$
$$= (D/H)_g/(D/H)_s$$

$$D_g = P_{D2} + ½ P_{HD}$$
$$H_g = P_{H2} + ½ P_{HD}$$
$$D_s = D/Pd$$
$$H_s = H/Pd$$

# Isotopic concentration detection:
## Previous techniques

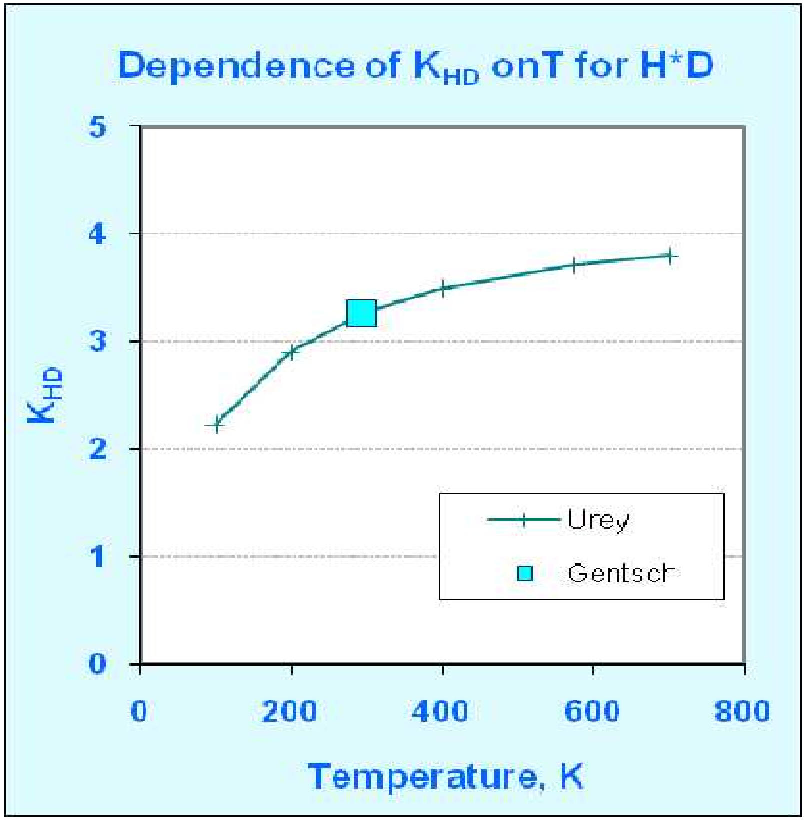
Isotopic concentrations in **solid**

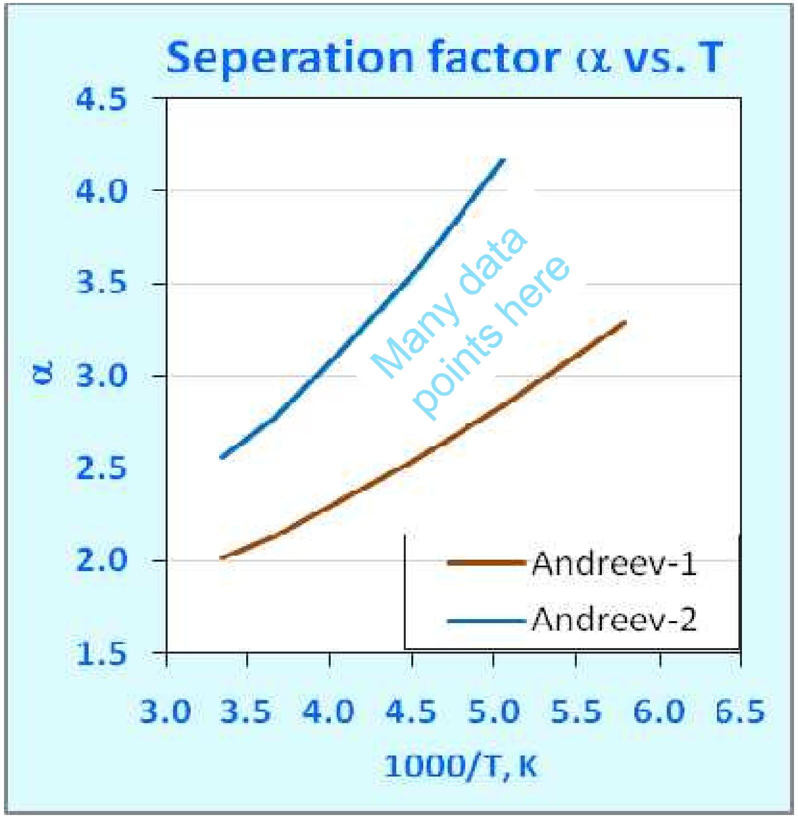
- Electric resistivity
- Reaction heat (Calorimetry)

Isotopic concentrations in **gas**:

- Thermal conductivity
- Gas chromatography
- Raman

# Reported $K_{HD}$ and $\alpha$ values in literature





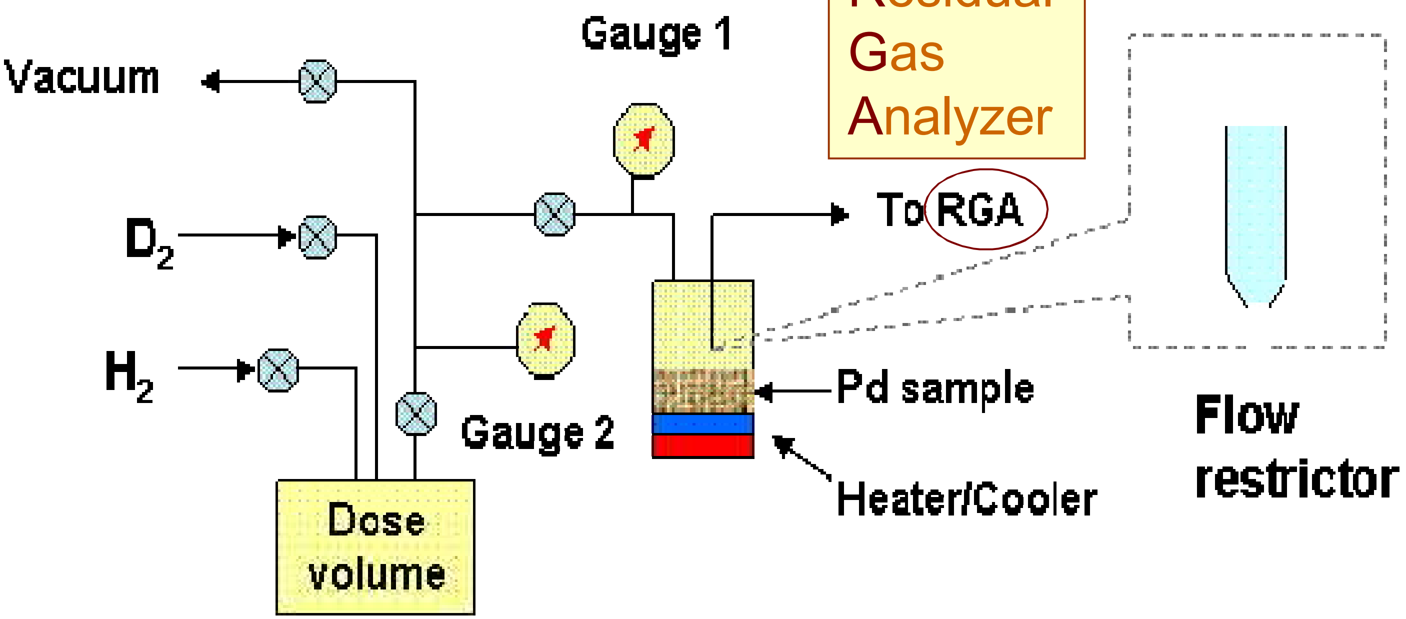
**Urey 's calculated results and Gentsch's experiment (the only one) on Pt**

Many data, but Scattered. The reason for scatter is unknown

- H.C. Urey, D. Rittenberg, *J. Chem. Phys*. **1** (1933) 137.
- B.M. Andreev, E.P. Magomedbekov and G. Sicking, "*Interaction of Hydrogen Isotopes with Transition Metals and Intermetallic Coumponds*", Springer, Ed. J. Kuhn *et al*., 1996 ISBN 3-540-58369-6.
- V.H. Gentsch, *Zeitschrift fur Physik Chem*., *NF*, Bd. **35 S.** (1962) 85.
- H. Brodowsky and D. Repenning, *Zeitschrift fur Physik Chem*. *NF*, Bd. **114** (1979) 141.

# Sieverts apparatus + RGA

New



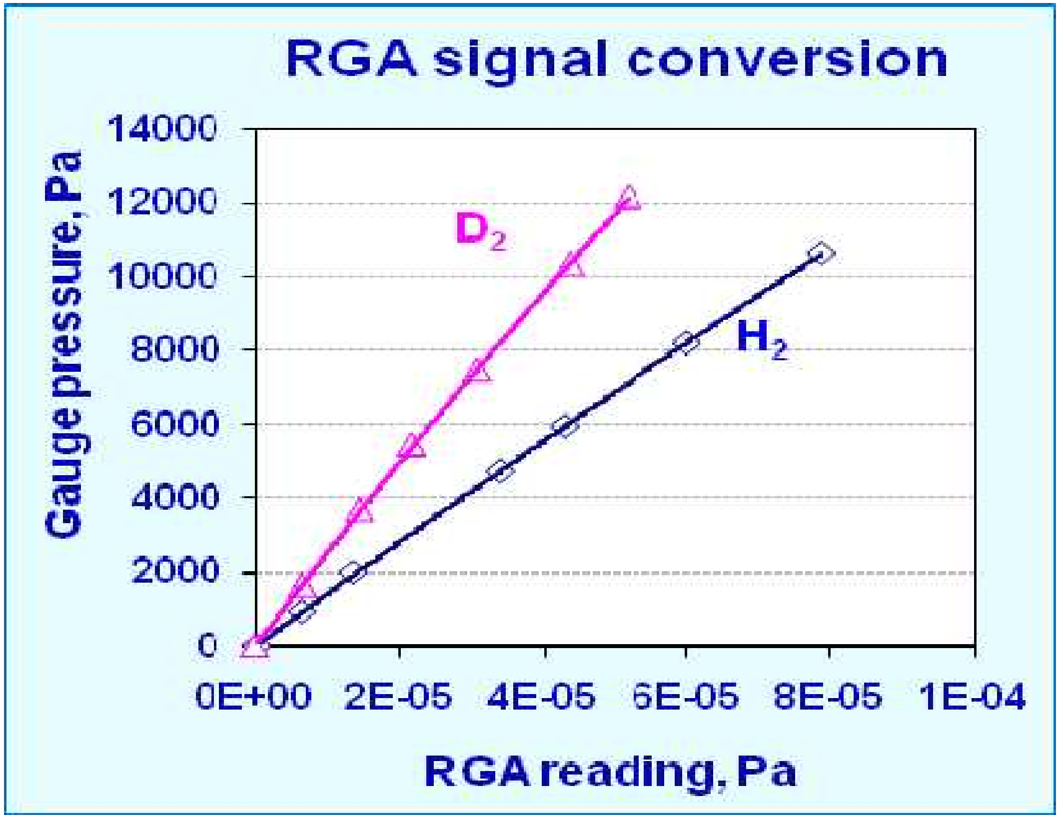
Residual Gas Analyzer

- Detect isotope composition
- No measurable gas loss during exchange: a closed system

The pressure difference between sample chamber and RGA is > $10^7$

**W. Luo, D. F. Cowgill, and R. A. Causey***J. Phys. Chem. C* ***2009, 113, 20076.***

# Calibration

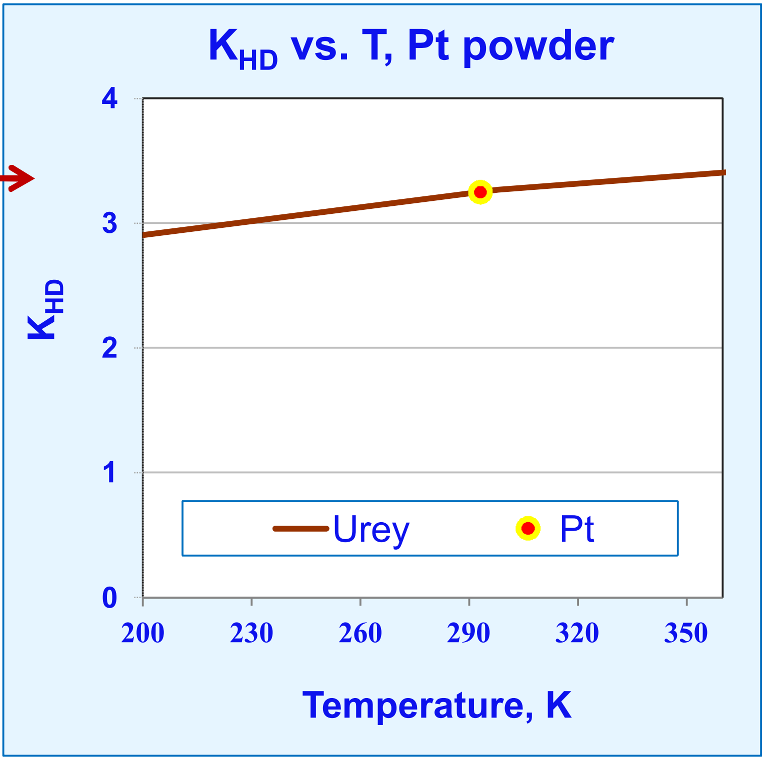


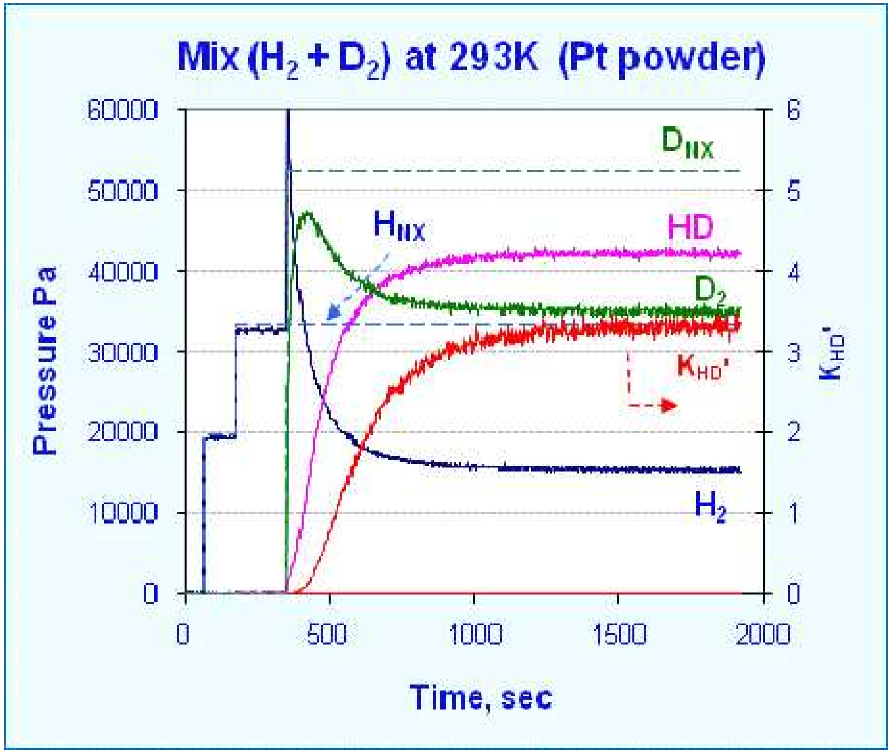
HD calibration: use the average of those for $D_2$ and $H_2$

W. Luo, D. Cowgill, R. Causey and K. Stewart, *J. Phys. Chem.*, B **112** (2008) 8099.

# Validate HD calibration by…

- Only one experimental $K_{HD}$ values reported in the literature
- Example for measured $K_{HD}$ in this work →

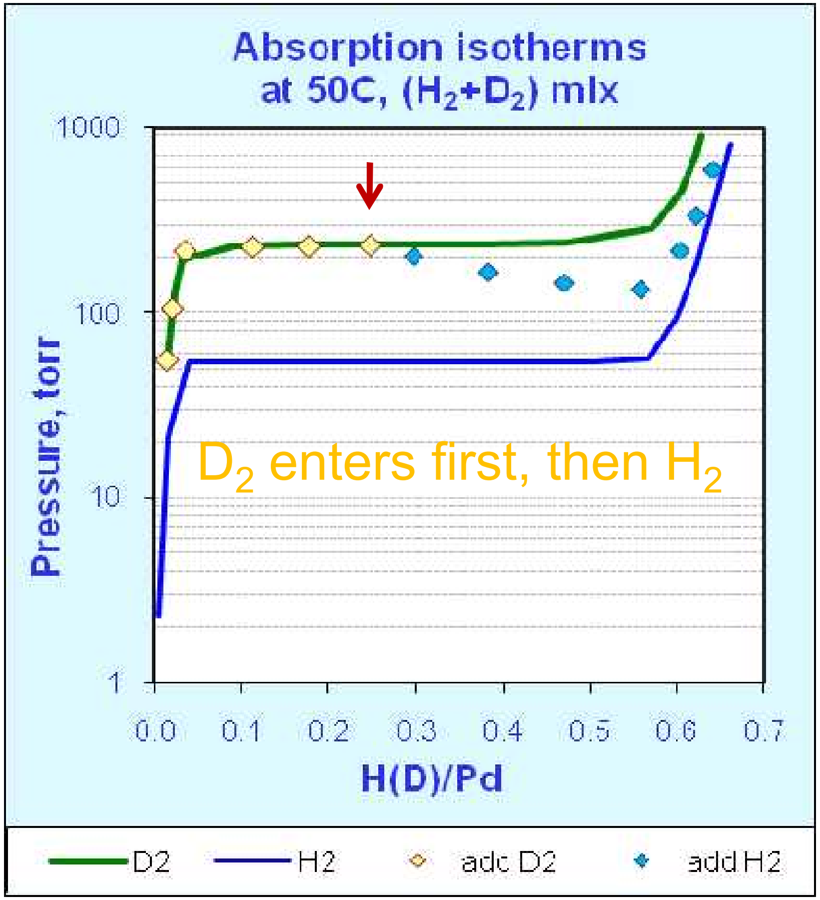




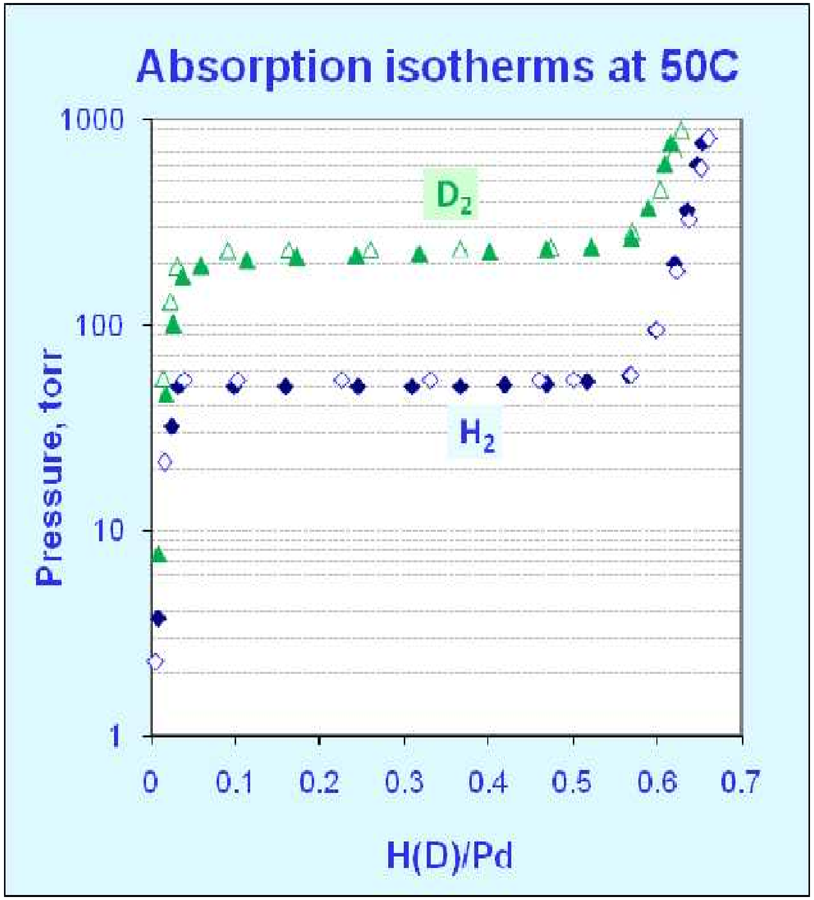
- $K_{HD}$ = 3.25 at 293K measured on Pt agrees with calculated value
- Validates the quality of our data and assumption of HD-calibration

1. H.C. Urey, D. Rittenberg, *J. Chem. Phys.*, **1** (1933) 137.
2. W. Luo, D.F. Cowgill , R.A. Causey, *J. Phys. Chem.* **B** 113 (2009) 12978.

# $H_2/D_2$ absorption in sequence



$D_2$ enters first, then $H_2$



Mixed H-D isotherm lies in between those of $H_2$ and $D_2$

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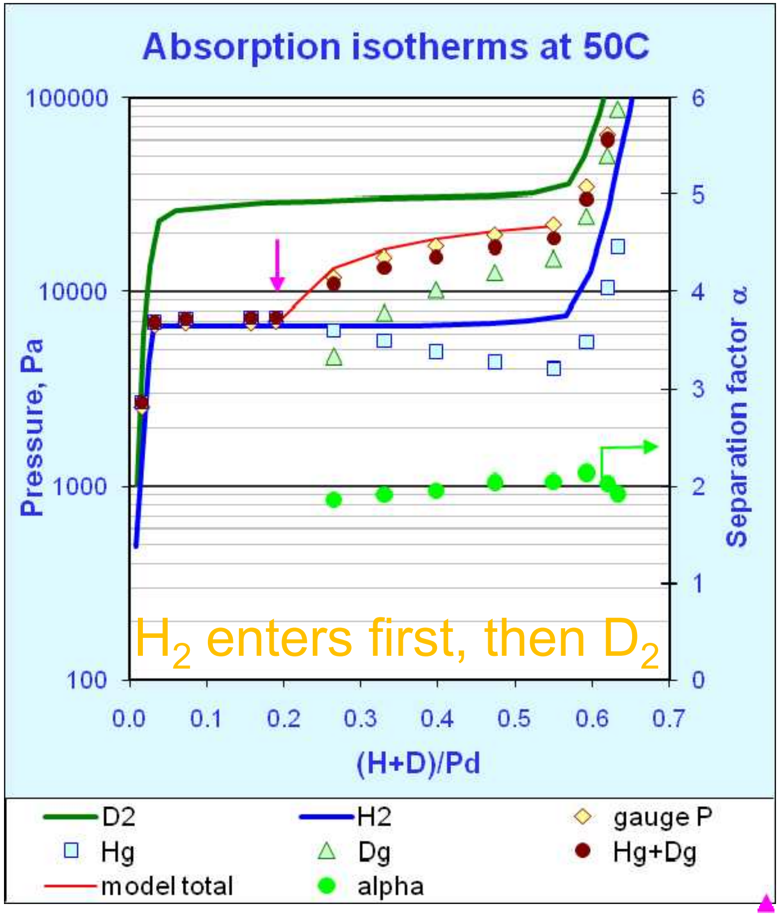
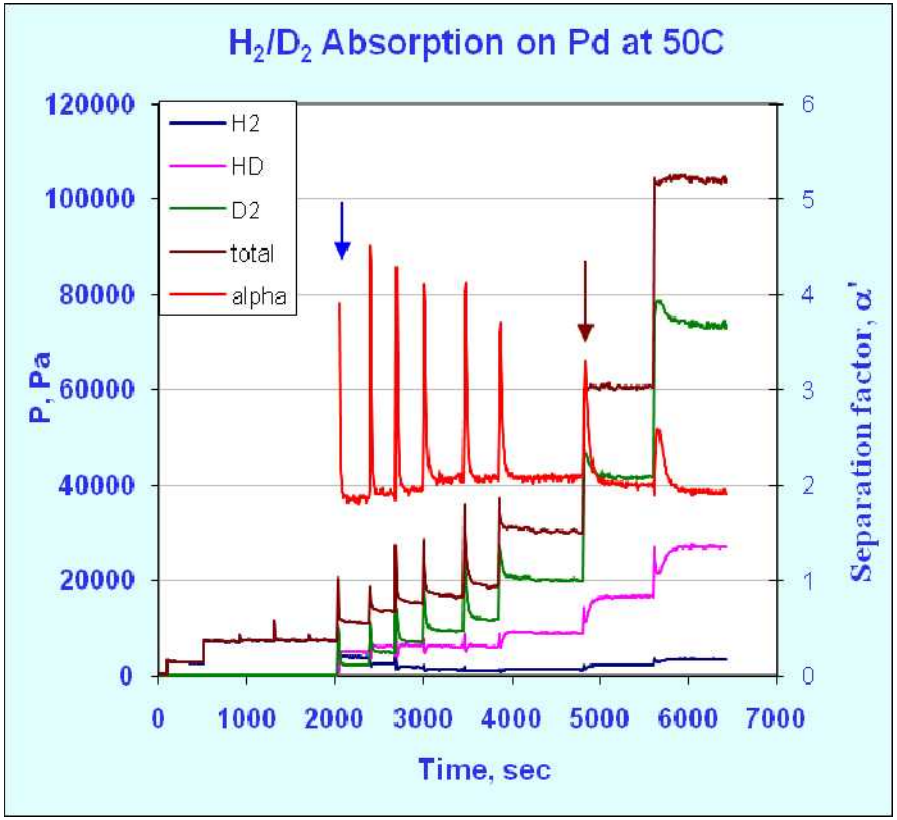
# $H_g$, $D_g$ in sequential $H_2/D_2$ absorption



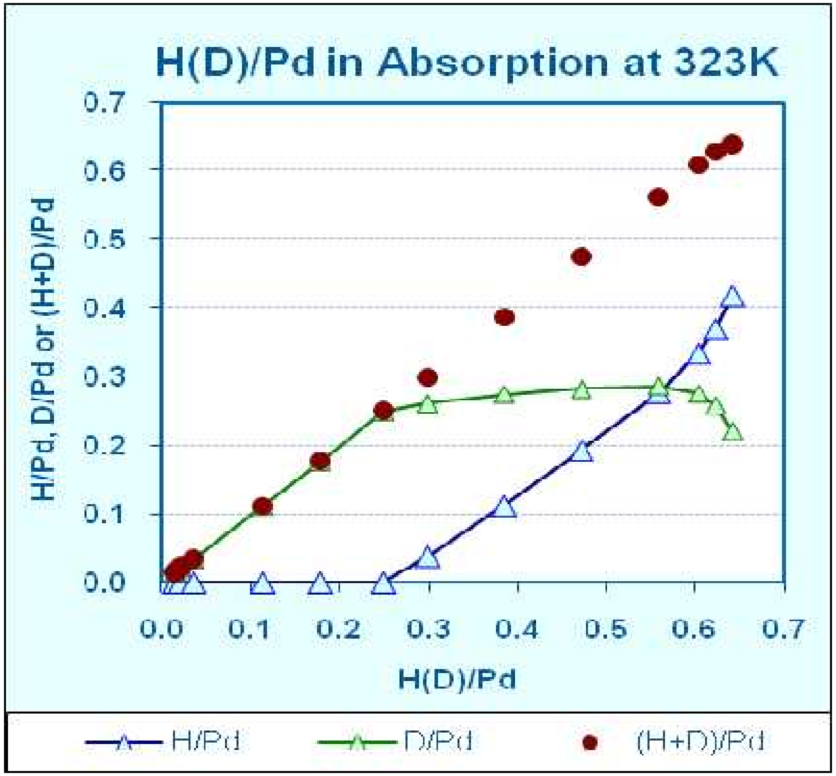


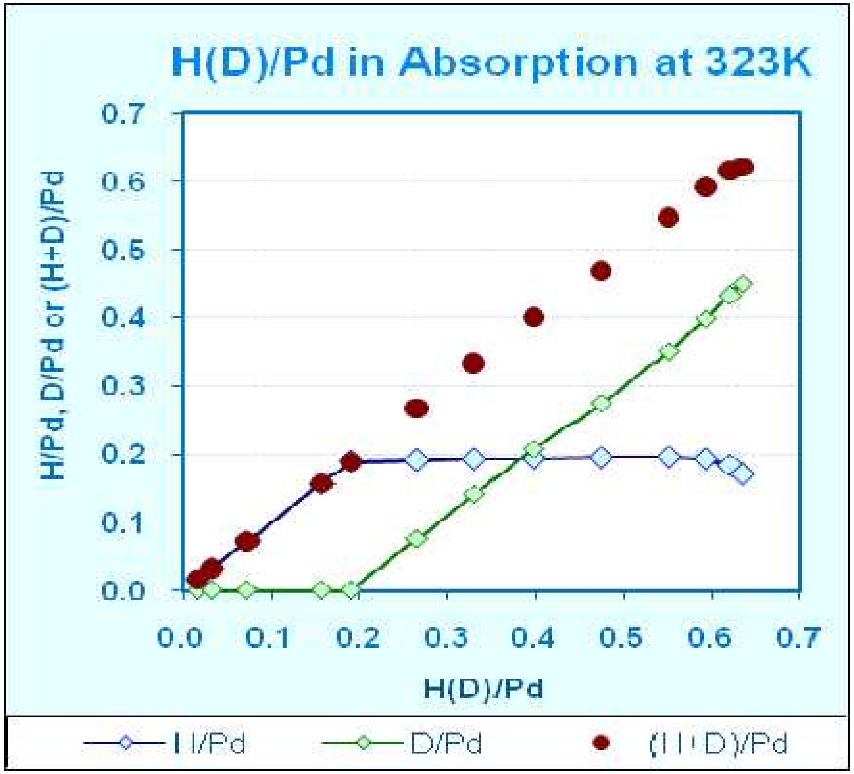
Absorption profile at 50C

- **Exchange reaches equilibrium when α reaches its equilibrium value.**
- **Model: $P_{mix} = x_H P_{H2} + (1-x_H) P_{D2}$, $x_H = H_s/(H_s+D_s)$ in plateau region**

**W. Luo, D. F. Cowgill, and R. A. Causey,** *J. Phys. Chem. C* ***2009, 113, 20076.***

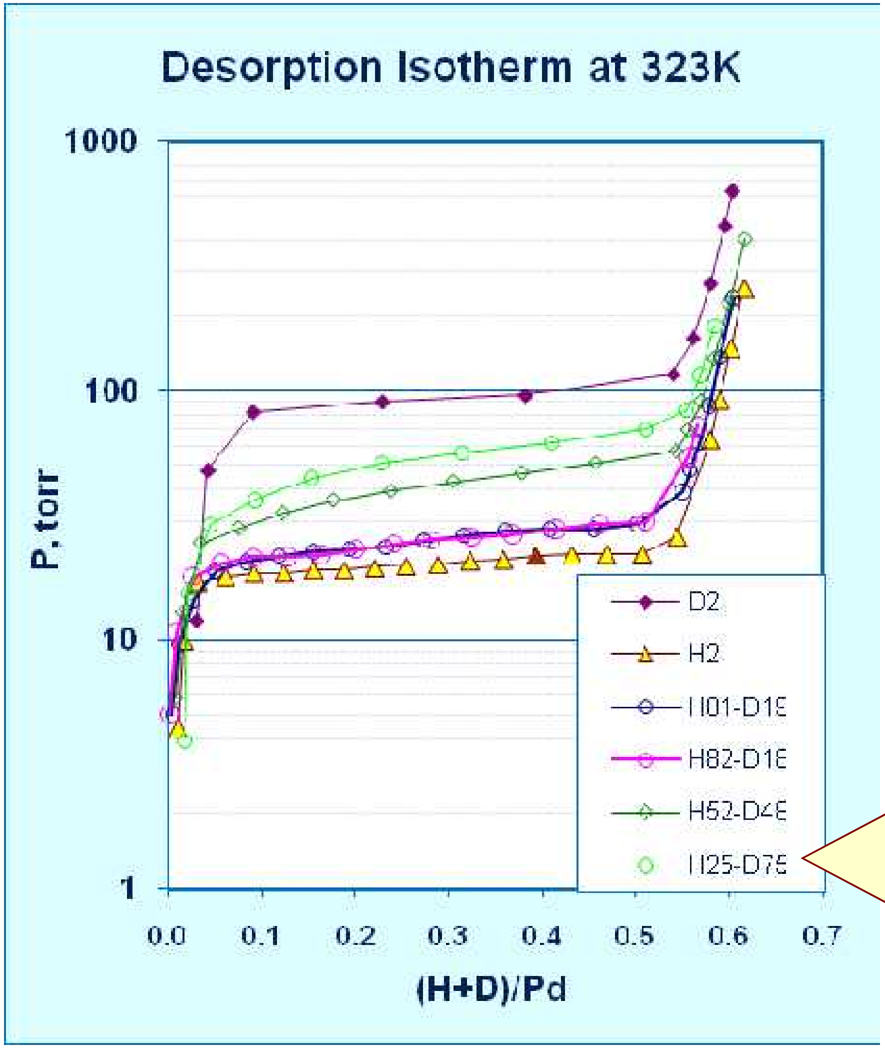
# $H_s$, $D_s$ in sequential $H_2/D_2$ absorption





When 2nd isotope enters solid in plateau region, the first isotope in solid is not displaced by 1st but, instead, enters the Pd until the β-phase is reached.

# Desorption isotherms of mixed hydrides



- **Isotherms of mixed hydrides are between those of $H_2$-Pd and $D_2$-Pd**
- **Higher initial D/H in Pd ⟶ higher equilibrium pressure**
- **Mixed hydride: sloping plateaus**
- **Plateau pressure slope increases with ratio H/D in solid**

**Initial H/D = 25/75 in Pd**

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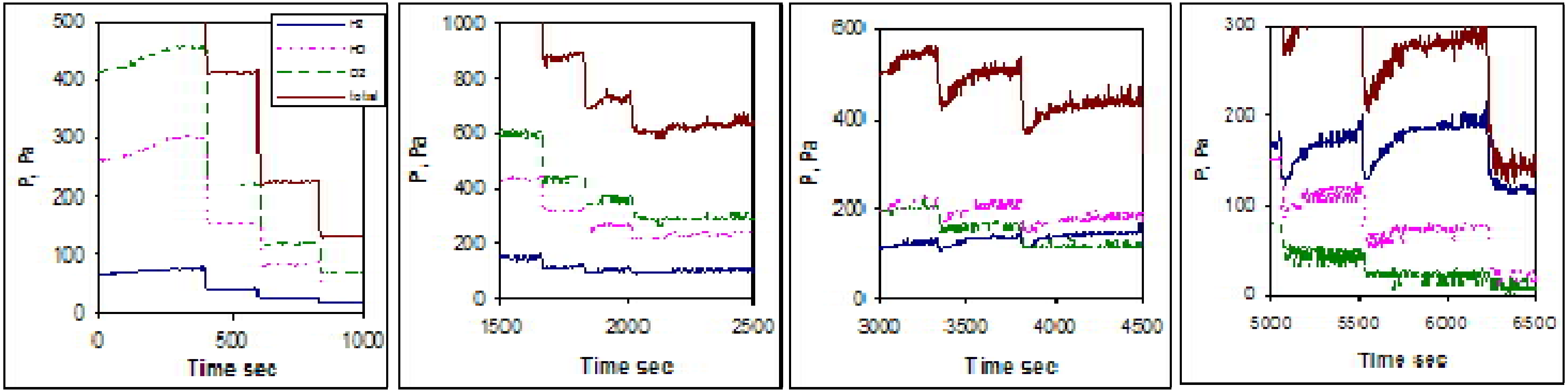
# Desorbed gas composition :

## $Pd(H_{0.52}D_{0.48})_{0.65}$ at 323K



← β- phase → | ← (α+β) two-phase → | ← α- phase →

**Composition of desorbed gas varies during desorption**

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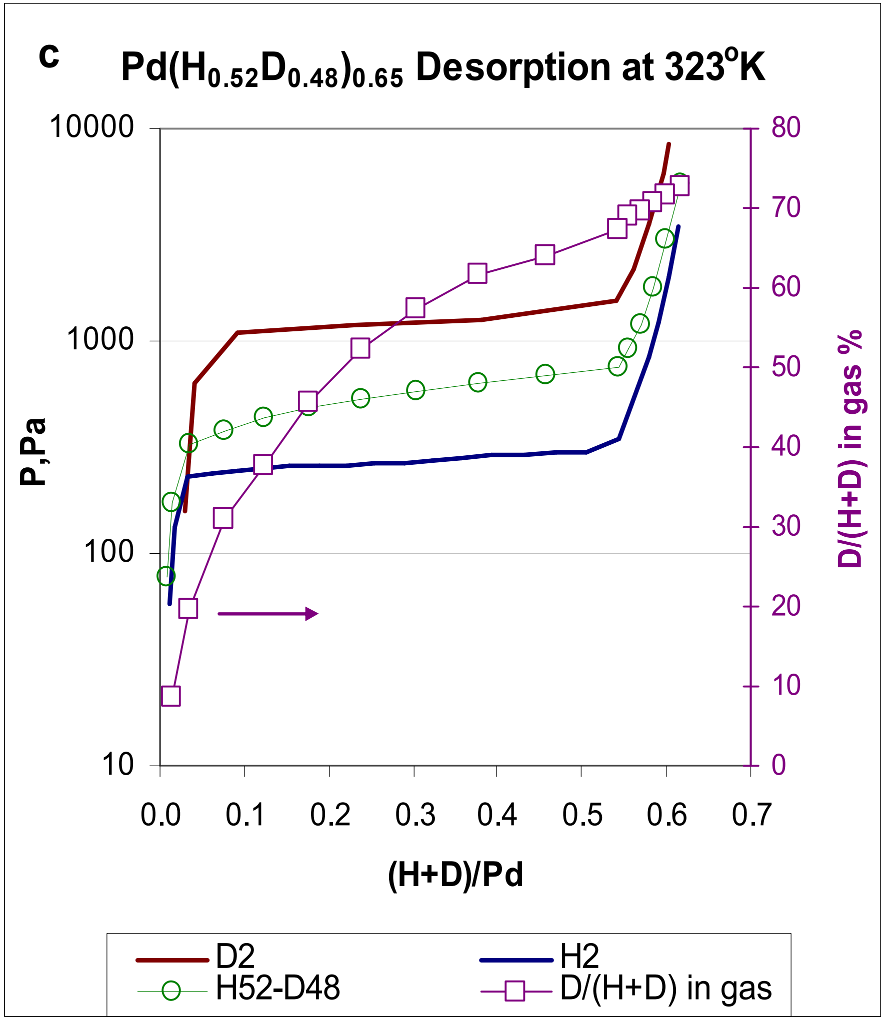
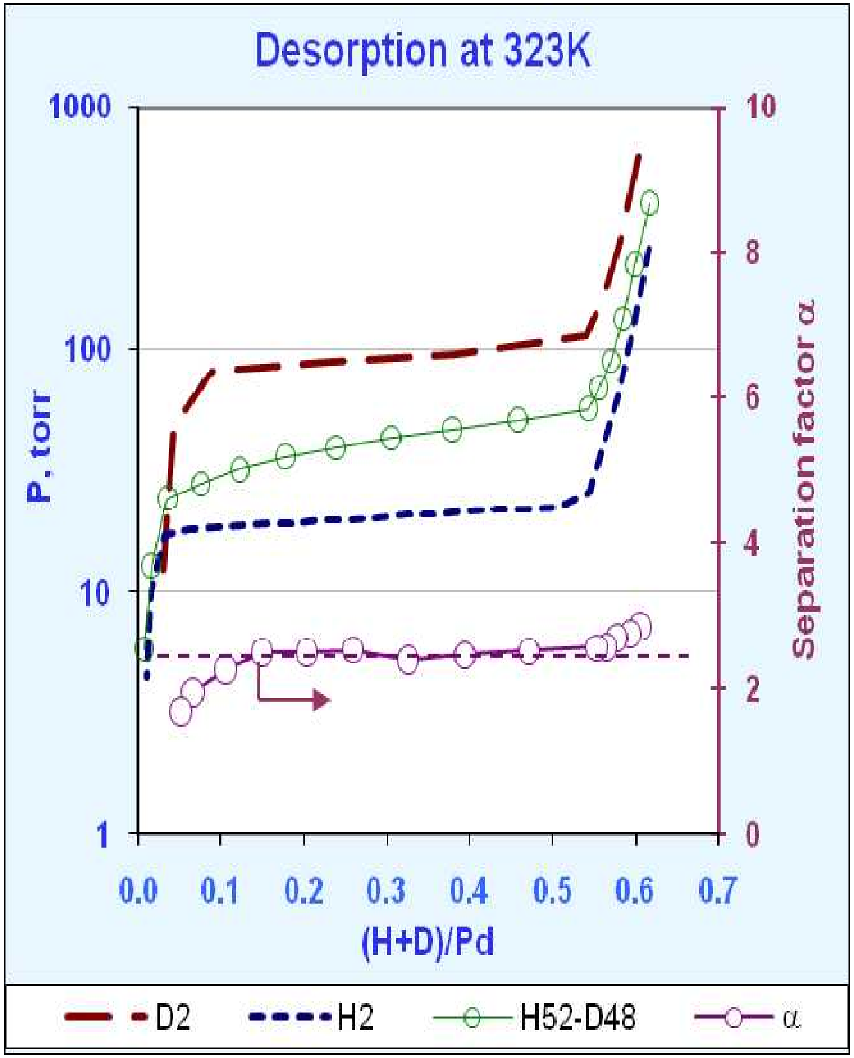
# D/(H+D) in Pd, $H_s/D_s$ and $D_g/H_g$ During Mixed Hydride Desorption



D-fraction in desorbed gas decreases when (H+D)/Pd reduces

# Separation factor during desorption



1. Both D and H desorb during desorption, but D/H ratio in desorbed gas is high when (H+D) in solid is high. This ratio decreases when (H+D) in solid is low.
2. Equilibrium desorption pressure higher when D/H in solid is high.
3. Plateau pressure for mixed hydride can be determined by:

$$P_{mix} = x_H P_{H2} + (1 - x_H) P_{D2},$$

$$x_H = H_s/(H_s + D_s)$$

$P_{H2:}$ plateau P for $H_2$-Pd,

$P_{D2:}$ plateau P for $D_2$-Pd

4. System reaches equilibrium when $(D_g/H_g)(H_s/D_s) = \alpha$

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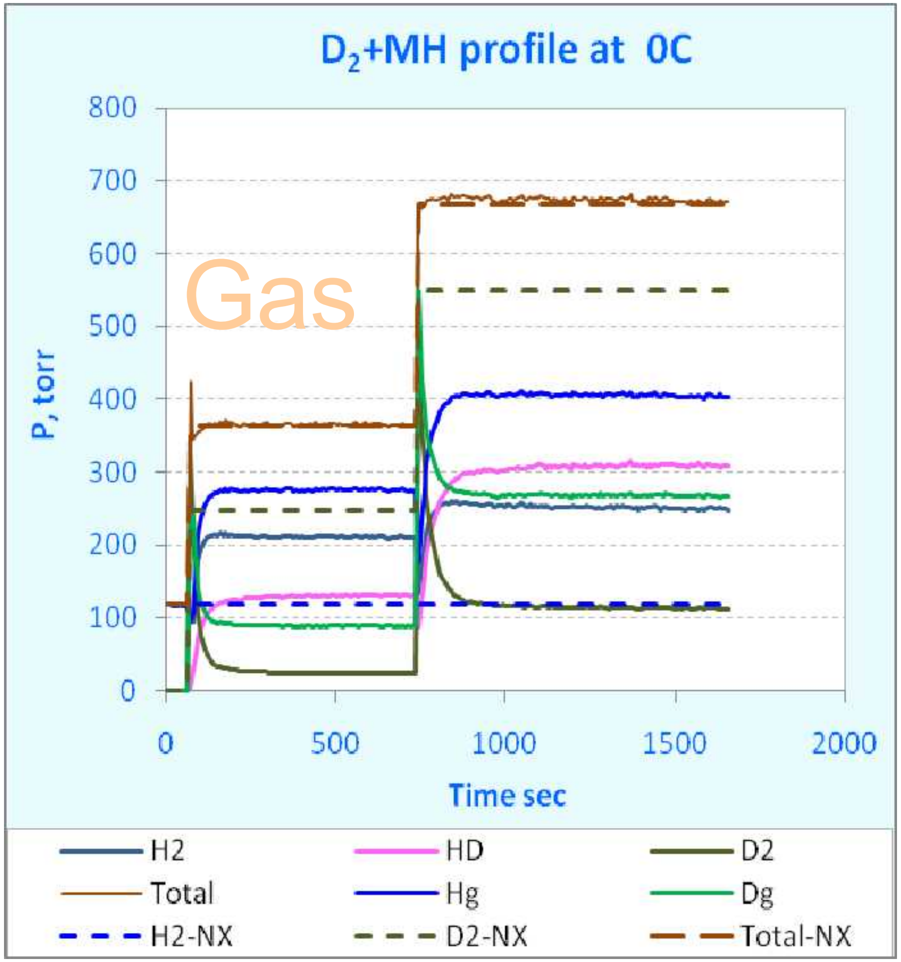
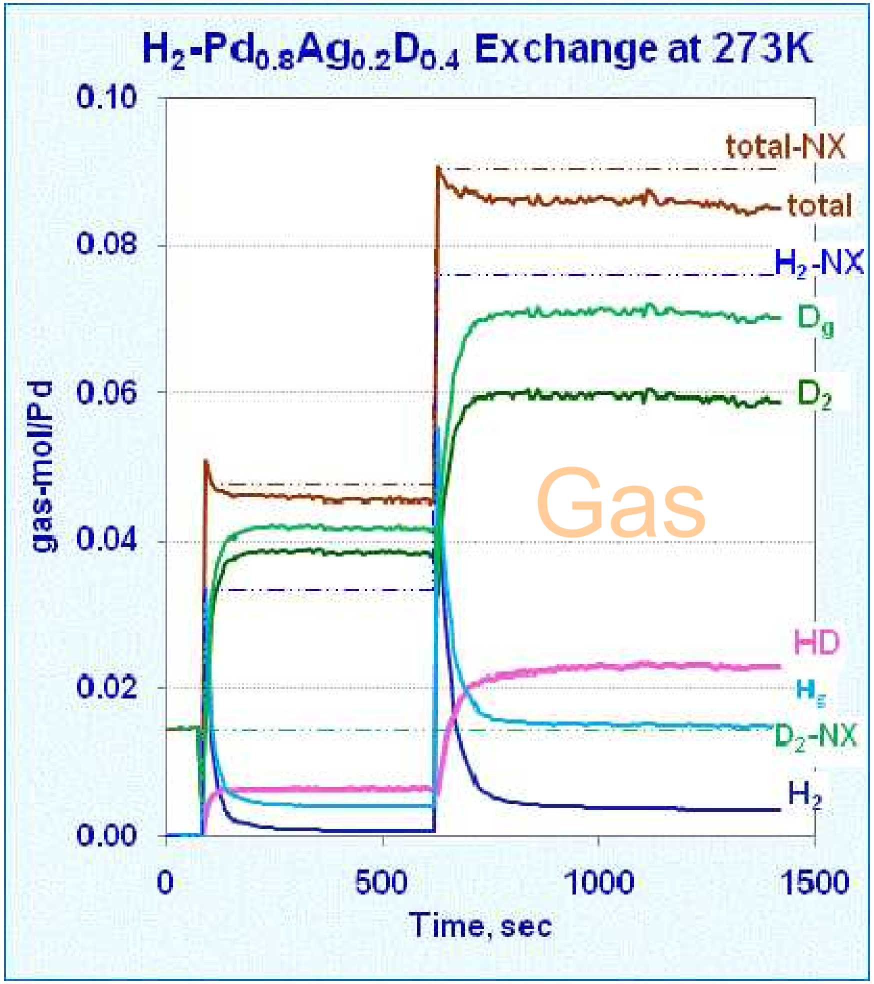
# H-D exchange in concentrated Pd and Pd alloys:

One isotope absorbed to β-phase, then the other isotope is introduced

- Almost no pressure change during H-D exchange
- H and D concentrations in solid can be calculated
- Exchange rate can be calculated



# H-D exchange profiles in ($H_2$+$Pd_{0.8}Ag_{0.2}D$)

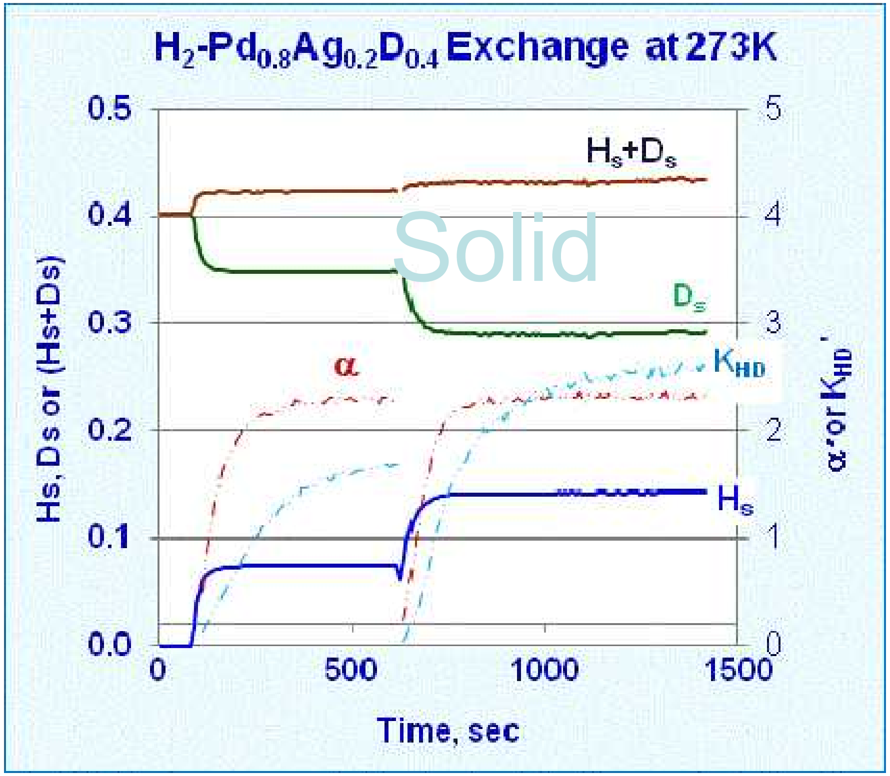


**Separation factor**

$$\alpha = \left(\frac{D_g}{D_s}\right)\left(\frac{H_s}{H_g}\right)$$

**Equilibrium constant**

$$K_{HD} = (HD)^2/(H_2D_2)$$



$\alpha$ and $K_{HD}$ govern the equilibrium partition of H & D in gas/solid

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# Exchange kinetic model

## 2-step Isotope exchange:

$$D_2 + Pd_mH = HD + Pd_mD$$
$$HD + Pd_mH = H_2 + Pd_mD$$

## Exchange rate model for Pd*

Driving force

for H*D: $dH_s/dt = k\, H_g\, D_s\, (\alpha-\alpha')$

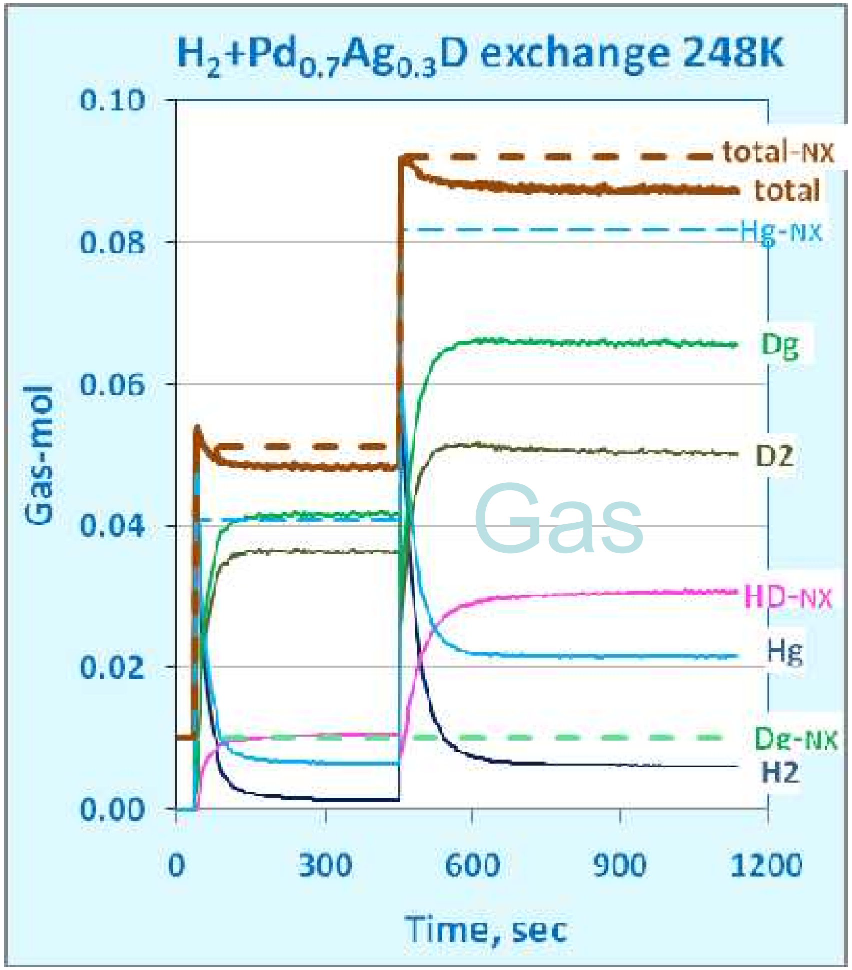
for D*H: $dD_s/dt = k\, D_g\, H_s\, (1-\alpha/\alpha')$

**To determine rate constant *k*:**

**plot $dH_s/dt$ vs $H_gD_s\,(\alpha - \alpha')$**

W. Luo, D.F. Cowgill R.A. Causey, *J. Phys. Chem.* **B 113** (2009) 12978.

# H-D exchange profiles in $(H_2+Pd_{0.7}Ag_{0.3})$

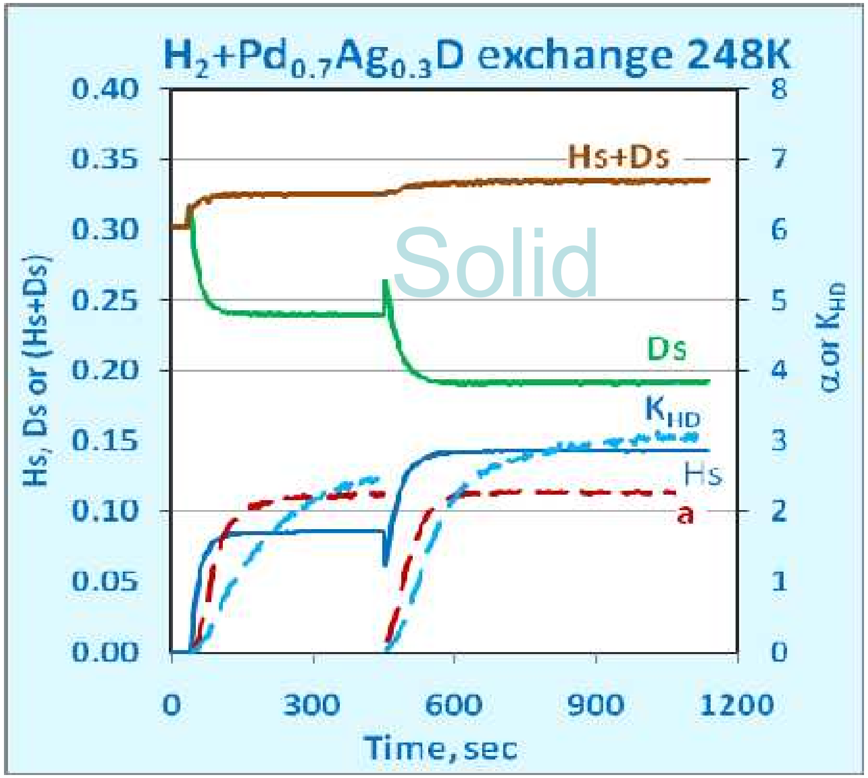


**Separation factor**

$$\alpha = \left(\frac{D_g}{D_s}\right)\left(\frac{H_s}{H_g}\right)$$

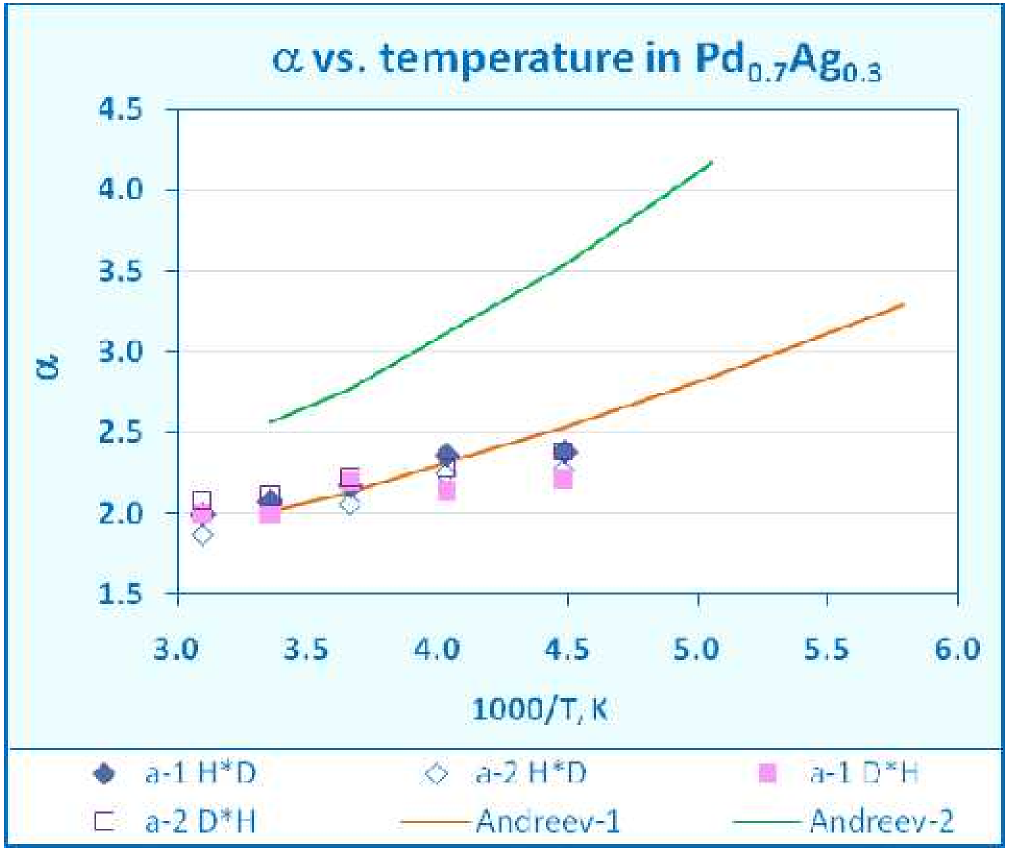
**Equilibrium constant**

$$K_{HD} = (HD)^2/(H_2{*}D_2)$$



α and $K_{HD}$ govern the equilibrium partition of H & D in gas/solid

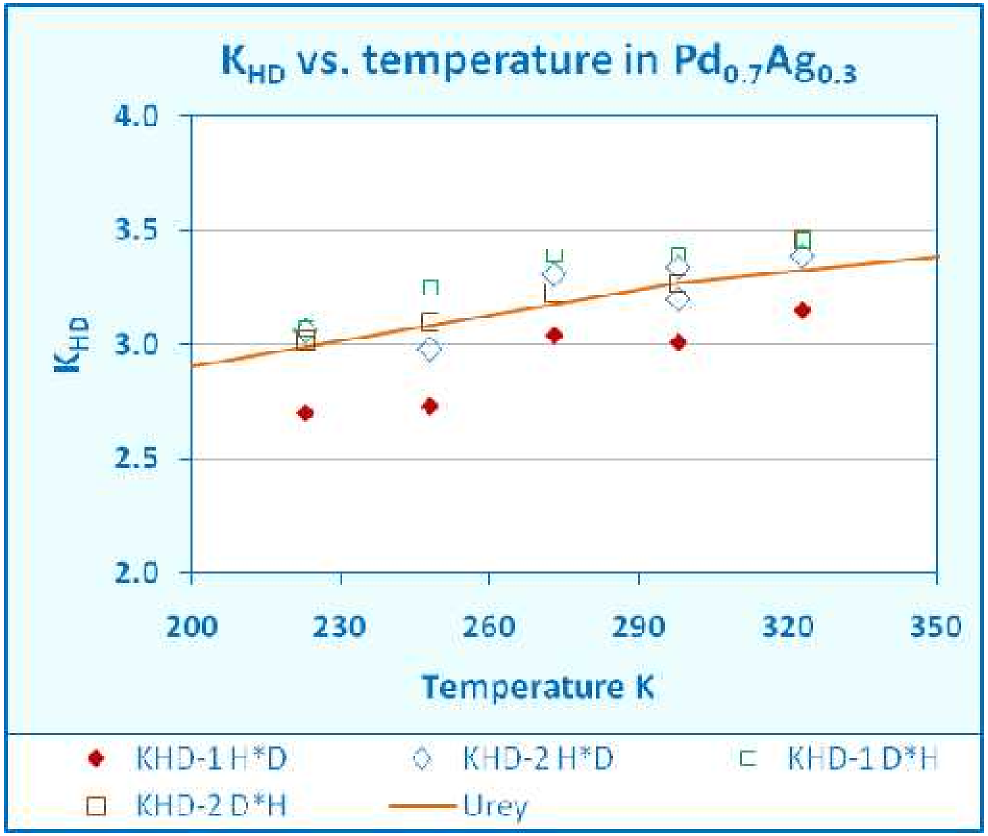
# $\alpha$ dependence on temperature



Limited experimental thermodynamic values were reported for Pd in literature. None for Pd alloys

Comparing the thermodynamic data, ($\alpha$ and $K_{HD}$) with those reported in literature can validate the obtained data.

# $K_{HD}$ dependence on temperature



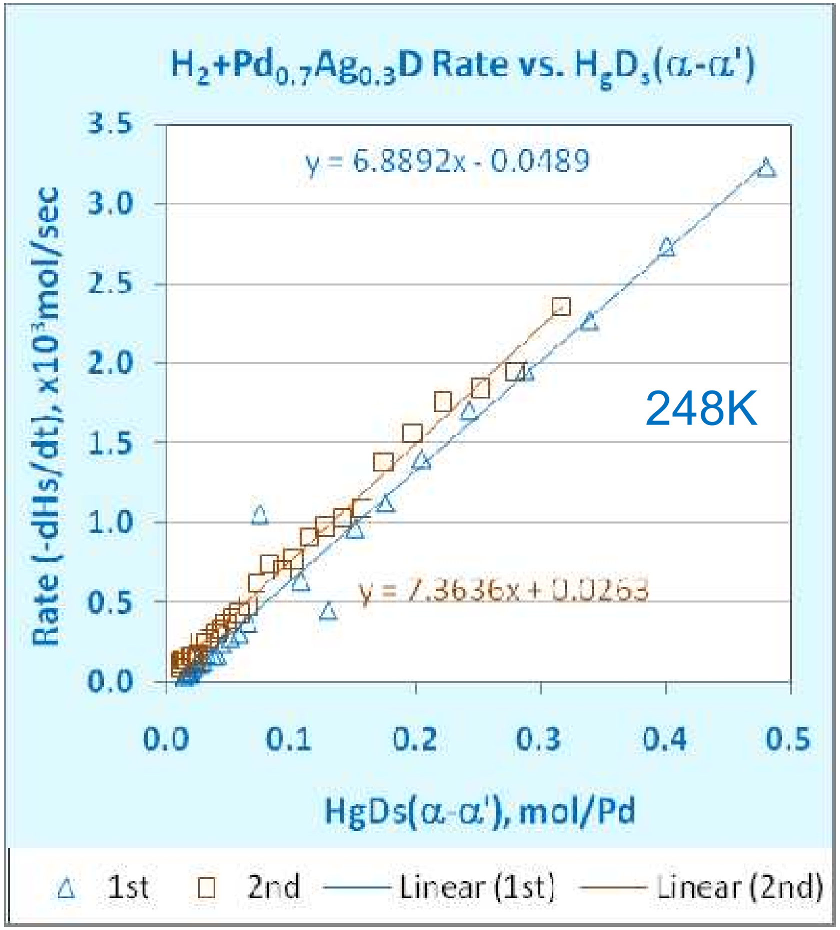
$$K_{HD} = \frac{P_{HD}^{2}}{(P_{H_2})\,(P_{D_2})}$$

$$\alpha = \left(\frac{D_g}{H_g}\right)\left(\frac{H_s}{D_s}\right)$$

$$D_g = P_{D2} + \tfrac{1}{2} P_{HD}$$

$$H_g = P_{H2} + 1/2\, P_{HD}$$

# Exchange rate constant determination

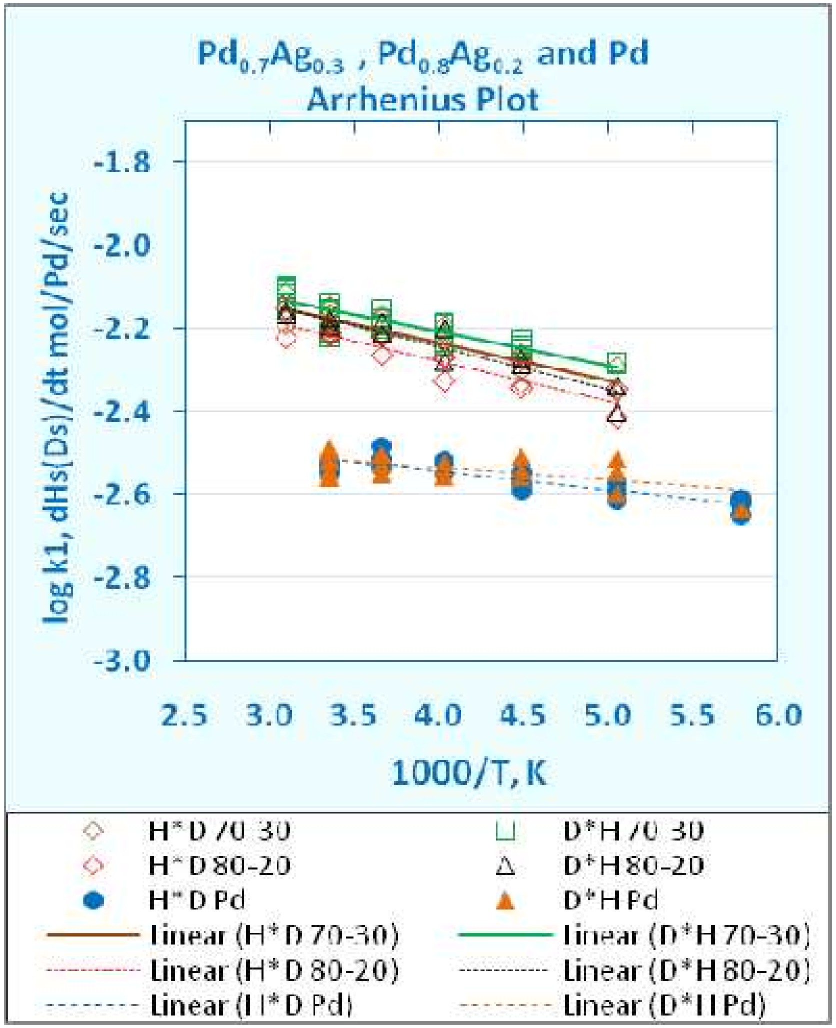


For the two doses of exchange for H*D in $Pd_{0.7}Ag_{0.3}$ at 248K

- A linear correlation for rate vs. exchange driving force
- K1 values can be determined by the slope

W. Luo, D.F. Cowgill and R.A. Causey, *J. Phys. Chem.* **B 113** (2009) 12978.

# Arrhenius plots



Arrhenius plot for H-D exchange in Pd, $Pd_{0.8}Ag_{0.2}$, $Pd_{0.7}Ag_{0.3}$ and Pd
Temperature range: 198-323K

Higher exchange rate for $Pd_{0.7}Ag_{0.3}$ and $Pd_{0.8}Ag_{0.2}$ could be resulted from its higher surface area (~3.5m$^2$/g) than that for Pd (~0.5m$^2$/g)

Plan: Test with samples of larger particle size will be carried out determine the correlation of particle size and exchange rate

# Conclusions-1

- (Sieverts' apparatus + RGA) is an effective method to detect the isotopic compositions during mixed hydride preparation and subsequent desorption
- $\beta$-phase $Pd(H_xD_{1-x})_y$ (x: 0.25 to 0.82 for y > 0.6), were prepared by isotope exchange, ($H_2$ + $PdD_y$) or ($D_2$ with $PdH_y$), at constant temperatures. The separation factor $\alpha$ during exchange was in good agreement with those in the literature

# Conclusions-2

- The absorption plateau pressures of a mixed-isotope system lie between those of single-isotope systems of H-Pd and D-Pd.
- Equilibrium absorption pressure in the plateau region of a mixed-isotope system at a given temperature varies with the ratio of H/D in the solid phase. Higher equilibrium pressures are associated with high D/H ratios in the solid phase.
- Isotope exchange does not take place in the solid phase if the system is in the plateau region. It will take place in the solid phase only when the system reaches $\beta$-phase.

# Conclusions-3

**Equilibrium properties of the mixed hydrides in desorption:**

- **Desorption isotherms lie between those of single isotope systems H-Pd and D-Pd and slope more than the latter**
- **Higher desorption pressures are associated with high ratios higher D fraction in solid, $D_s/(H_s+D_s)$**
- **D/H ratio in the desorbed gas decreases with the total isotopic content in the solid, $(H_s+D_s)$**

# Conclusions-4

- The rates of H-D exchanges in β-phase of Pd and $Pd_{0.7}Ag_{0.3}$ hydrides are obtained for both the forward and backward exchange directions over a temperature range of -100 to 50C.
- A comprehensive model is proposed that correlates the exchange rate and the exchange driving force composed of the reactant concentrations and the extent of deviation from the equilibrium.
- Very low exchange activation energies obtained ~0.7 kJ/mol and ~0.3 kJ/mol for Pd and $Pd_{0.7}Ag_{0.3}$, respectively, and the difference between the two exchange directions are insignificant.

# Acknowledgement

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- Thanks Prof. T.B. Flanagan of The University of Vermont for valuable suggestions and Dr. Tom Felter at Sandia for great advice

- It is impossible to complete this work without the discussion and support from all colleagues, Don Cowgill, Ken Stewart, Craig Tewell.

Thanks for your attention