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Equilibrium Measurement of Hydrogen Isotope Self Exchange in PdH by Spin Relaxation

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Background

- Palladium is useful for storage, pressurization and helium control in tritium systems.
- We need to understand the detailed kinetics of hydrogen transport through the surface of hydride materials.

Problem

- Conventional techniques measure the exchange between ***different*** isotopes leaving a gap in the fundamental knowledge of isotope exchange.

Solution

- Sandia is the originator of the technique for examining isotope exchange with a single isotope.

Approaches

Self Exchange — NMR

We can now measure the exchange of a hydrogen atom with another hydrogen which is called ***Self Exchange***.

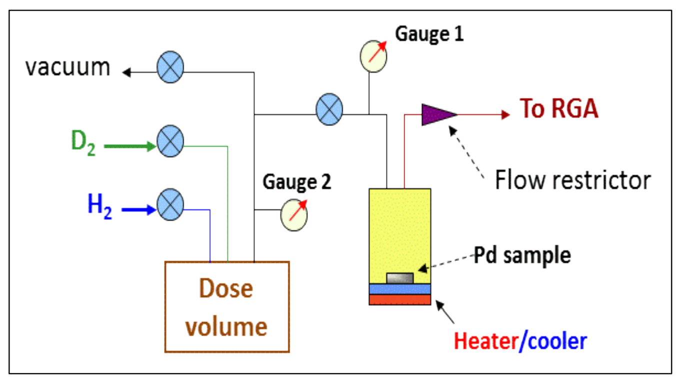
This is done by aligning spins and measuring the relaxation rate. One can also determine the activation energy for each isotope independently.

$$R_1^{app} = AT + (1/b + 1/K_{pg})^{-1}$$

$$K_{pg} = K_0 \exp(-E/k_B T)$$

- A, b = constants
- T = temperature
- K_{pg} = Temp-dep. Exchange rate from the solid to gas
- E = exchange energy or energy for H/D to get in and out of the solid

Isotope Exchange



Schematic isotope exchange system.

Sievert's – Type Batch

Conventional methods for determining isotope exchange require two different isotopes, e.g. hydrogen and deuterium that are resolved by a mass spectrometer/ RGA. These are non-equilibrium measurements.

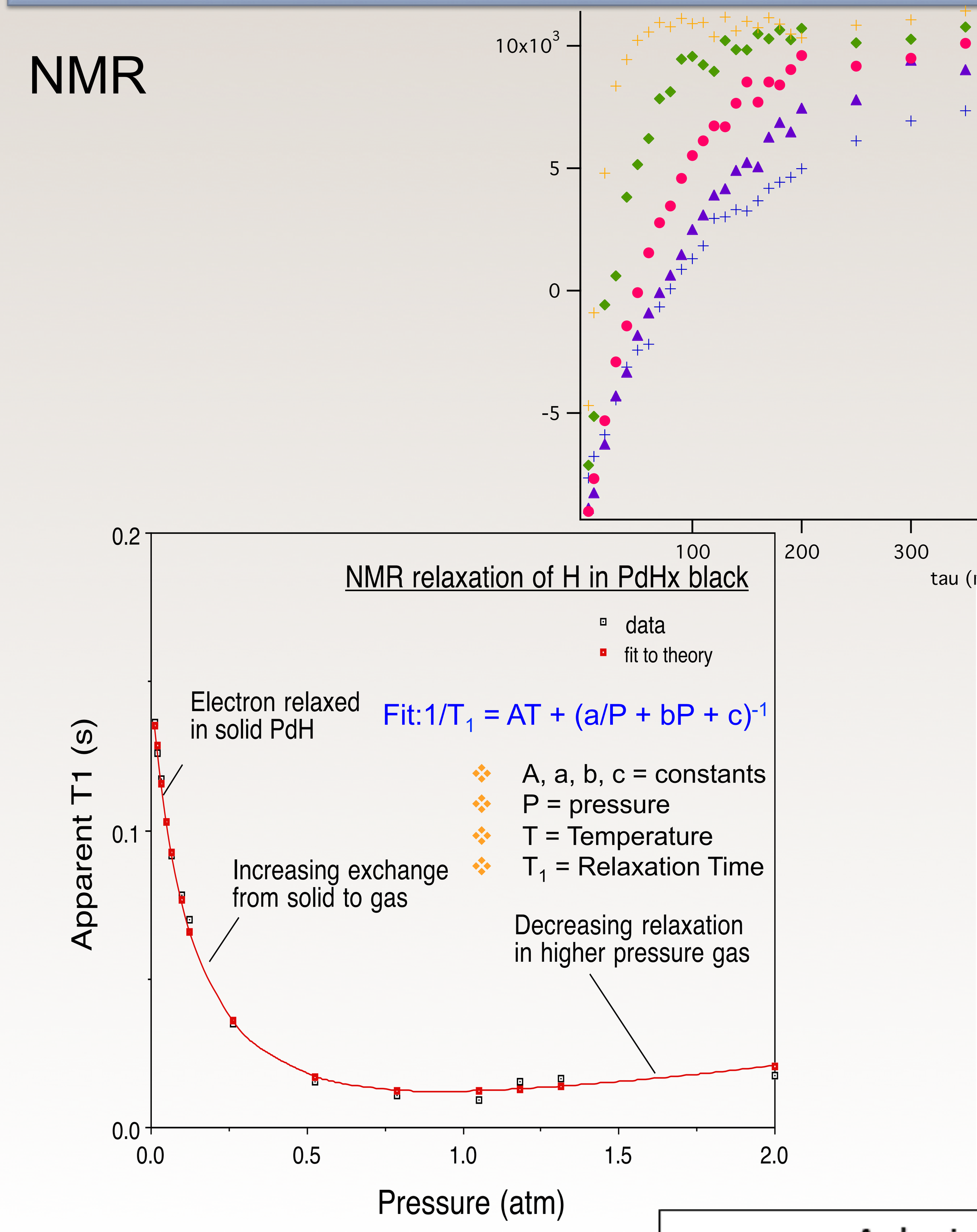
Arrhenius expression for the exchange probability in Sievert's – Type batch experiment:

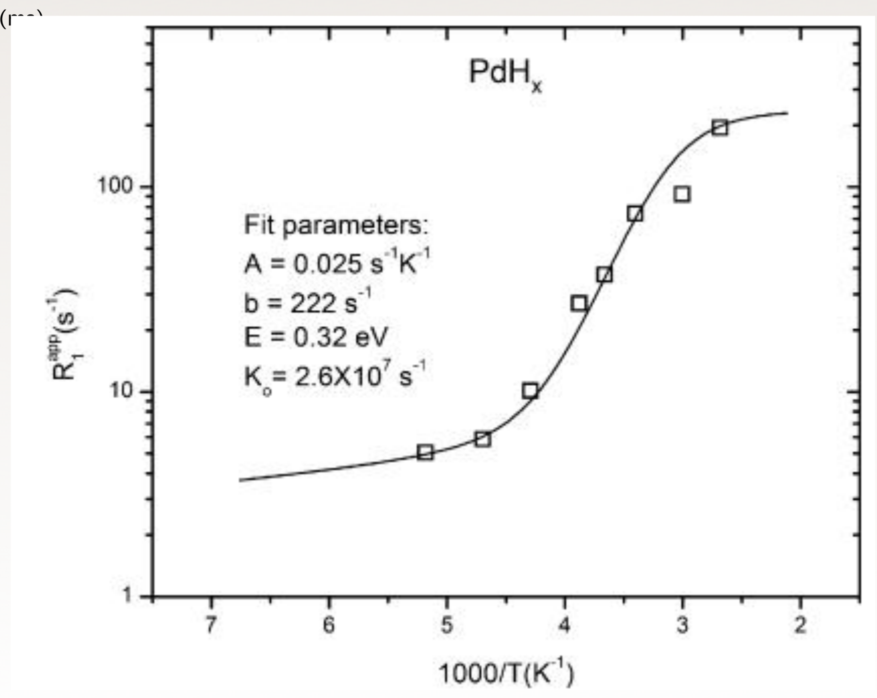
$$p_{ex} = p_o \exp(-E_{ex}/R_g T)$$

- T = temperature
- R_g = Solid intrinsic relaxation rate.
- E_{ex} = exchange energy

Results

NMR





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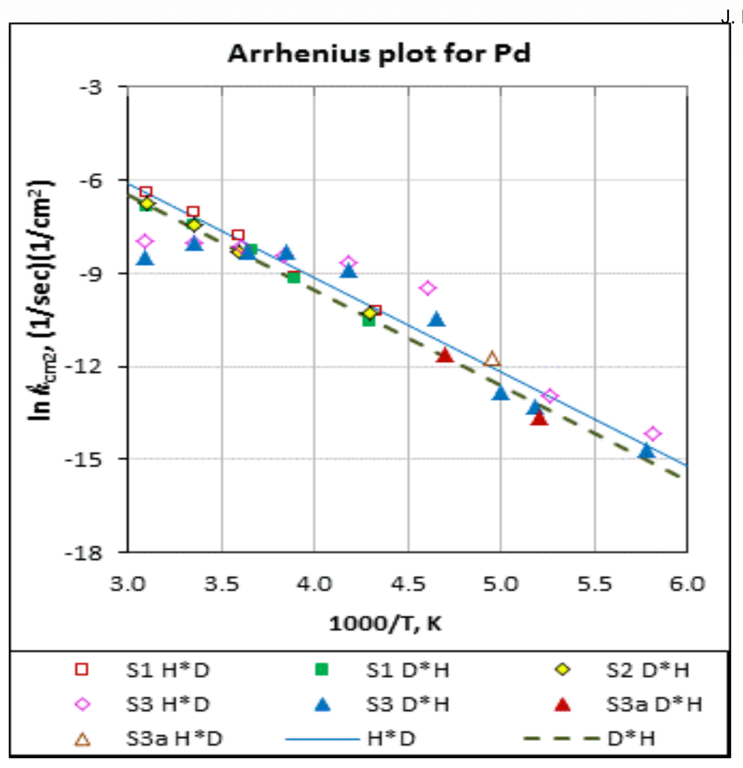
Sievert's - Type Batch

Arrhenius plot for four samples. H*D and D*H indicate the exchange directions.



Comparison

NMR / Sievert's-Type Batch

Material (T=300 K)	H_2+PdH Black	D_2+PdD Black	H_2+PdD Fine	D_2+PdH(a Coarse	D_2+PdH(b Coarse	H_2+PdD(a) Coarse	H_2+PdD(b Coarse
Gas Pressure, P_{atm}	0.9	1.0	0.92	0.78	.84	.99	.87
Obs. Exchange Rate, k (s^{-1}	108	66.6	1.6	.038	.036	.064	.062
Exchange Coefficient, k' (moles-H/atm-cm^2-s)	1.74 E-6	0.91 E-6	0.71 E-6	0.92 E-6	0.87 E-6	1.55 E-6	1.50 E-6
Exchange Probability, p_{ex}	4.8±.5 E-	3.5±.4 E-	5.3±1.7 E-	2.7±.6 E-7	2.7±.5 E-7	6.0±1.2 E-	5.7±1.1 E

Exchange results from recent NMR and Batch measurements.

- p_{ex} is the probability that an atom enters the solid.
- Better accuracy in NMR experiments
- D_2 + PdD vs H_2 + PdH exchange probabilities are different due to the different surface states.

Impact

Self Exchange has filled the gap in the fundamental understanding of hydrogen transport properties.

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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