Does Gas Loading Produce Anomalous Heat?

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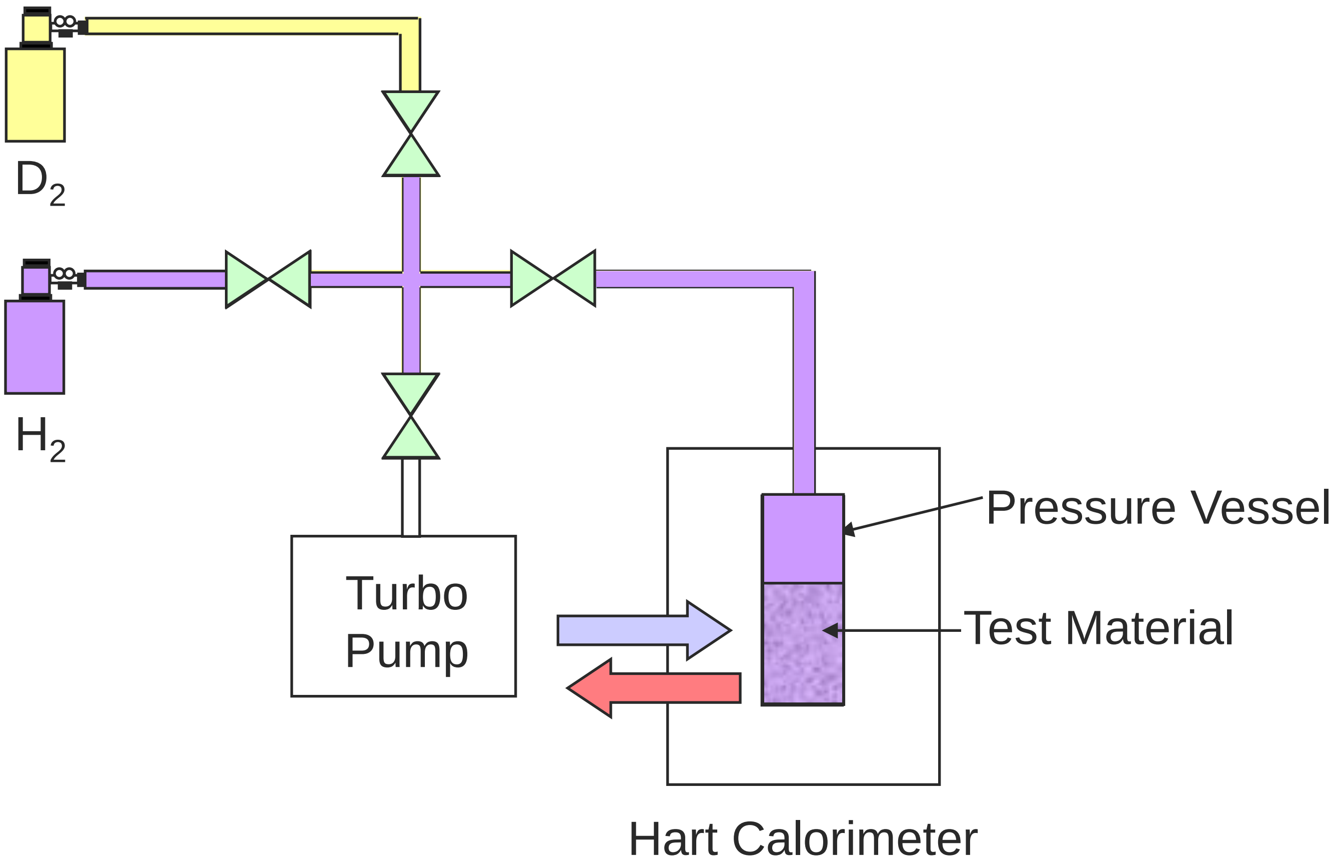
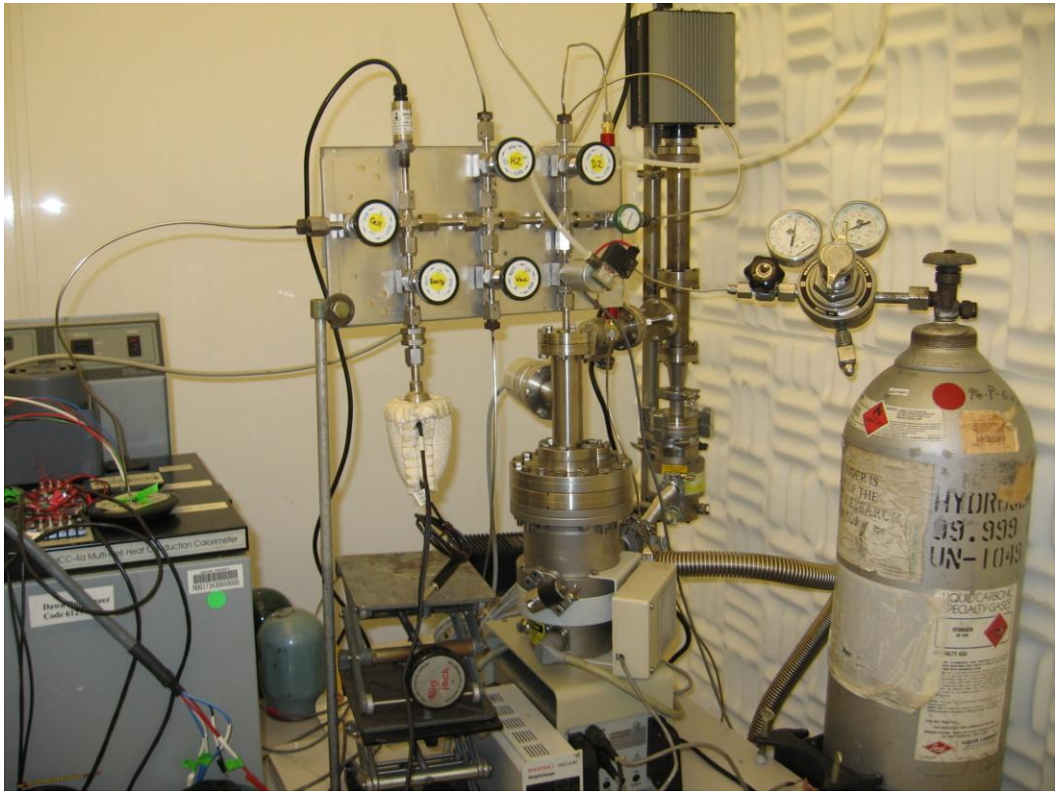
October 6, 2009

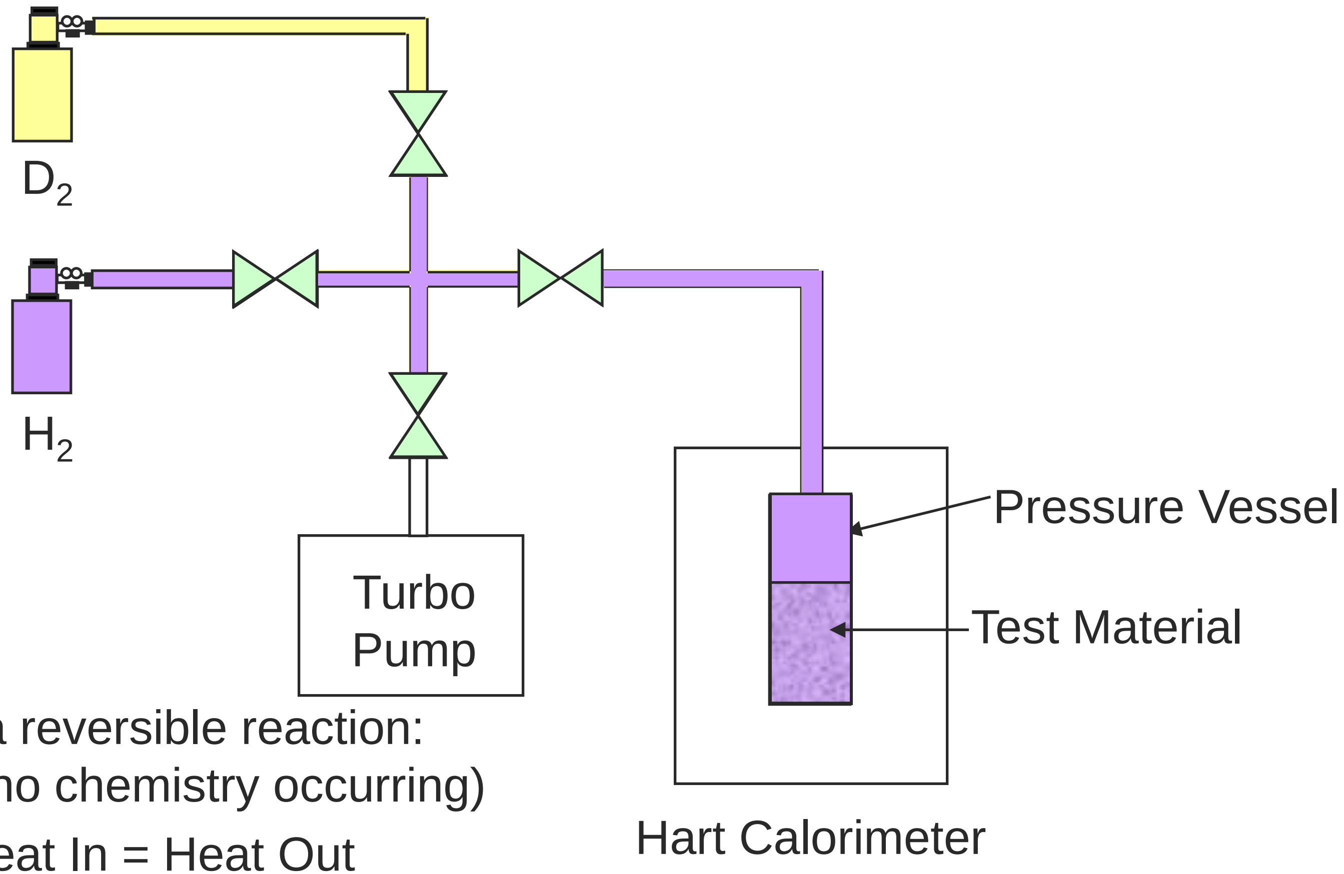
Basic gas loading experiment



Set-up in Hart calorimeter in NSI

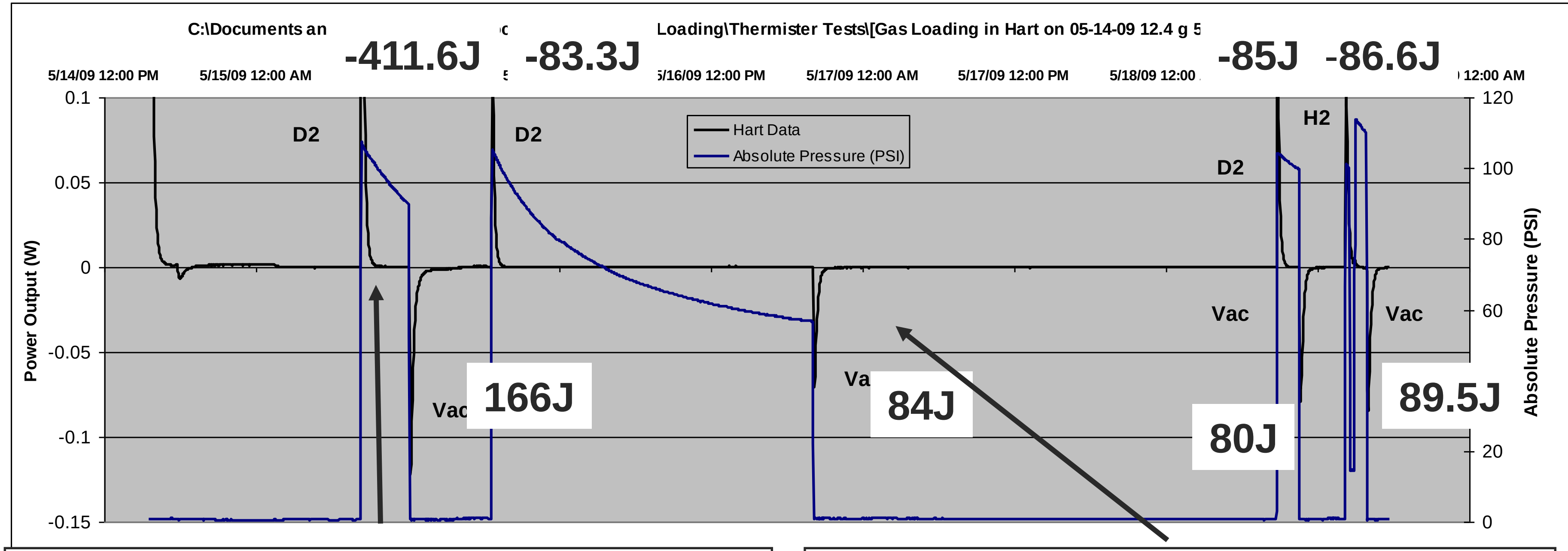


Basic gas loading experiment



- For a reversible reaction:
  (*i.e.* no chemistry occurring)
  - Heat In = Heat Out
    (Internal Control)
  - $H_2 = D_2$
    (External Control)

Loading using commercial 5% Pd/BaCO3 - Control



Exothermic:

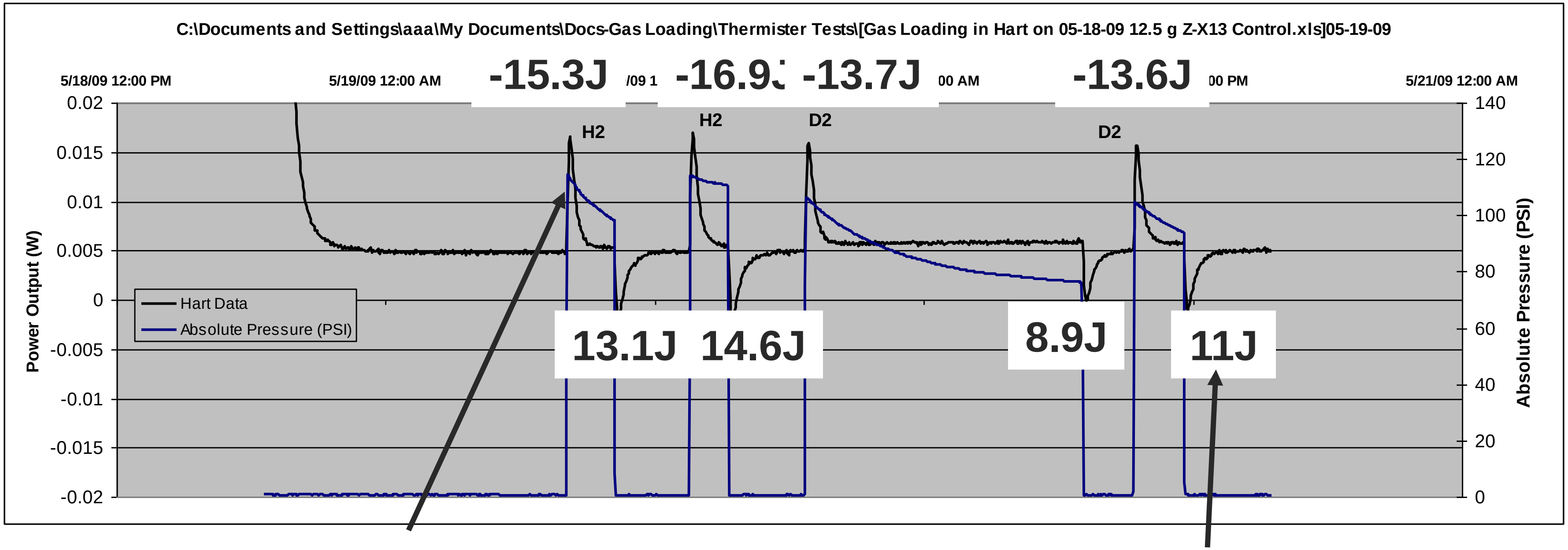
- Heat of Chemical Reaction
- Heat of D_2 uptake
- Heat of Pressurization (PV work)
- **Other Heat**

Endothermic:

- Heat of D_2 release
- Heat of Evacuation (PV work)C

- Hart calorimeter - no excess heat is observed
  - Heat In = Out; $D_2 = H_2$
  - Internal and External Controls OK

Matrix without Pd - Control



Endothermic:

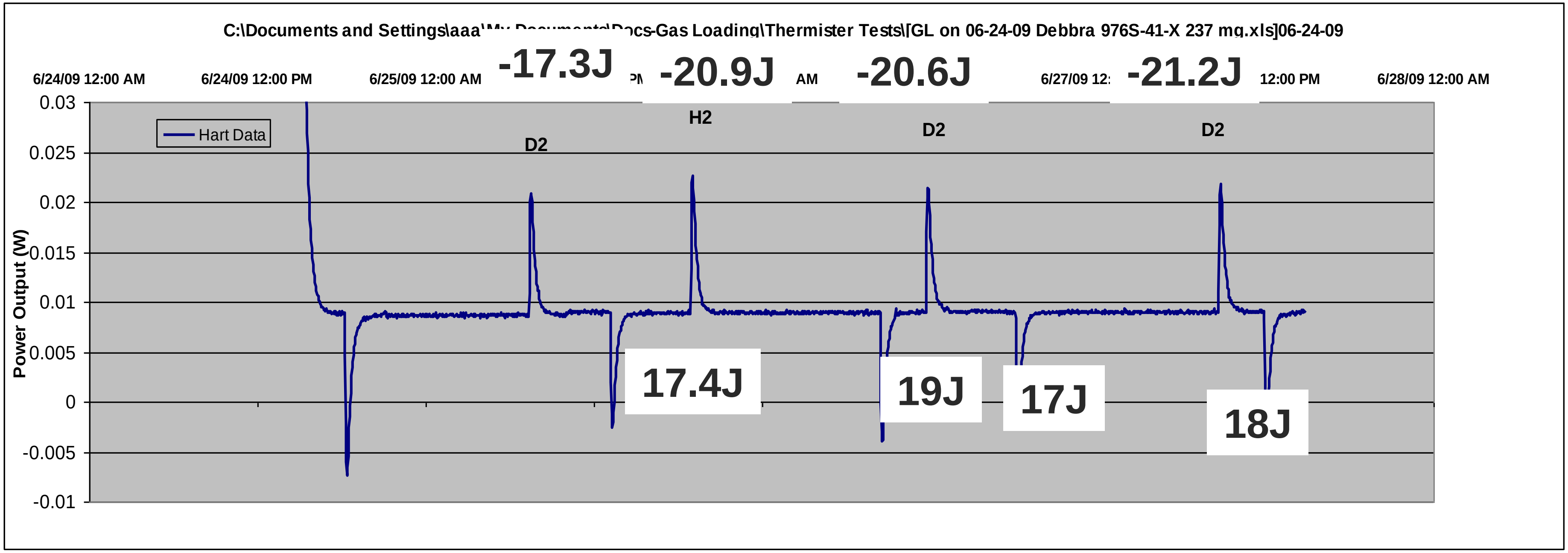
- Heat of Pressurization (PV work)

Endothermic:

- Heat of Evacuation (PV work)

- Hart calorimeter- no excess heat is observed
  - Heat In = Out; $D_2 = H_2$
  - Internal and External Controls OK

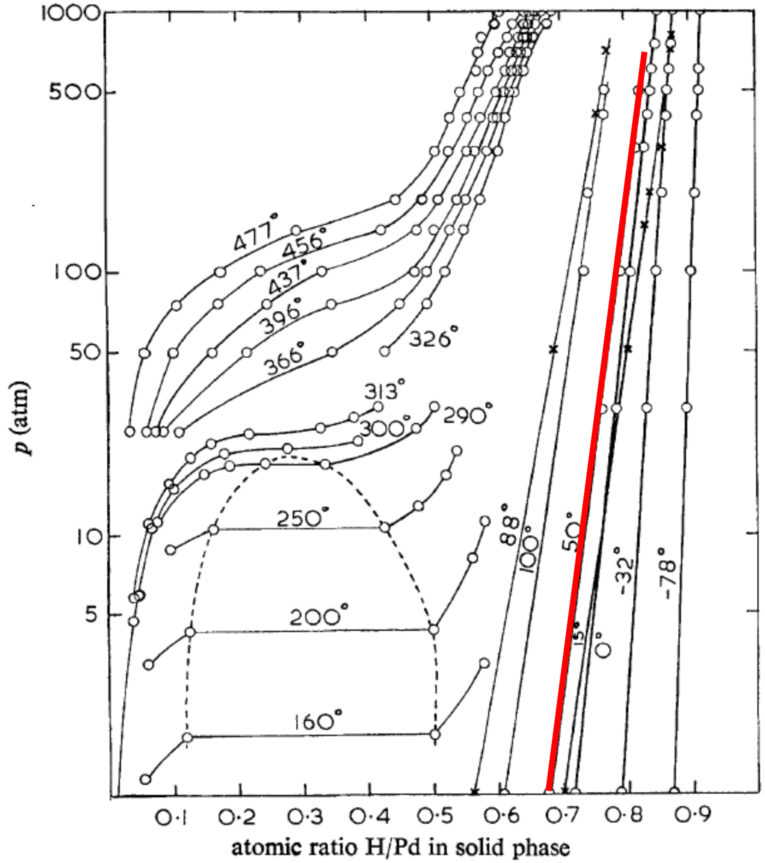
Loading using Pd/Graphite Paper



- Hart calorimeter- no excess heat is observed
  - Heat In = Out; $D_2 = H_2$
  - Internal and External Controls OK

Tying Gas Loading to Electrolytic Loading

- Hydrogen diffusin
- Because of this c 0.5-0.7 parts hydrogen
- Generally very hi um to uptake hydrogen ach PdH_1
- In 1908, Paal anc ium black prepared with hy



From: P.L. Levine and K.E. Weale, "The Palladium + Hydrogen Equilibrium at High Pressures and Temperatures", *Transactions of the Faraday Society*, **56** (1960) 357-362.

Literature Results – Particle Size

Certain size particles (< 2 nm) take-up hydrogen 1:1

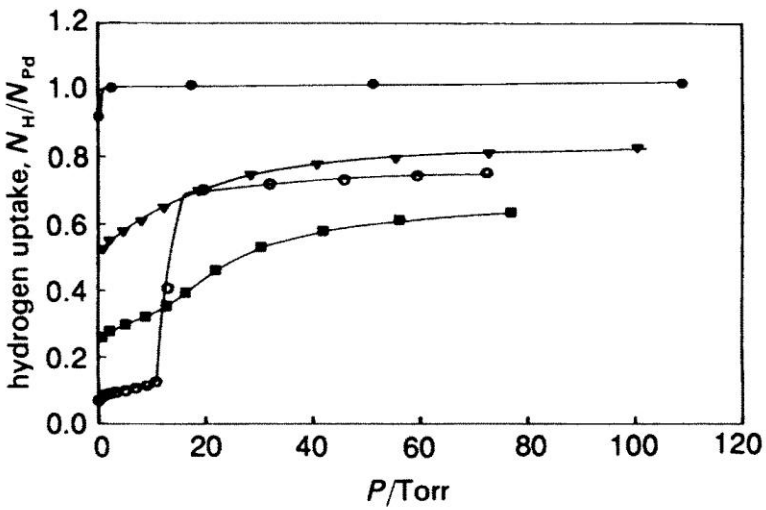


Fig. 1 Uptake isotherms for sorption of hydrogen on Pd/Al_2O_3 sample at 298 K: ○, 2% $Pd(N)/Al_2O_3$; ■, 2% $Pd(Cl)/Al_2O_3$; ▽, 1% $Pd(Cl)/Al_2O_3$; ●, 0.5% $Pd(Cl)/Al_2O_3$

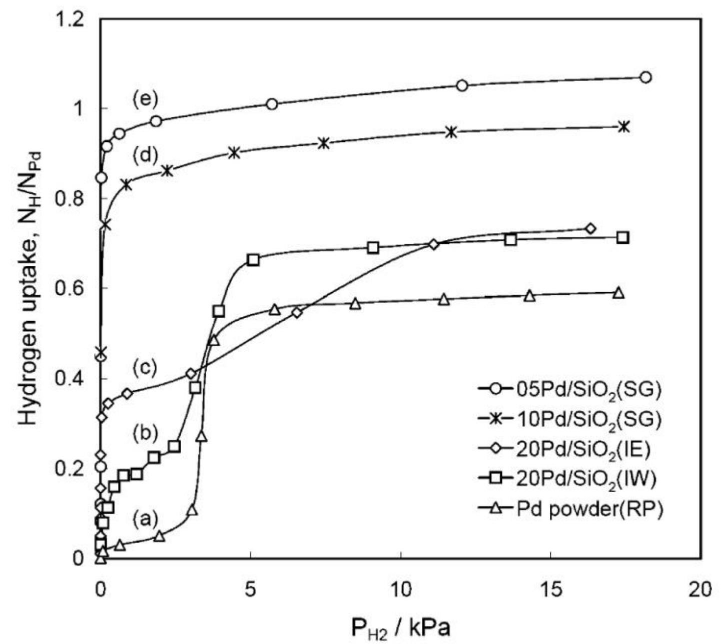


Figure 1. Adsorption isotherms of hydrogen uptake at 313 K for different palladium samples: (a) Pd powder (RP); (b) $20Pd/SiO_2$ (IW); (c) $20Pd/SiO_2$ (IE); (d) $10Pd/SiO_2$ (SG); and (e) $05Pd/SiO_2$ (SG).

From: Shu-Chin Chou, Shu-Hui Lin, and Chuin-Tih Yeh, "Isosteric Heat of Sorption of Dihydrogen on Alumina-supported Palladium", *J. Chem. Soc. Faraday Trans.,* **91**(1995) 949-951.

From: Sheng-Yang Huang, Chin-Da Huang, Boh-Tze Chang, and Chuin-Tih Yeh, "Chemical Activity of Palladium Clusters: Sorption of Hydrogen", *J. Phys. Chem. B*, **110** (2006) 21783-21787.

Literature Results – Particle Size

Certain size particles (< 2 nm) take-up hydrogen 1:1

Preparation	Estimated Particle Size (nm)	Heat of Hydrogen Adsorption (kJ/mole)	Ratio H:Pd @ 0.2 Atm
Pd Powder	9	94	0.55
1.86% Pd/SiO_2 (IW)	~4	92	0.68
10% Pd/SiO_2 (SG)	1.1	131	0.9
5% Pd/SiO_2 (SG)	1	183	1.05

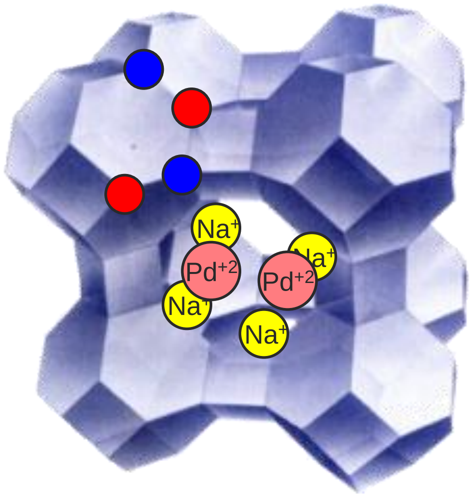
Data from: Sheng-Yang Huang, Chin-Da Huang, Boh-Tze Chang, and Chuin-Tih Yeh, “Chemical Activity of Palladium Clusters: Sorption of Hydrogen”, *J. Phys. Chem. B*, **110** (2006) 21783-21787.

Hypothesis for Excess Heat

- Particle size is important
  - <2 nm allows rapid loading to Pd:D 1:1
  - Need isolation to keep from sintering – used Zeolites

Type A Zeolite

Type X Zeolite

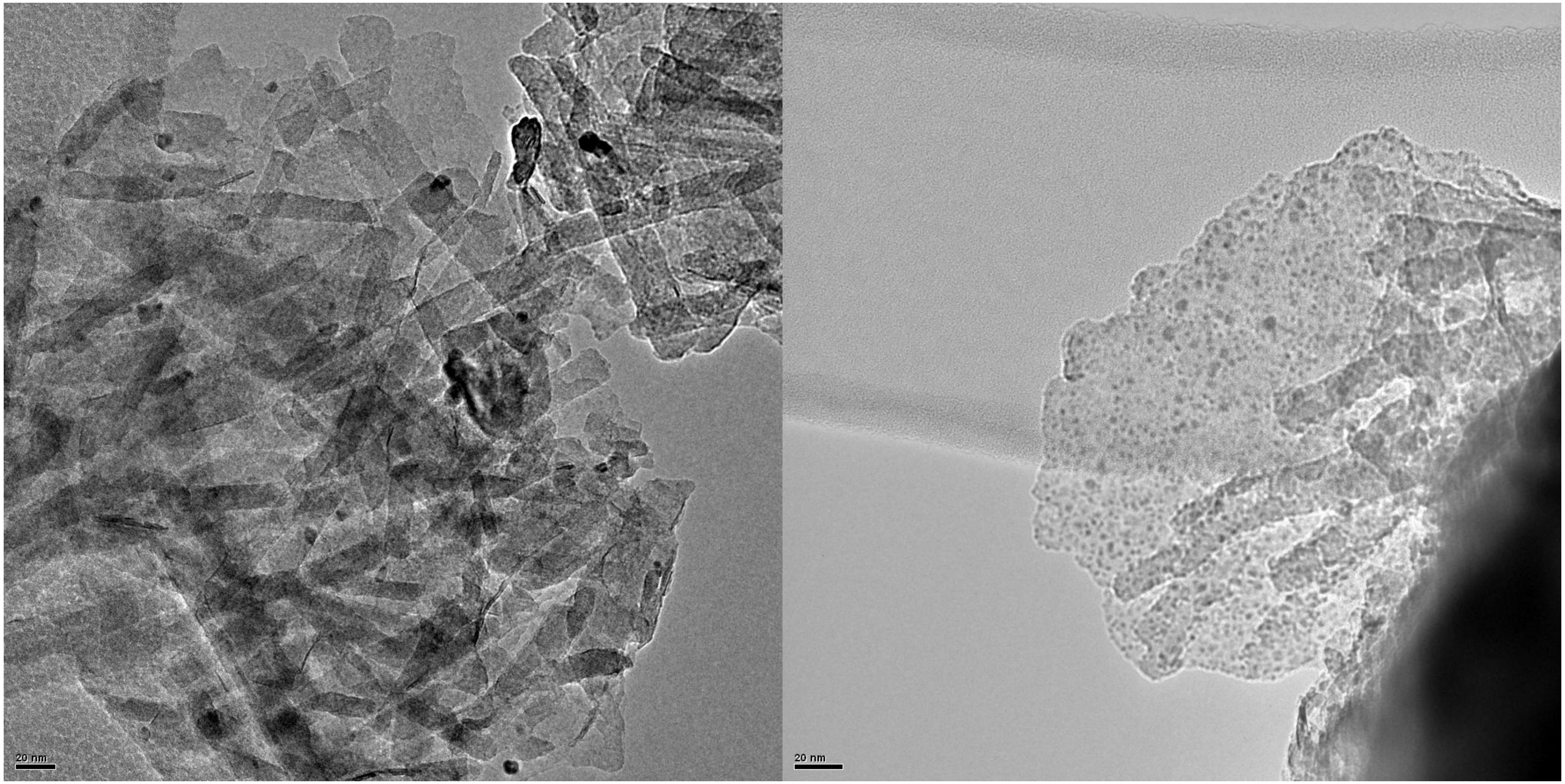


$Na_{88}Al_{88}Si_{104}O_{384}$

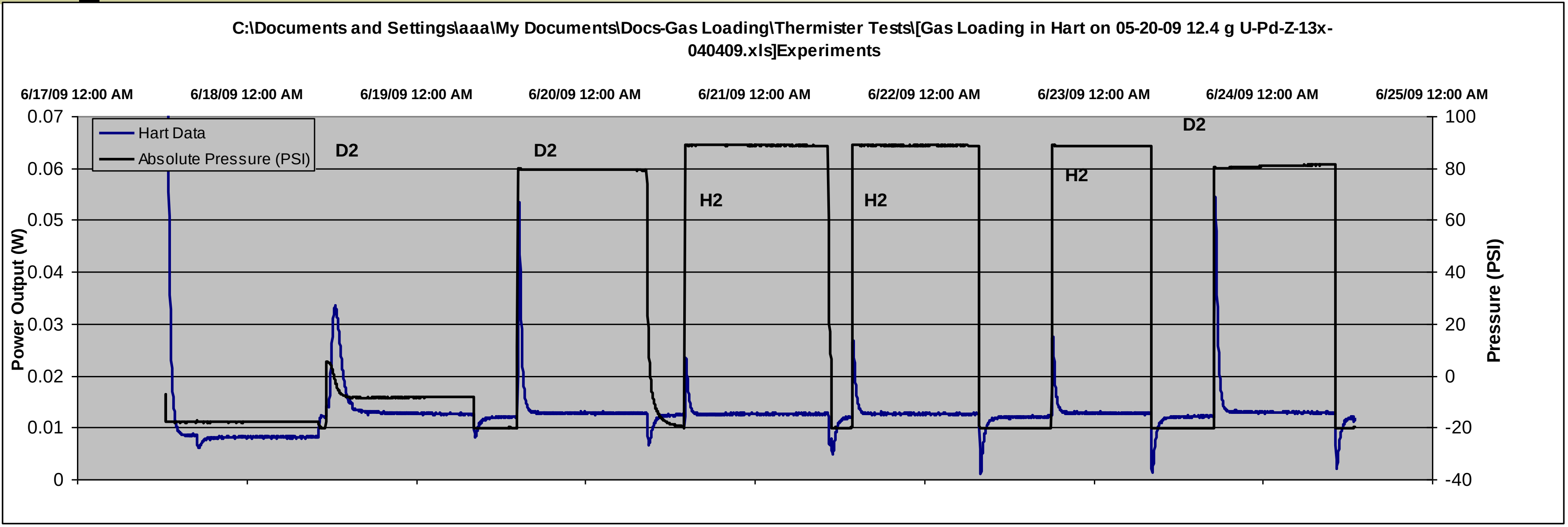
From: http://www.molecularsieve.org/Zeolite_Molecular_Sieve.htm

Characterization of Particle Size

- Not readily visible via TEM due to matrix



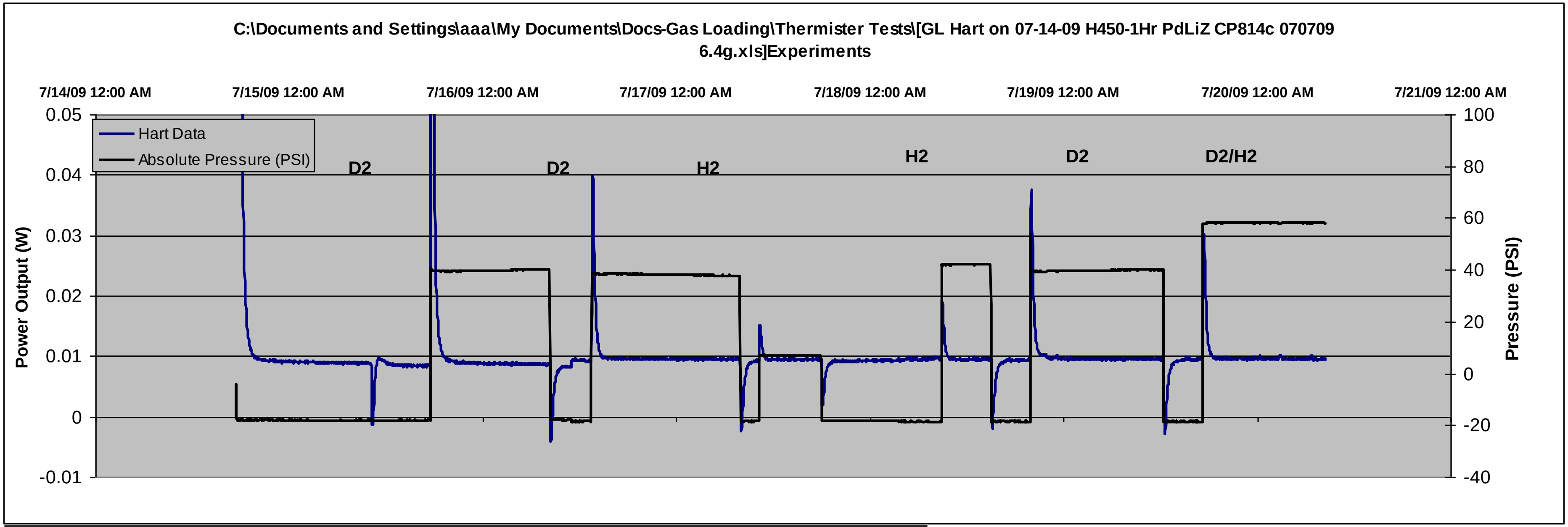
Matrix with Pd – 0.5% Pd on NRL Matrix



Heat from 2nd D2 pressurization	-77.6
Endothermic heat from 2nd D2 evacuation	19.7
Heat 3rd H2 pressurization	-26
Endothermic heat from 3rd H2 evacuation	31.5

- Hart calorimeter- no excess heat is observed
  - Heat In ≠ Out; $D_2 \neq H_2$
  - Internal and External Controls NOT OK for D_2 but OK for H_2

Matrix with Pd – 1% Pd on NRL Matrix



Measured Heat Deuterium pressurization at 17:35 on 07/15/09	-154.7
Measured Heat Deuterium removal at 8:21 on 07/16/09	22.4
Measured Heat of Deuterium pressurization at 13:48 on 07/16/09	-43.1
Measured Heat of Deuterium removal at 7:58 on 07/17/09	20.9
Measured Heat Hydrogen pressurization at 10:17 on 07/17/09	-7.2
Measured Heat of Hydrogen removal at 18:02 on 07/17/09	13.5
Measured Heat Hydrogen pressurization at 8:54 on 07/18/09	-12.9
Measured Heat Hydrogen removal at 15:04 on 07/18/09	20
Measured Heat Deuterium pressurization at 19:54 on 07/18/09	-46.5
Measured Heat Deuterium removal at 12:29 on 07/19/09	20.1
Measured Heat Hydrogen/Deuterium Mix pressurization at 17:54 on 07/19/09	-28.8

- Hart calorimeter- no excess heat is observed
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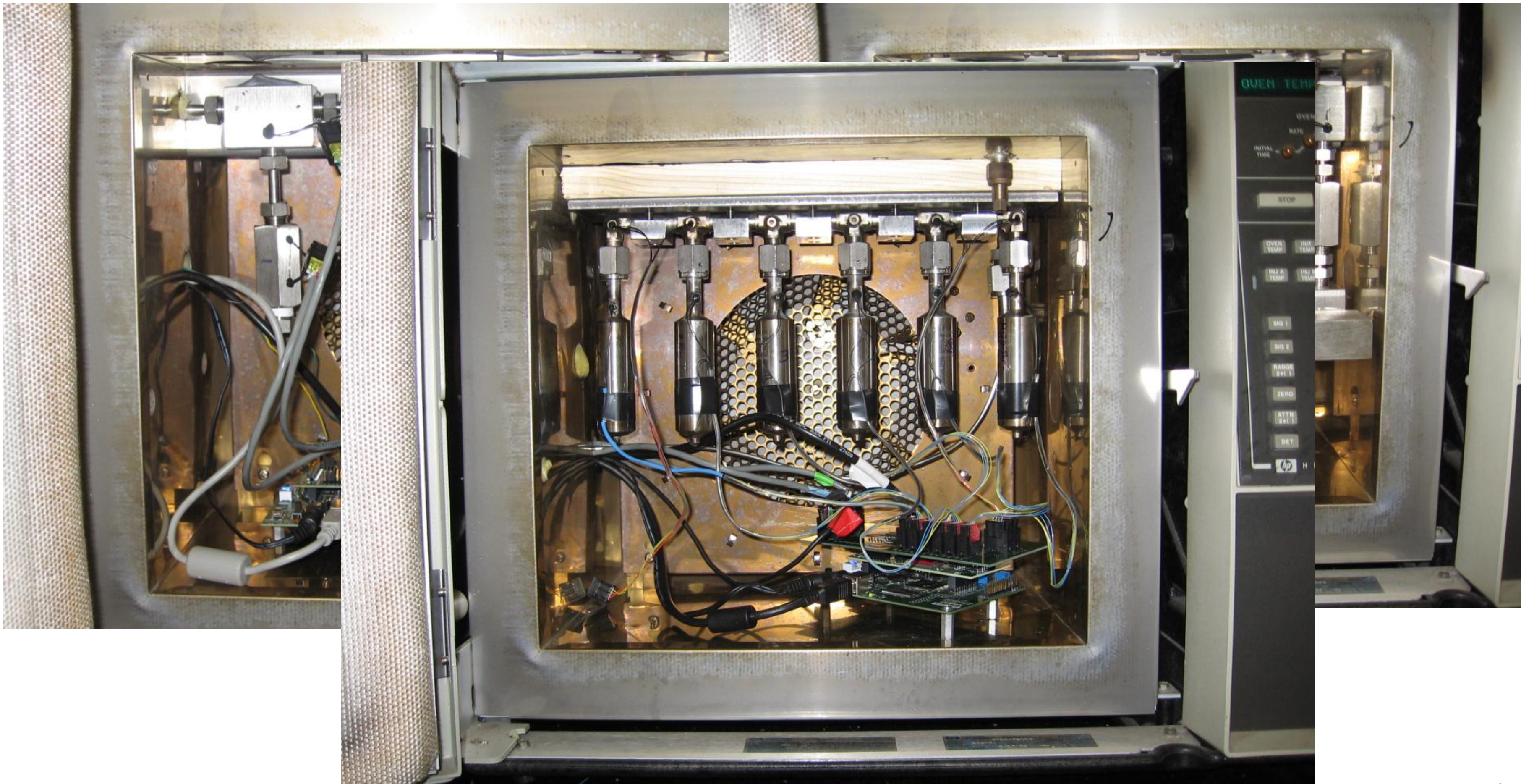
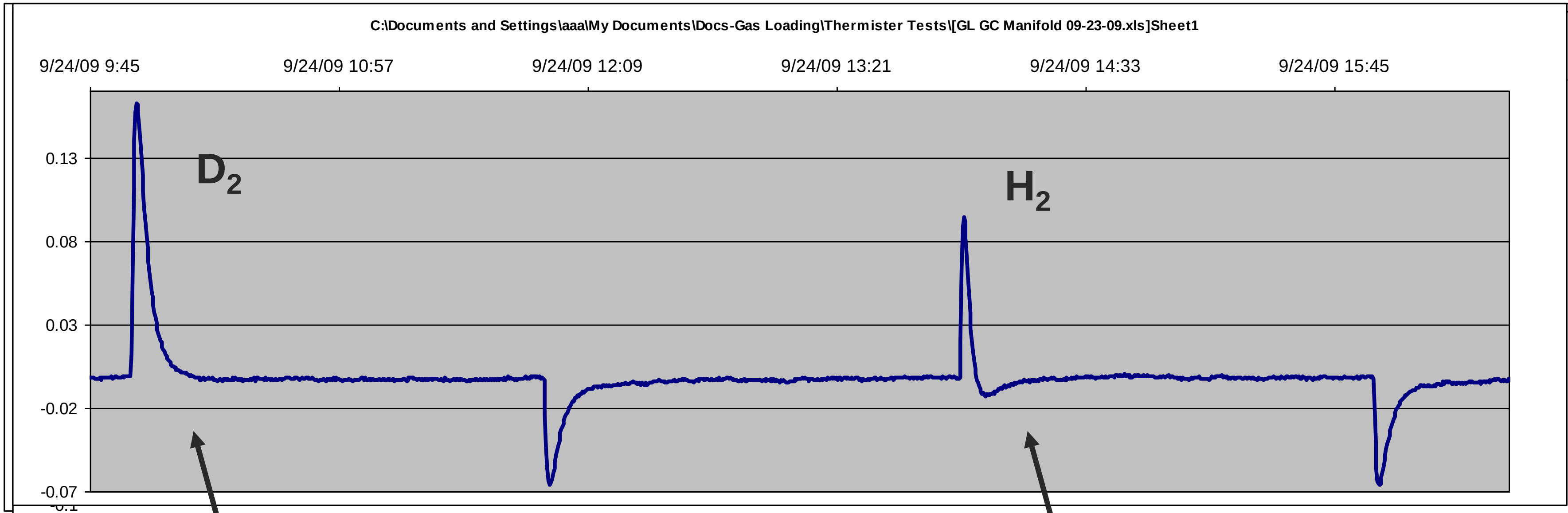
  - Internal and External Controls NOT OK for D_2 but OK for H_2

Examples of set-up in GC Oven



Closer Look of a Run in the GC

Various matrices



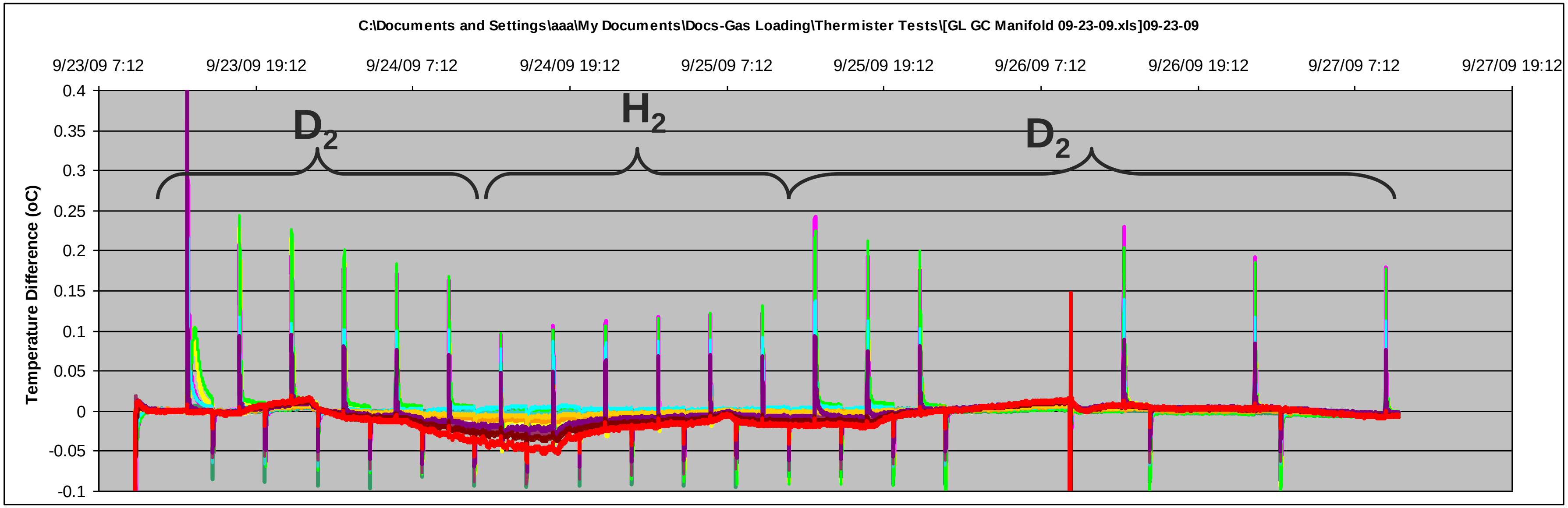
Heat of Chemical Reduction
Heat of D_2 uptake
Heat of Pressurization (PV work)
Other Heat

Heat of H_2 uptake
Heat of Pressurization (PV work)
Other Heat

- **Results from GC:**
  - Excess <u>other</u> heat is observed
  - Heat In ≠ Out for D_2 but equal for H_2, $H_2 \neq D_2$

Closer Look of a Run in the GC

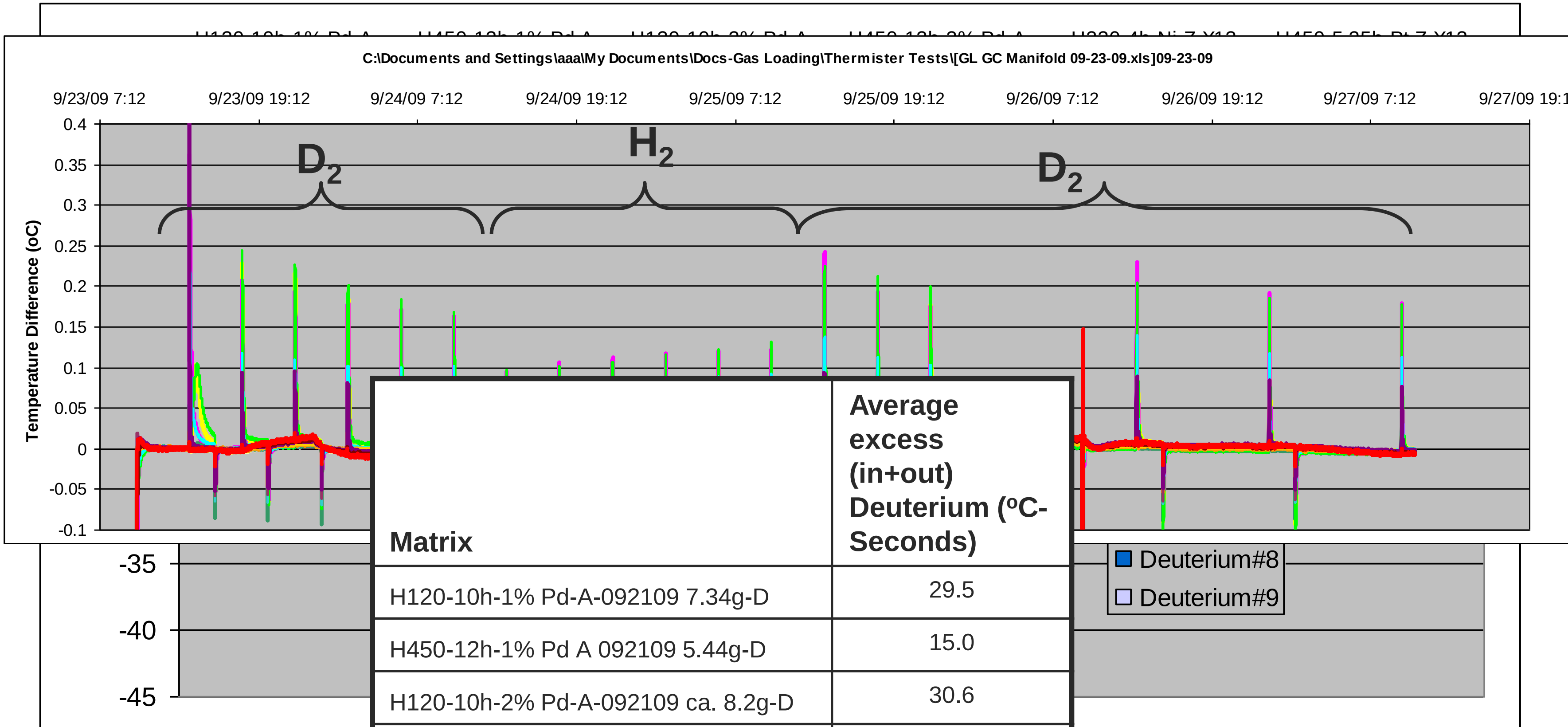
Various matrices



- **Results from GC:**
  - Excess <u>other</u> heat is observed
  - Heat In ≠ Out for D_2 but equal for H_2, $H_2 \neq D_2$

Closer Look of a Run in the GC

Reproducibility of Depressurizations



Matrix	Average excess (in+out) Deuterium (°C-Seconds)
H120-10h-1% Pd-A-092109 7.34g-D	29.5
H450-12h-1% Pd A 092109 5.44g-D	15.0
H120-10h-2% Pd-A-092109 ca. 8.2g-D	30.6
H450-12h-2% Pd-A-092109 6.92g-D	9.4
H230-4h-Ni-Z-X13-082709 5.0g-D	2.2
H450-5.25h-Pt-Z-X13-090409 5.61g-D	5.7

But

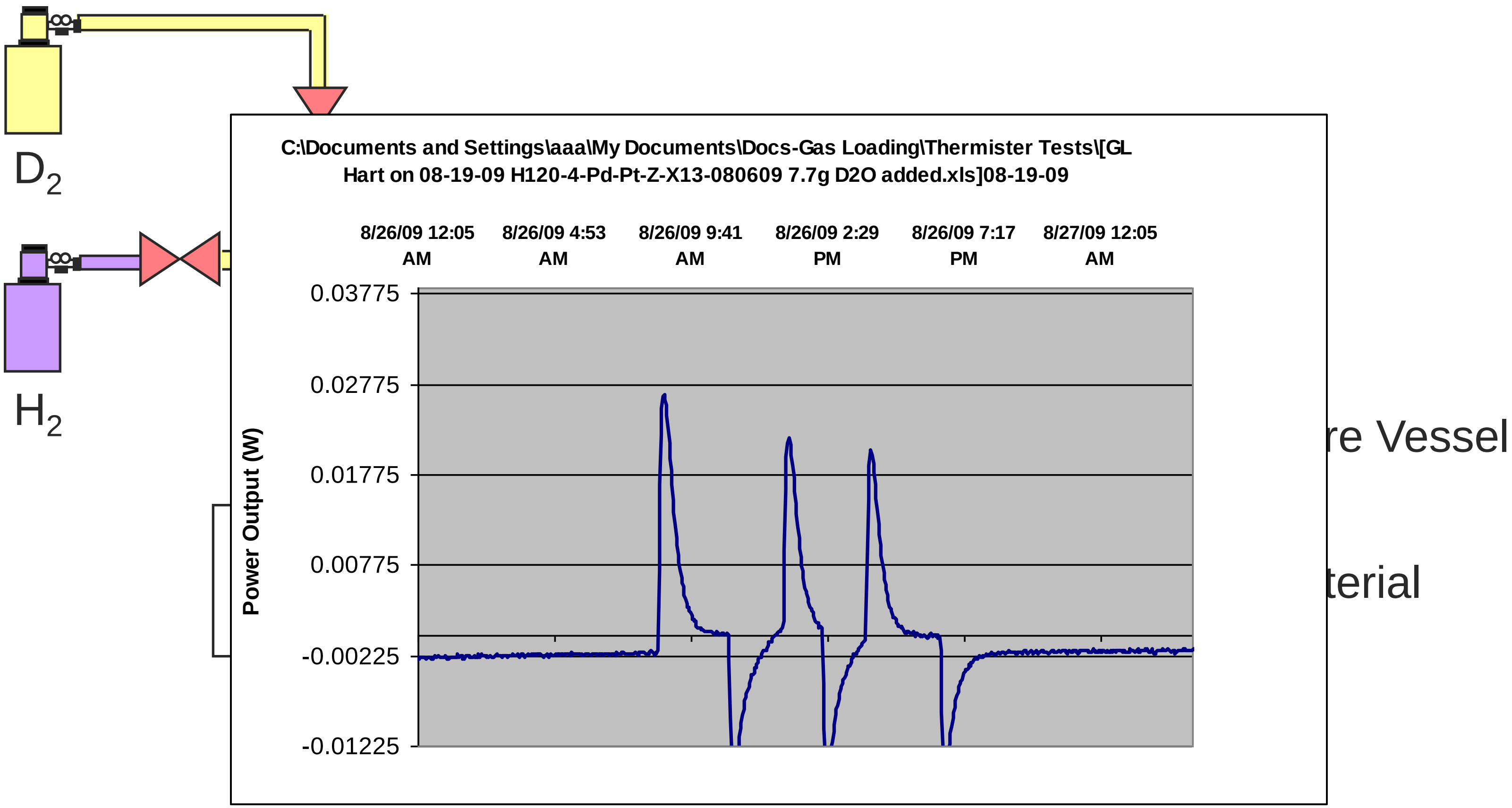
Is there an explanation for the "other" heat repeatedly observed?

Possible Sources of Heat #1

Chemical energy in the deuterium but not in the hydrogen

- Example O_2
- Argue against:
  - Increase pressure – no proportionate increase in heat
  - Other palladium particles show no effect
    - Hypothetically could be dependant on particle size but this is not supported chemically

Recycling of Fill Gas



Initial Pressurization to 125 PSI	-48.9J
Recycle #1 to 122 PSI	-38.7J
Recycle #2 to 120 PSI	-31.3J

Possible Sources of Heat #2

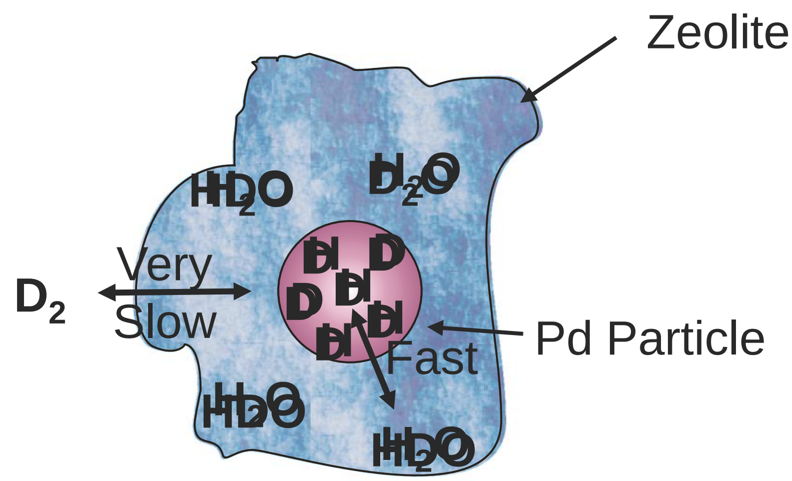
Mechanism consistent with some observations

D_2

- Chemical exchange of D_2 with H2O

  $D_2 + H_2O \rightarrow HD + HDO$ -4.13 kJ/mole

  $D_2 + H_2O \rightarrow H_2 + D_2O$ -8.71 kJ/mole

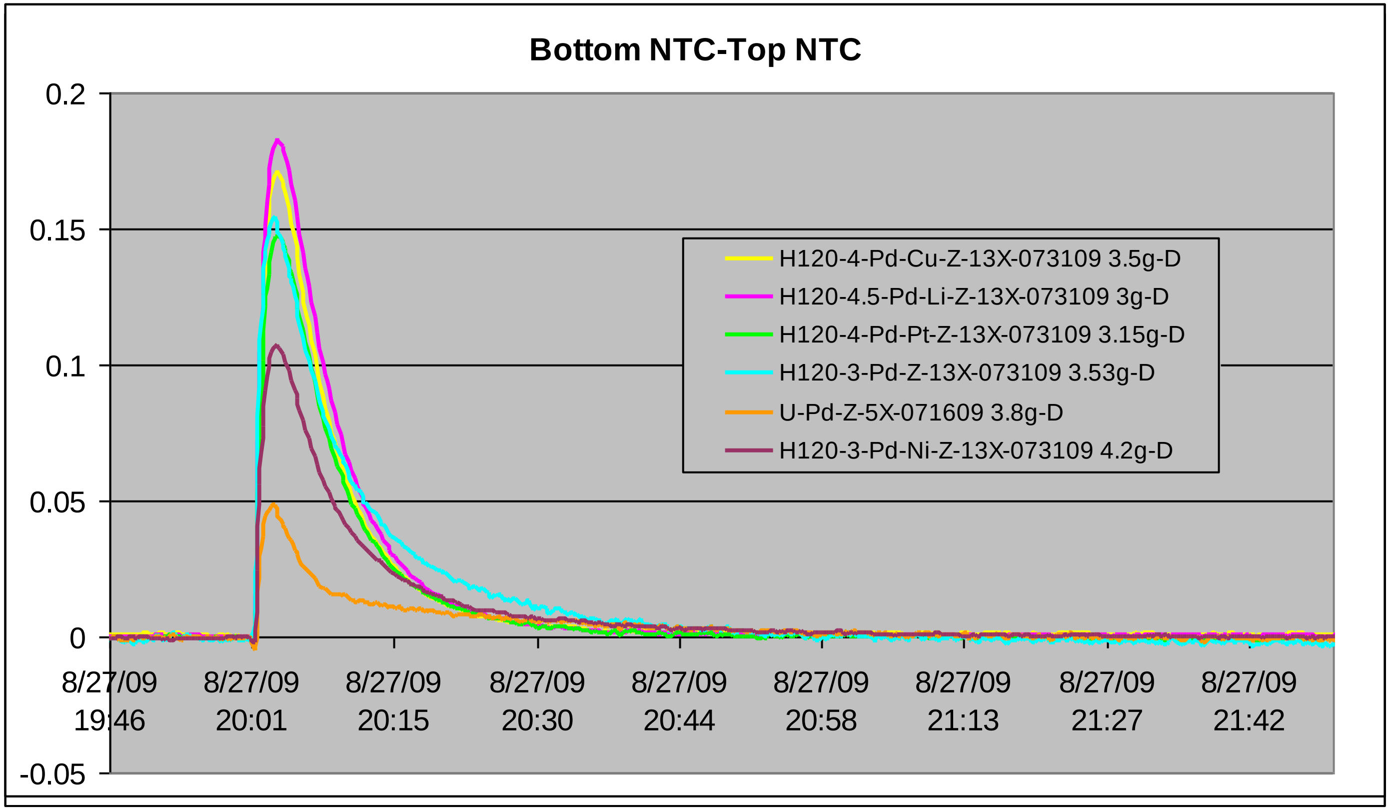


- Heat produced but no signature of H-D exchange in gas phase
  - Signature only upon removal of residual gas in Pd particle
    - Observed – D_2 gives some HD and H_2 gives some HD
- Calculations suggest for the amount of Pd present and going to D_2O (worse case)
  - Ignoring the spillover effect, only 7J heat available
- Using D_2O saturated Zeolite should see less heat with H_2
  - Observed – can be endothermic

Possible Sources of Heat #2

Some observations

- Chemical exchange of D_2 with H2O
  - $D_2 + H_2O \rightarrow HD + HDO$ -4.13 kJ/mole
  - $D_2 + H_2O \rightarrow HD + D_2O$ -8.71 kJ/mole



GL GC Manifold 08-25-09 at 70C then 29C.xls

Why Consider D-H Exchange as a Possible Source of Heat?

- Chemical exchange of D_2 with H2O
  - $D_2 + H_2O \rightarrow HD + HDO$ -4.13 kJ/mole
  - $D_2 + H_2O \rightarrow HD + D_2O$ -8.71 kJ/mole

- Can explain:
  - Internal controls – In <> Out
  - Why D_2 (exothermic) <> H_2 (endothermic)
- Effect still pesent with some “dry” matrices
  - Make water in initial reactions
    - $PdO + D_2 \rightarrow PdDx + D_2O$
    - D_2O + Matrix → Hydrated Matrix
- Many pressurization/depressurization cycles decreases contribution

Conclusions

- Preparing Pd nano-particles inside Zeolites is reproducible and easy
  - Zeolites appear to provide Pd particles of the correct dimensions
- Interesting heat pattern was measured by two independent principles
  - Many iterations with unexpected heat present
  - Heat in presence of Deuterium but not Hydrogen
- Chemical effect due to Hydrogen-Deuterium exchange may account for some of the anomalous heat
  - Hydrogen may not be best control
  - Requires all the species present – Zeolite, Pd catalyst, water. D_2/H_2
  - But simple calculations do not account for all the heat observed
- Although chemistry of Zeolites is complex, because of the ease of preparation, further exploration of these systems is warranted

Acknowledgements

Funding from DTRA is gratefully acknowledged. The views, opinions, and/or findings contained in this presentation are those of the presenter and should not be interpreted as representing the official views or policies, either expressed or implied, of the Naval Research Laboratory or the Department of Defense.

Questions

Publication Approval Number 09-1226-3219