SAND2017-9292C

Compact Determination of Hydrogen Isotopes and Helium

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2nd Asia-Pacific Symposium on Tritium Science

Pleasanton, CA

September 2017

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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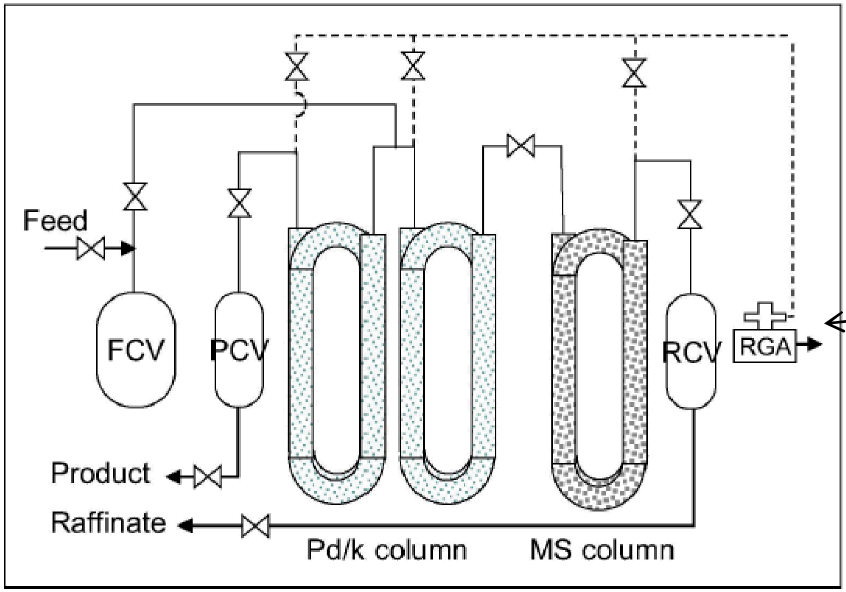
Tritium and helium-3 operations

- ^{1}H, ^{2}H, ^{3}H, ^{3}He, ^{4}He can all get mixed together during generation, storage, use, and recycling
- It can be useful to know what is present
- Mass spectrometry requires bulky vacuum chambers and pumps that get contaminated with tritium, exhaust dilute tritium, consume kW of power
- Limits number of measurement points

Example: isotope separation

- TCAP hydrogen isotope separation process developed by Savannah River National Laboratory
- Flows gas mixture repeatedly through sorbent columns
- More composition monitors would be useful

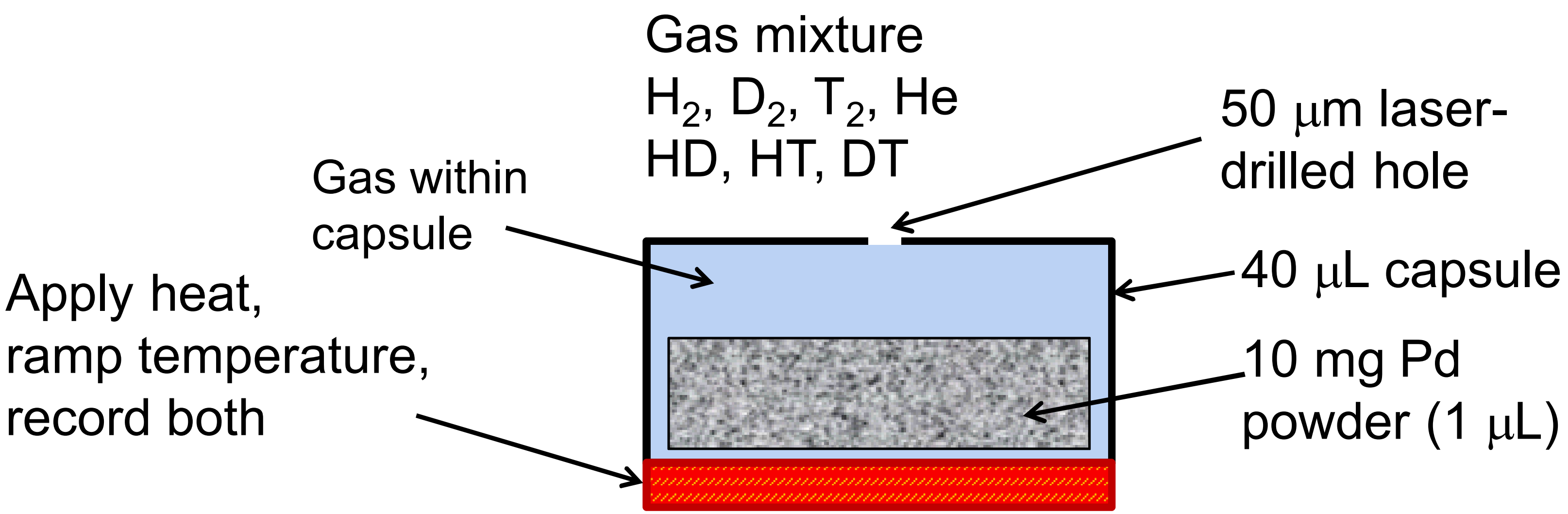


Replace this, or monitor in more locations

L. K. Heung *et al.*
Fusion Sci Tech 60 1331 (2011)

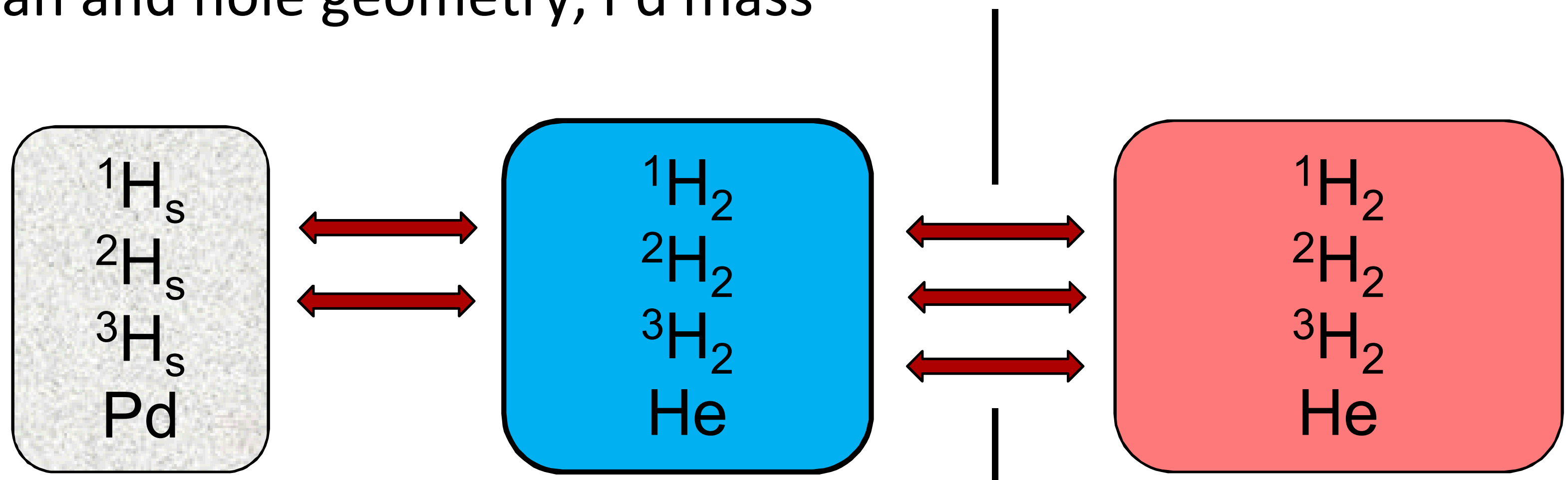
Detection concept

- Absorption of H, D, T by Pd is temperature, pressure dependent; reversible
- Absorption releases heat, desorption absorbs heat
- Flow restriction controls local gas environment
- He buildup near Pd affects H, D, T partial pressure
- Ignoring diatomic speciation, He isotope



Predictive modeling

- 7 variable concentrations, 7 transport equations
- Inputs include outside gas concentration, temperature vs. time, pan and hole geometry, Pd mass



Only H absorbs,
by first-order rate law

All gases:
Pressure-driven flow
Diffusion

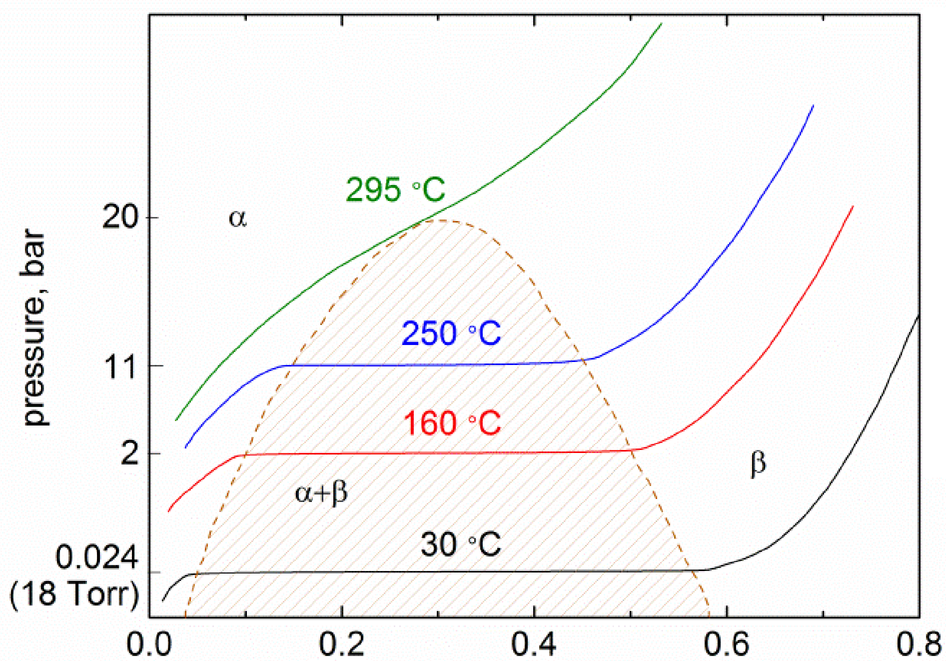
Fixed concentration,
temperature

Mixed diatomic isotopologues accounted for implicitly

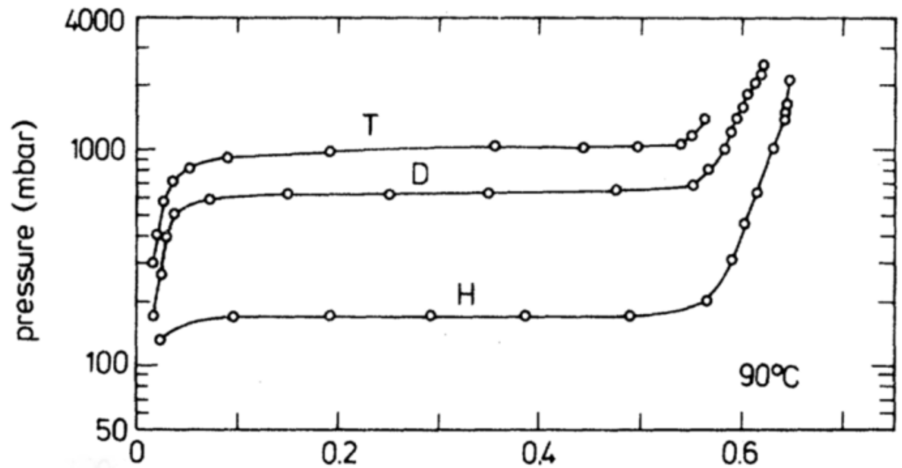
Account for heat capacities, thermal expansion of gas in pan

Prediction of ${}^{i}H_{eq}$

- Traditional “PCT” experiment holds temperature constant and ramps pressure



A.G. Knapton
Plat. Met. Revs 21:44 (1977)



Atomic ratio H:Pd
Lässer and Klatt
Phys. Rev. B 26 3517

Math model of PCT curve

- Equate solid and gas chemical potentials (*i* or *j* = H, D, or T)
- Gas phase: standard state term, ideal pressure-dependent term
  - μ^0 captures translational, vibrational, rotational partition functions and bond dissociation energy (Lässer and Powell, Phys Rev B 34 578 1986)
- Solid phase: standard state term, concentration-dependent terms
  - μ^0 captures absorption enthalpy, vibrational modes
  - "Excess" chemical potential includes elastic, electronic effects
    - Polynomial fit to beta-phase PCT experiments, intersecting at zero

$$\mu_{ij}^{g} = \mu_i^s + \mu_j^s$$

$$\mu_{ij}^{g} = \mu_{ij}^{0} + RT\ln\left(P_{ij}/1\,\text{atm}\right)$$

$$\mu_i^s = \mu_i^0 + RT\ln\left(\frac{x_i}{x_v}\right) + \mu_i^{ex}$$

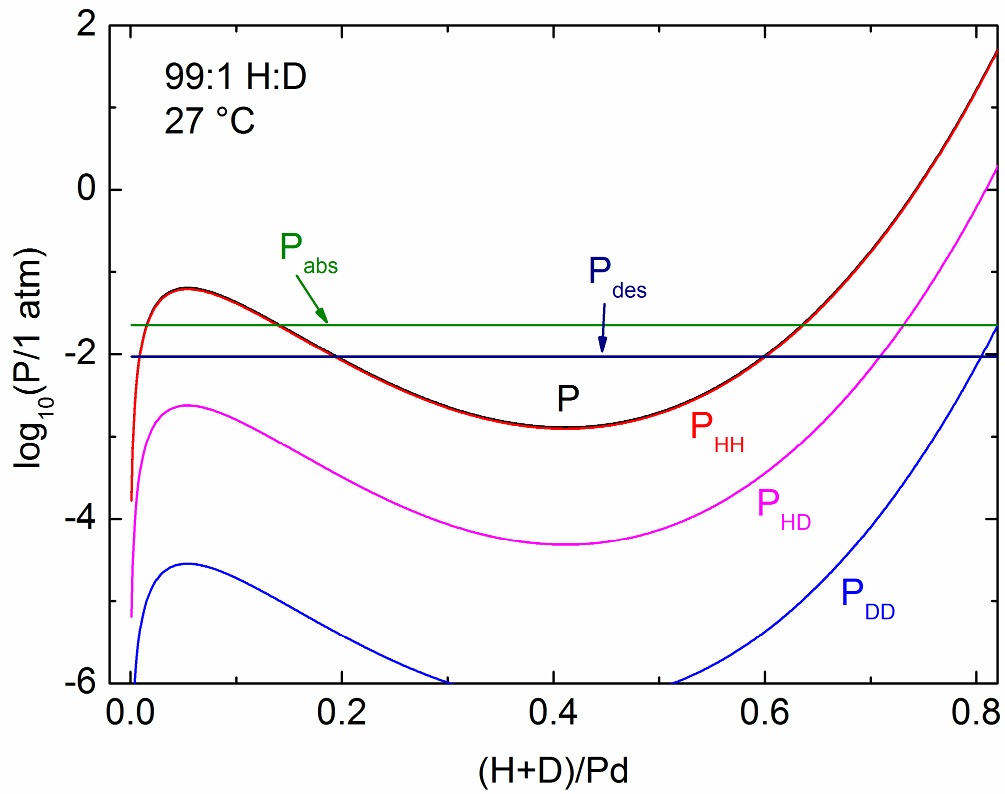
Oates, Lässer, Kuji, Flanagan
J Phys F 15(11) 2273 1985
J Phys Chem Solids 47(4) 429 1986

$$x_v = 1 - \sum_i x_i$$

$$^{i}H_{eq} = \frac{P_{ii}}{2RT} + \sum_j \frac{P_{ij}}{2RT}$$

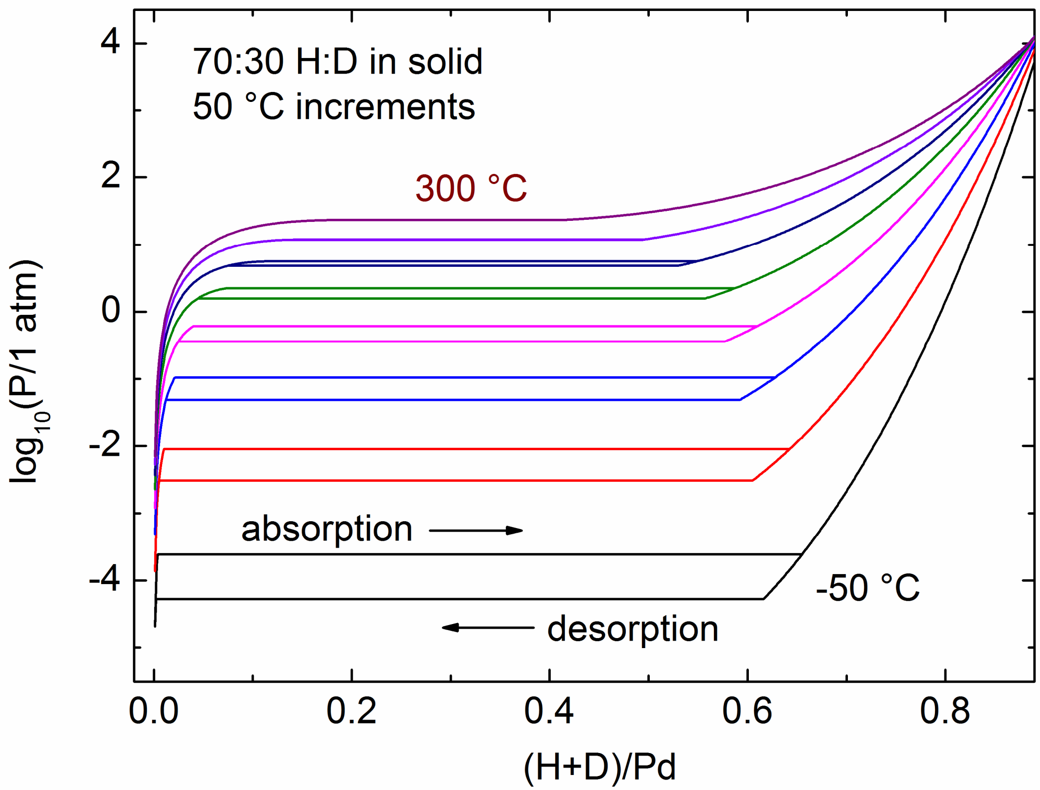
Plateau pressures

- Solve for $P_{ij}(x)$ at fixed x_H:x_D:x_T ratio
- Correlation of experimental pure-gas plateaus to peak and trough
- Maxwell construction (equal area) does not improve



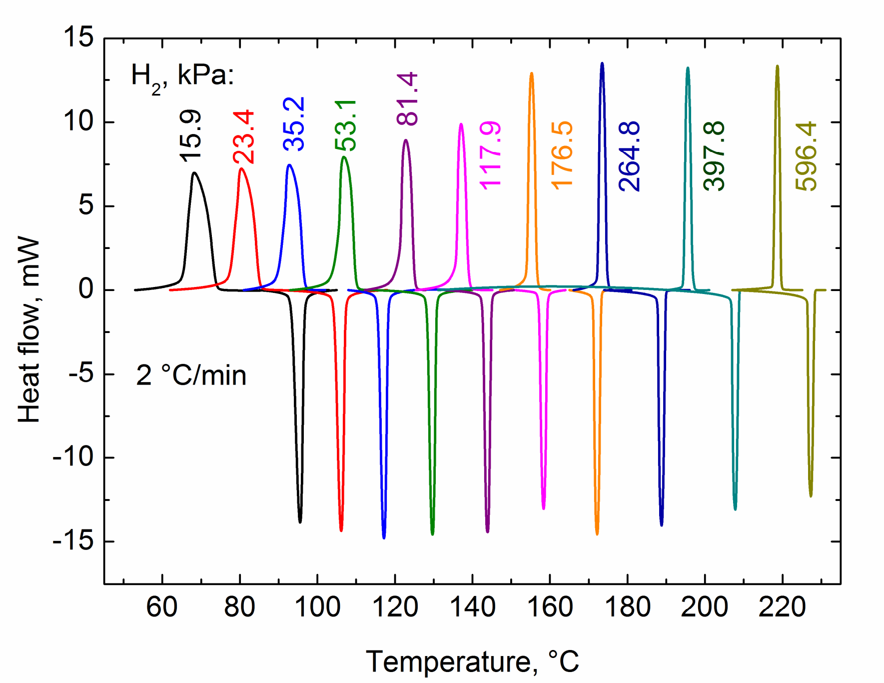
Mixed-isotope PCT curves

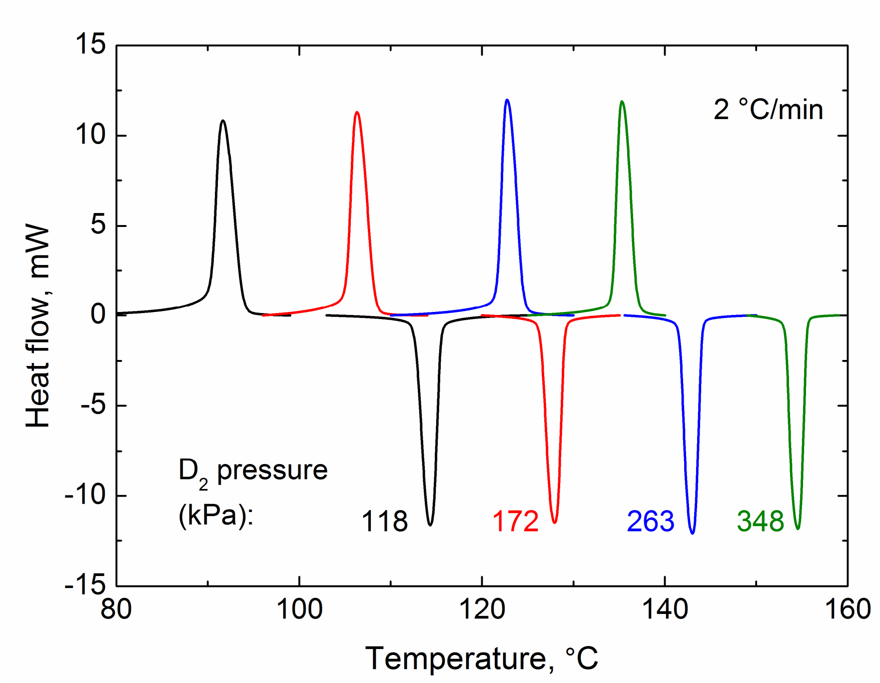
- PCT curves with absorption and desorption plateaus can be predicted for fixed isotopic ratio in solid
- Specific points can be evaluated without computing entire curve



Calorimetry in pure H_2 and D_2

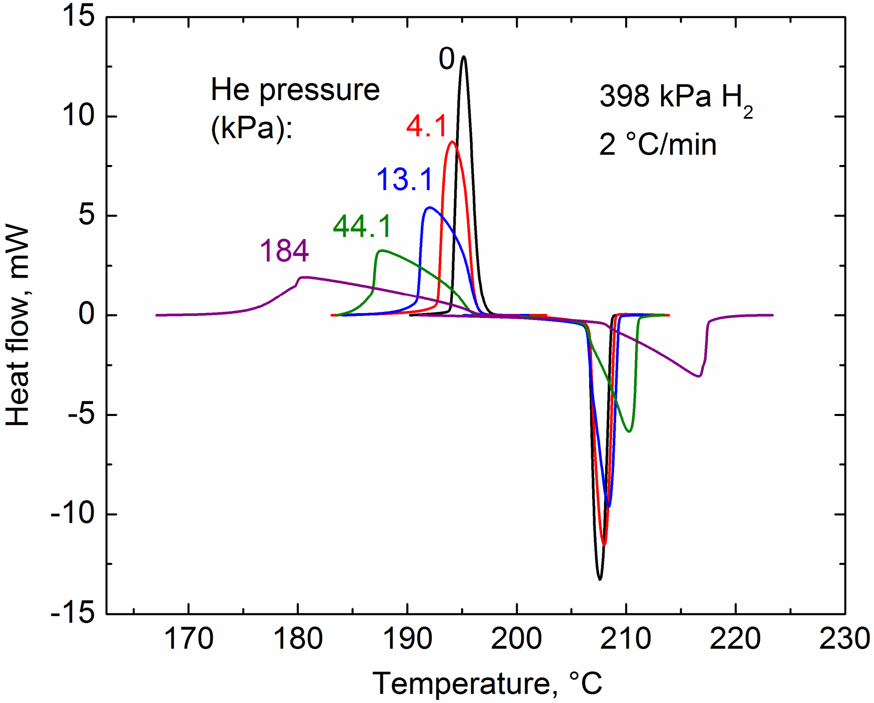
- Peak temperature depends on gas pressure, isotope

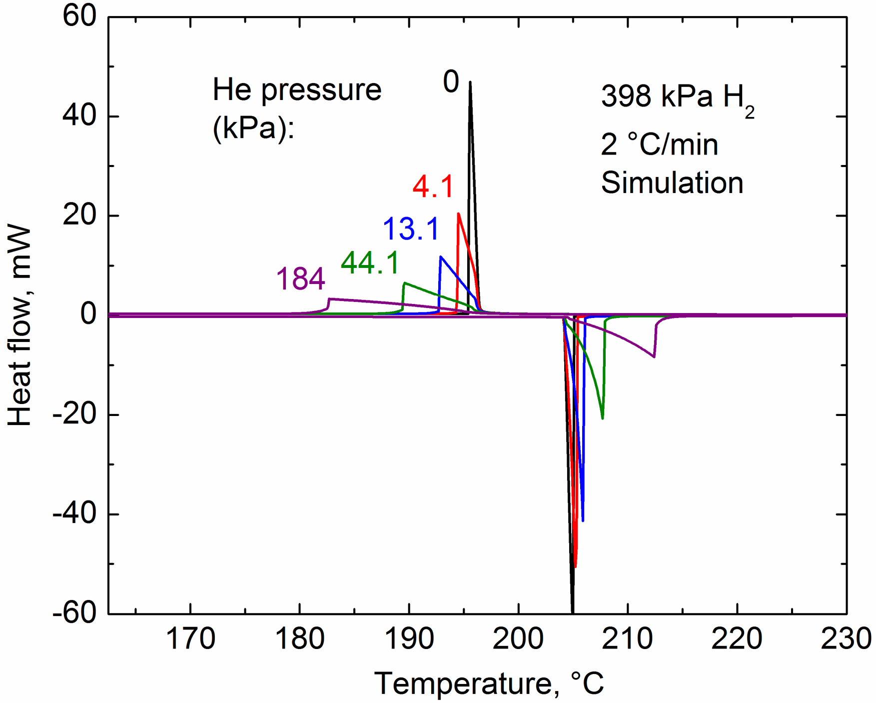




Helium smears H_2 peaks

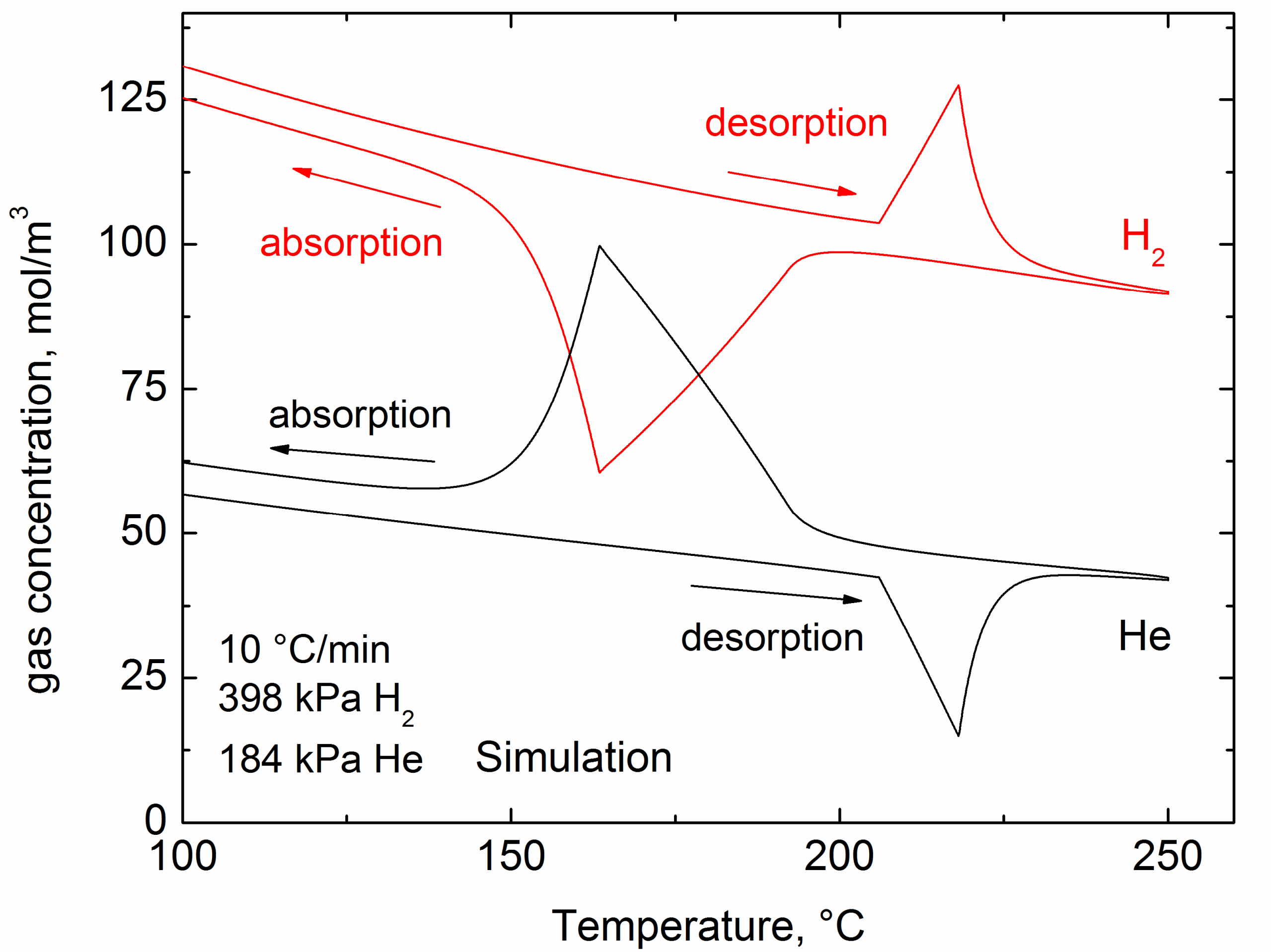
- He enters capsule along with H_2, but does not absorb
- He blanket reduces H_2 partial pressure, shifting peak temperature
- With blanket, H_2 transport is diffusion-limited through hole
- H_2 blanket creates opposite effect during desorption





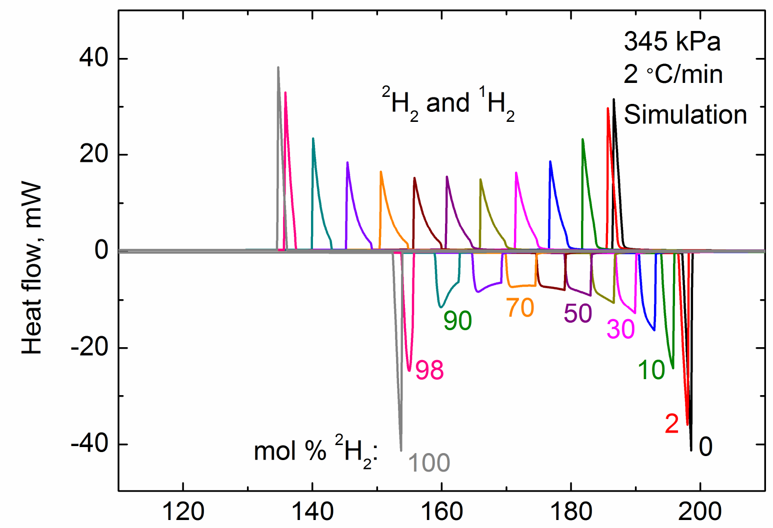
Modeled He blanketing effect

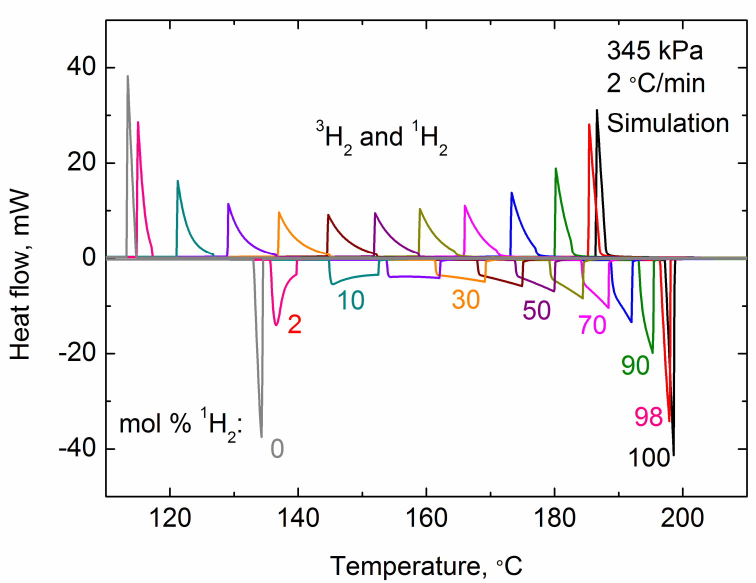
- He strongly perturbs H_2 concentration

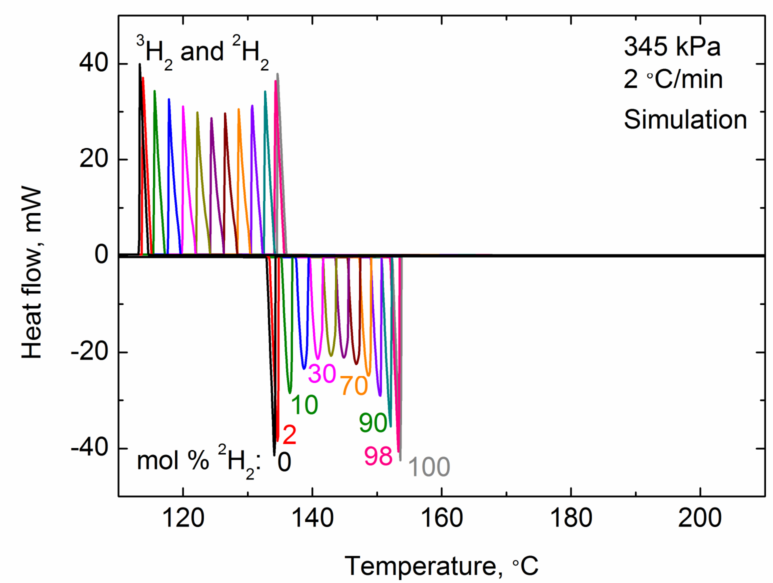


Isotopic pairs: Simulation

- Constant pressure
- Varying composition
- Mixtures have broader peaks at intermediate temperatures
- Broadest peaks near 1:1 composition in solid

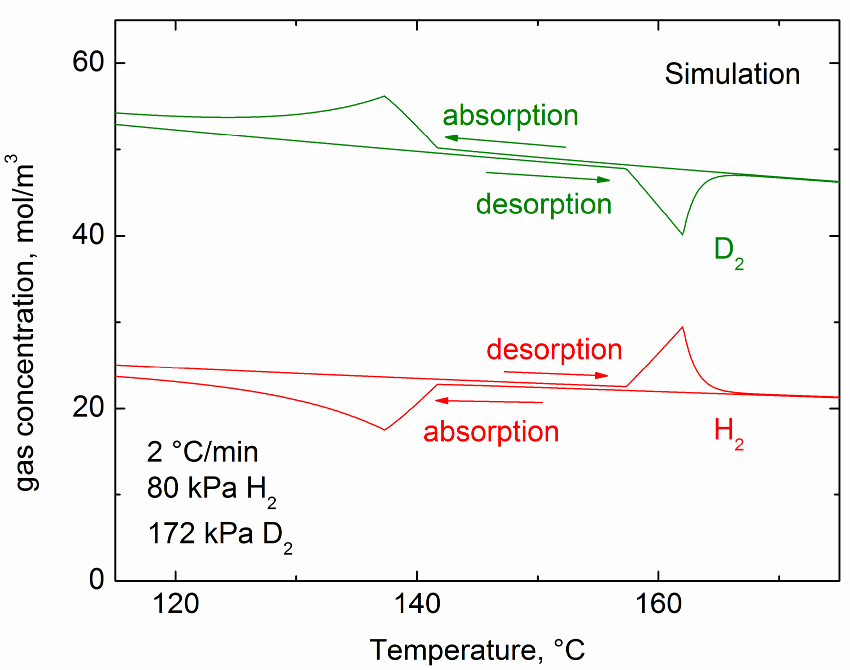


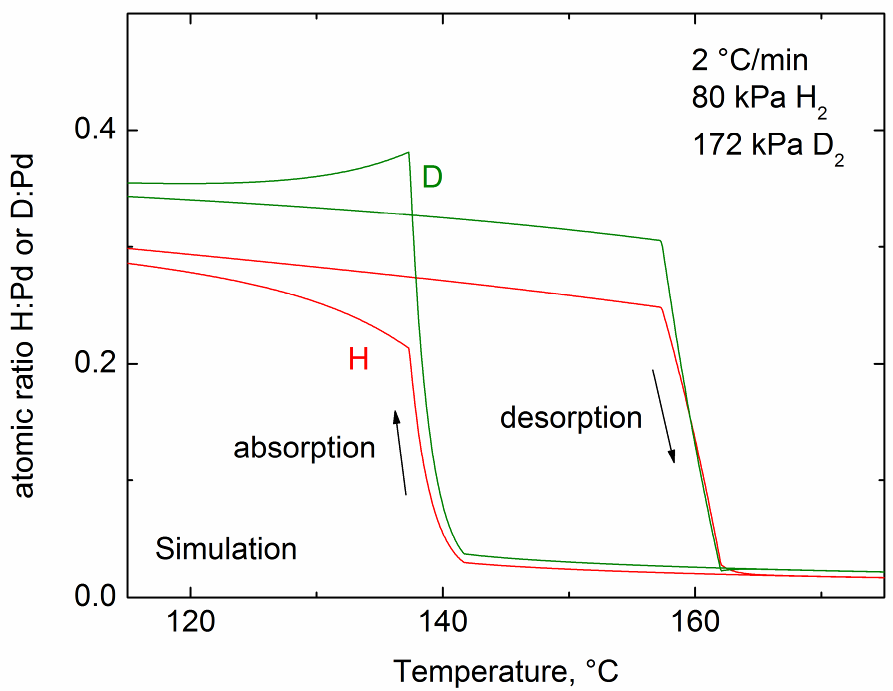




Concentrations for H_2-D_2 mix

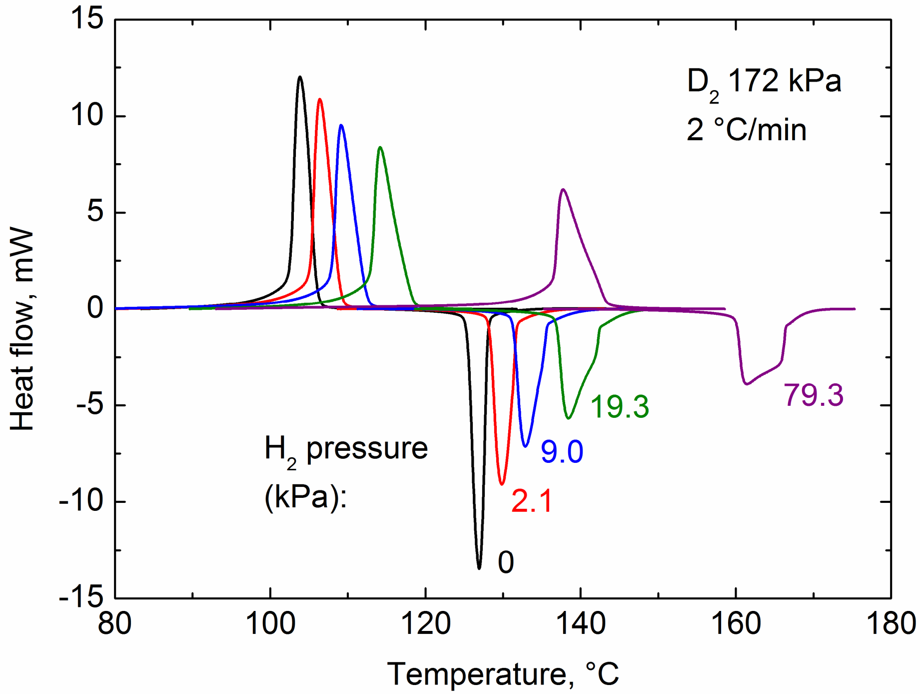
- H_2:D_2 balance is perturbed
- solid H:D > gas H_2:D_2

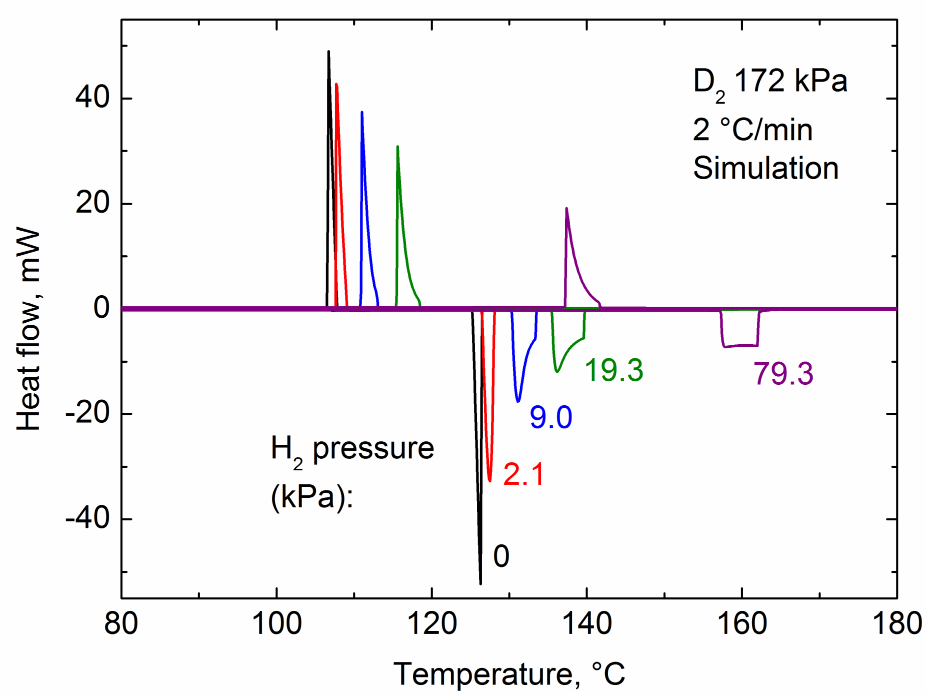




Experiment: Adding H_2 to D_2

- Peak shapes and positions are captured well by model





Adding D_2 to H_2

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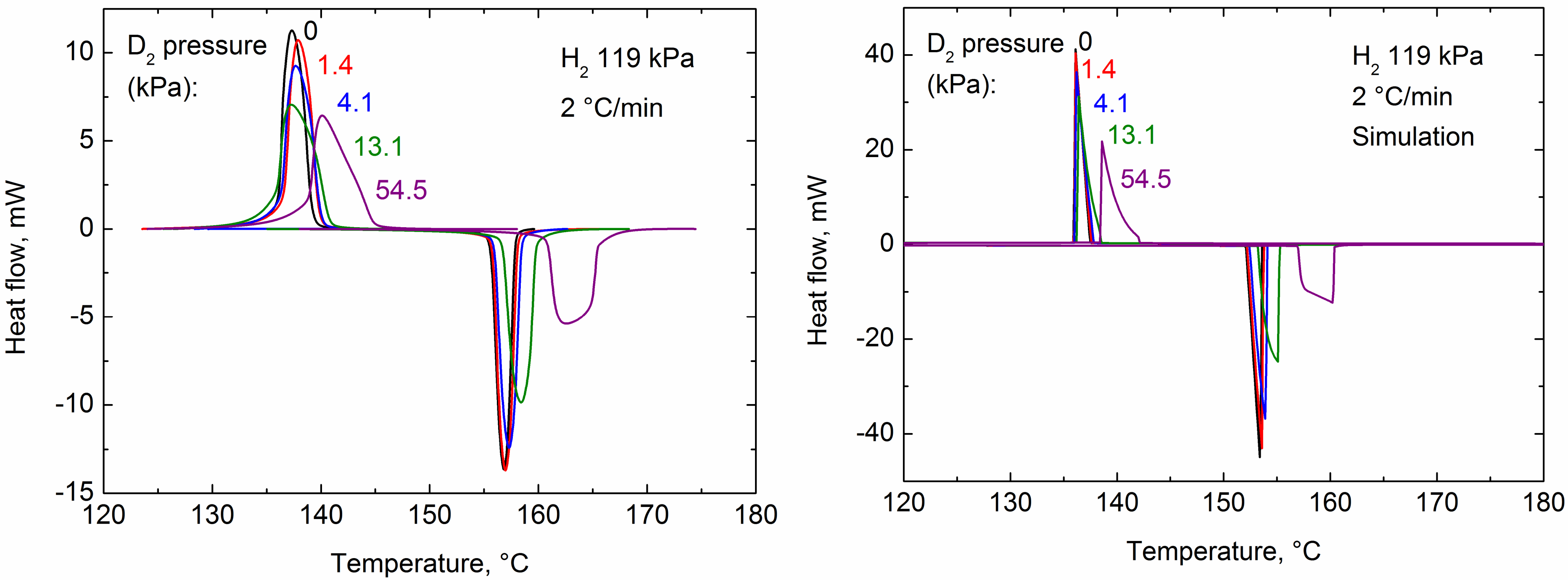
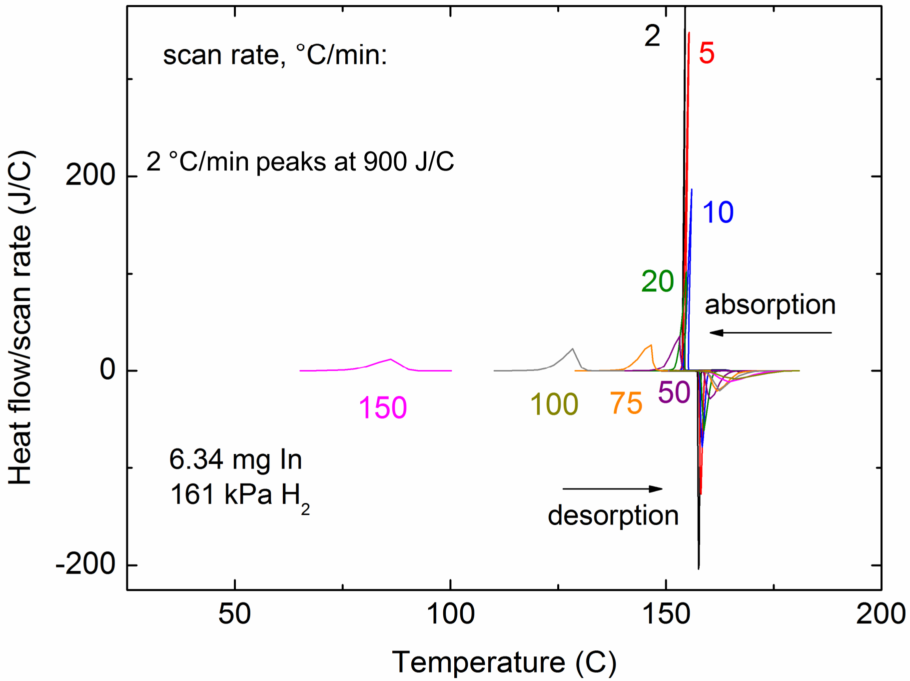
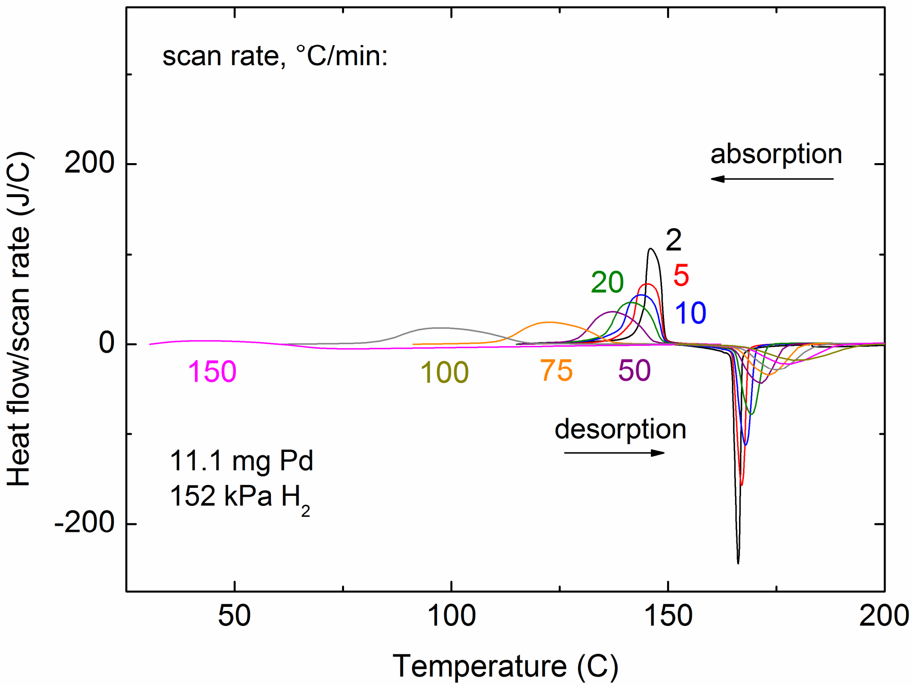


Limits of measurement speed

- Indium melting/freezing shows limits of instrument response time
- H_2 absorption, desorption appear slightly slower
- Absorption is slower than desorption
  - Activation barrier accelerates desorption, slows absorption
  - Instrument heats more quickly than it cools
- Simulations suggest that flow through orifice is not rate limiting; small ΔP





Conclusions

- Distinguishable signals are produced in Pd calorimetry upon variation of H_2, D_2, He partial pressure
- Can detect about:
  - 1% He in H_2 (or presumably D_2)
  - 1% H_2 vs. D_2
- For temperatures of 30 to 230 C, relevant pressures are:
  - 2-600 kPa H_2
  - 12-1600 kPa D_2
  - Comparable amounts of He
- Behavior can be predicted by simple model
  - Should allow deduction of unknown partial pressures from experimental data

Future opportunities

- Optimization of sensitivity, time resolution:
  - Geometry: scaling hole size, pan volume
  - Scan rate
- Parallel sensing, peak tracking could further increase time resolution
- Optimize Pd powder composition and structure to modify pressure range, absorption kinetics
- These efforts may improve size, power consumption

Acknowledgements

- Calorimetry: Weifang Luo, Ken Stewart
- Modeling: Trevor Cai, Bill Wolfer

BACKUP SLIDES

No-pump detection options

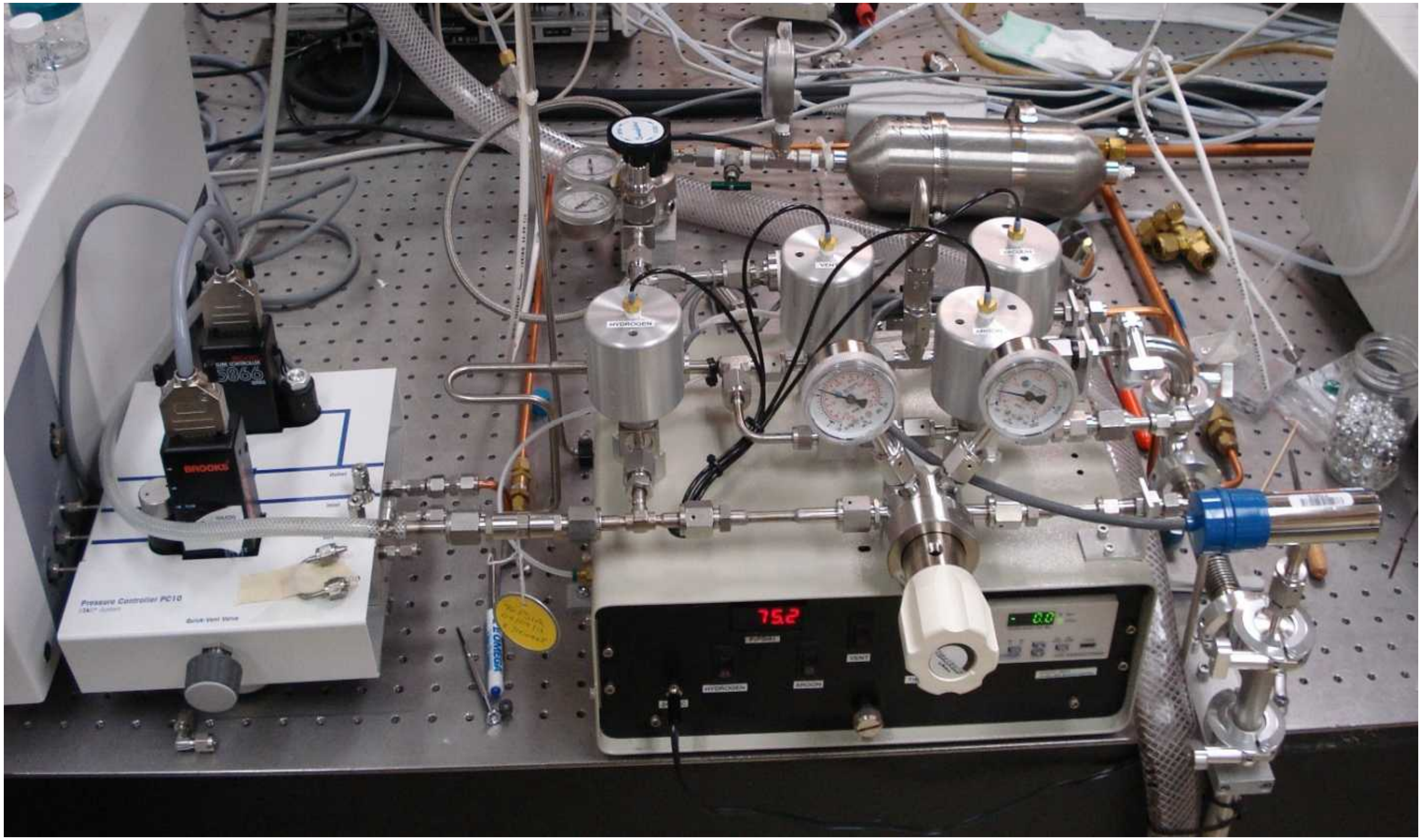
- Detect tritium-induced ionization current (ion chamber)
  - Currents can be nA to uA range
- "Exit sign": measure light from phosphor-coated window
  - Difficult to test without tritium; challenging compositional dependence
- Spectroscopy: Raman or optical properties of ions
  - Requires high-gain sensors, light sources, signal integration; bulky
- Physical properties: thermal conductivity, sound speed
  - All quite similar among these gases
- Chemical transduction: thermal, electrical
  - significant heat of absorption as metal hydrides

Virtual lab tour

- Mettler Toledo HP-DSC 1 (DSC in 0-10 MPa vessel)

Virtual lab tour

- H_2, D_2, He, Ar, vacuum manifold
- 0-100 psi transducer

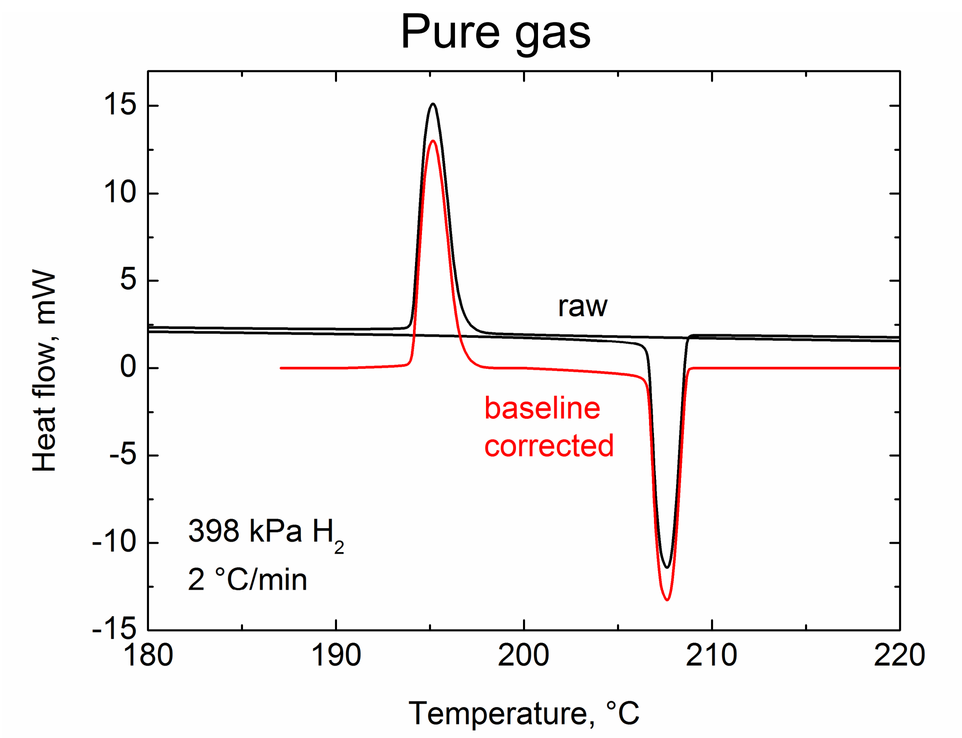


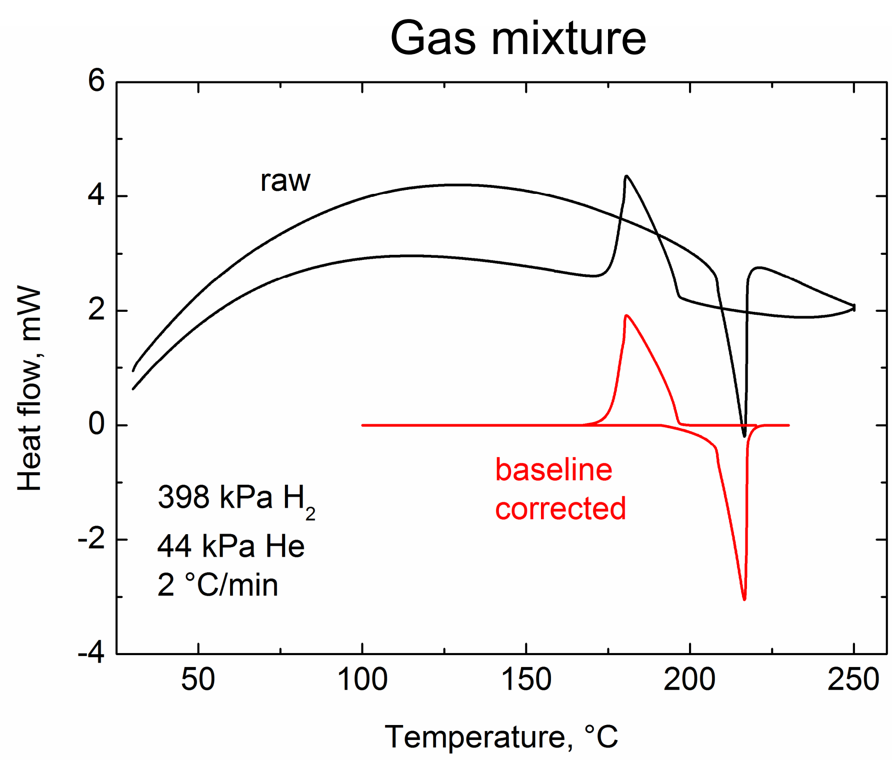
Inside pressure vessel

- Lid is crimped onto pan
- Sample and empty reference pans sit on heating element

Processing of calorimetry data

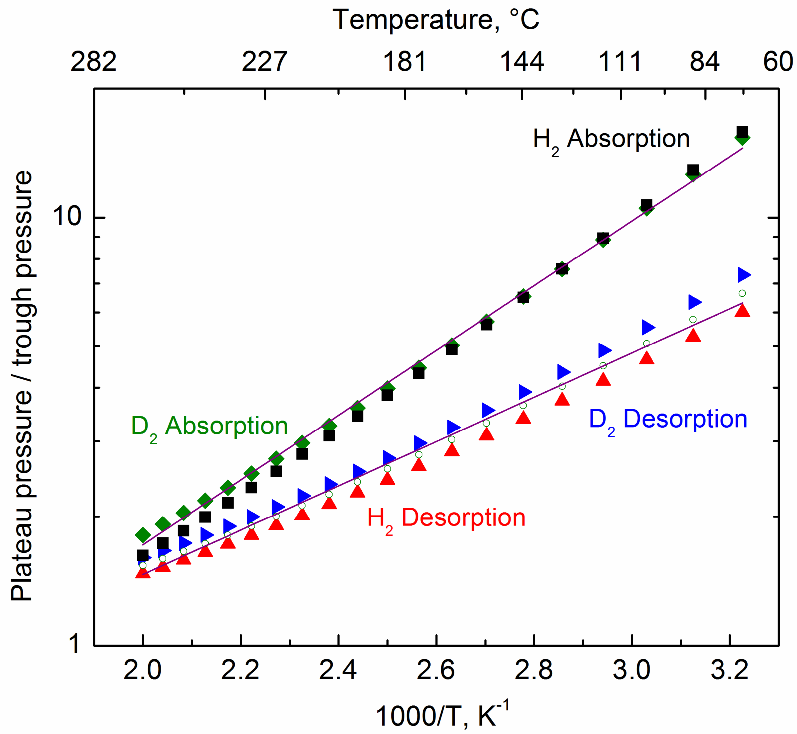
- Baseline is influenced by heat capacity, convection differences vs. reference pan
- We only care about gas absorption and desorption by Pd

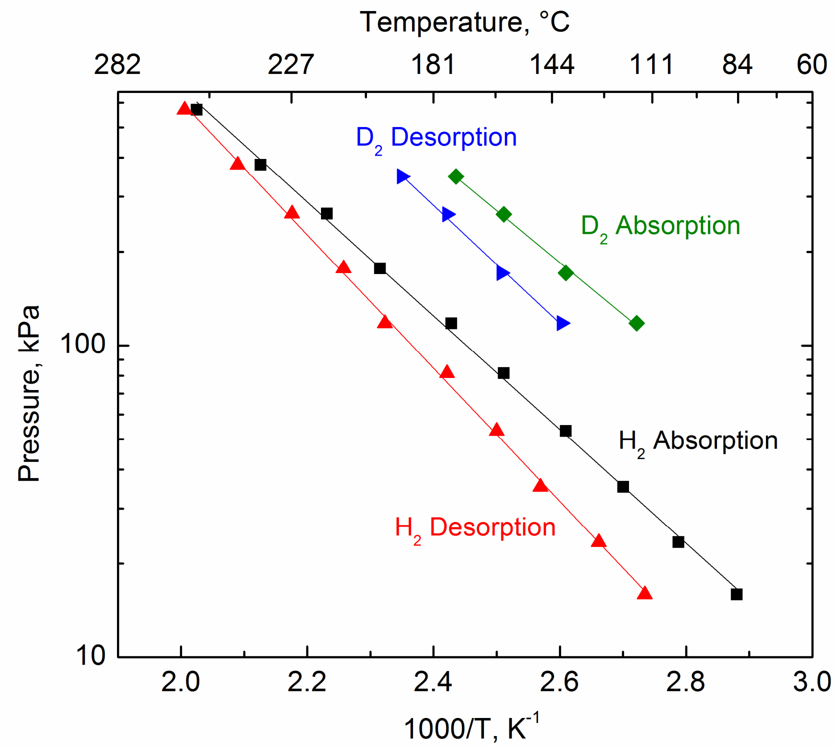




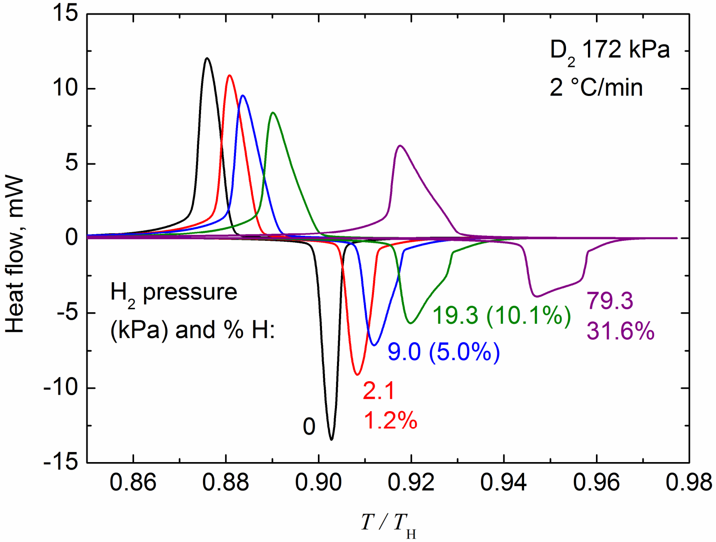
Empirical fits for plateau pressures

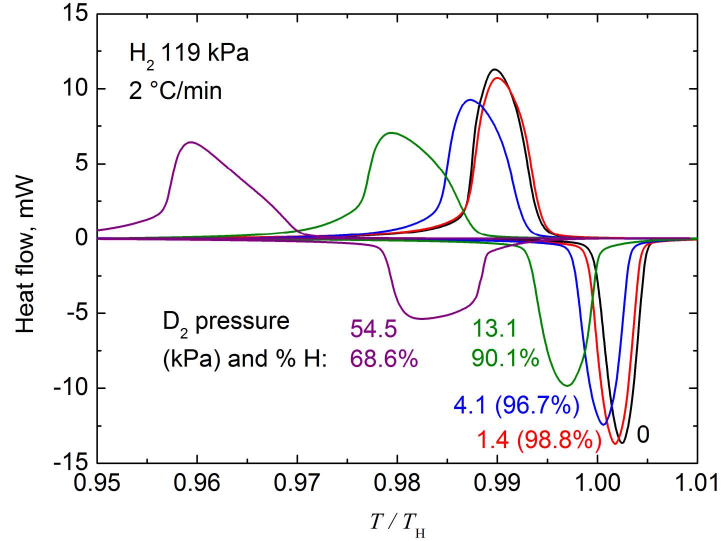
- We compared DSC peak onsets to predicted μ troughs

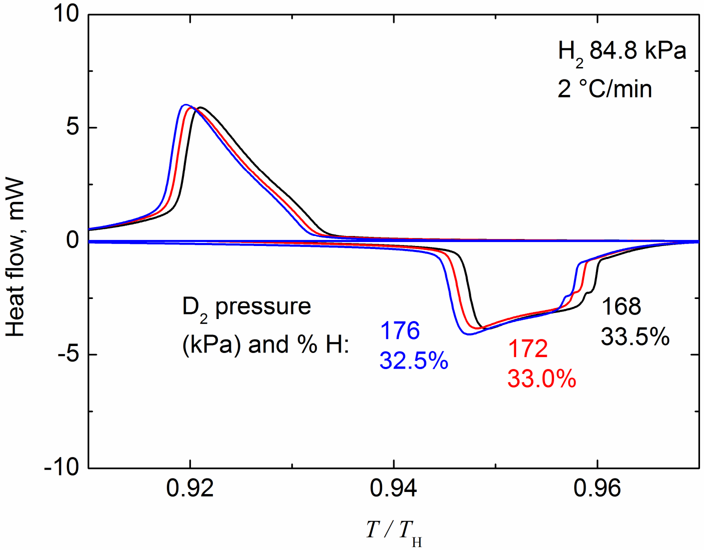


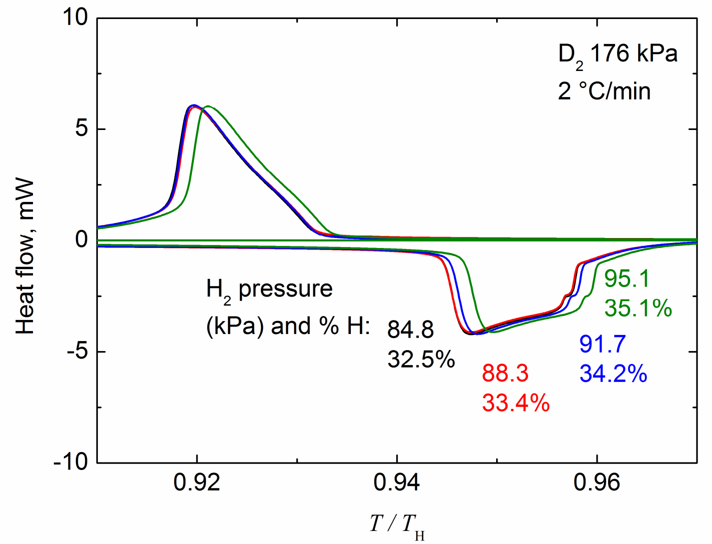


Sensitivity is about 1% for H vs. D



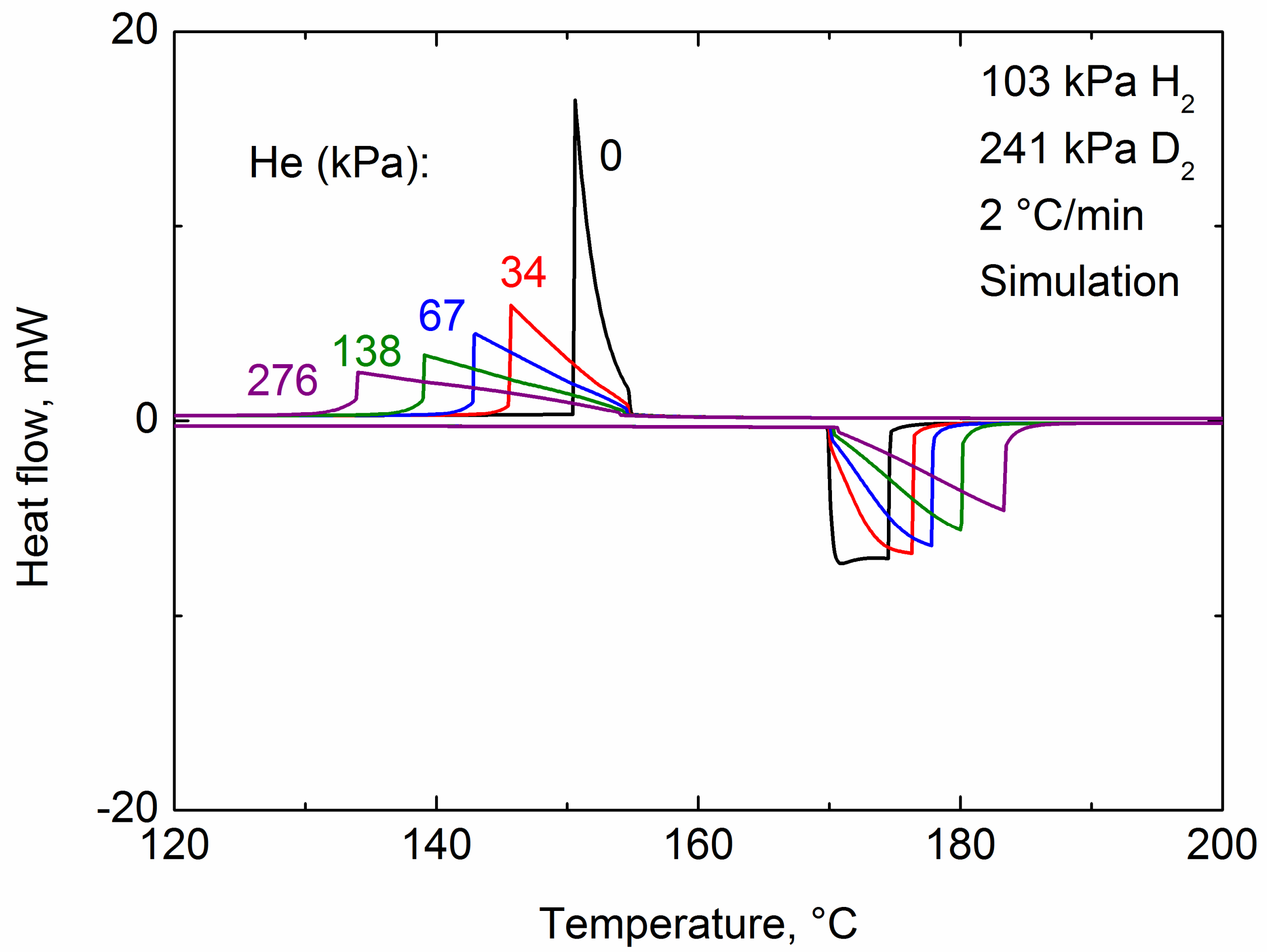






Ternary gas mixture

- Helium blanketing shifts simulated peaks of H-D mixtures



Predictive modeling

- 7 variable concentrations, 7 transport equations (i = 1,2,3)

$$V\frac{d^{i}H_2}{dt}=\frac{\pi r^4}{8\mu L}\frac{{}^{i}H_2^{*}}{n}\left(n_o RT_o - nRT\right)+D\frac{\pi r^2}{L}\left({}^{i}H_o - {}^{i}H_2\right)-km\left({}^{i}H_2 - {}^{i}H_{eq}\right)$$

$$V\frac{dHe}{dt}=\frac{\pi r^4}{8\mu L}\frac{He^{*}}{n}\left(n_o RT_o - nRT\right)+D\frac{\pi r^2}{L}\left(He_o - He\right)$$

$$\frac{d^{i}H_s}{dt}=2km\left({}^{i}H_2 - {}^{i}H_{eq}\right)$$

* These are replaced with ${}^{i}H_0$ and He_0 when this term is positive (flow into capsule)

- Initially:

$${}^{i}H_2 = {}^{i}H_0$$

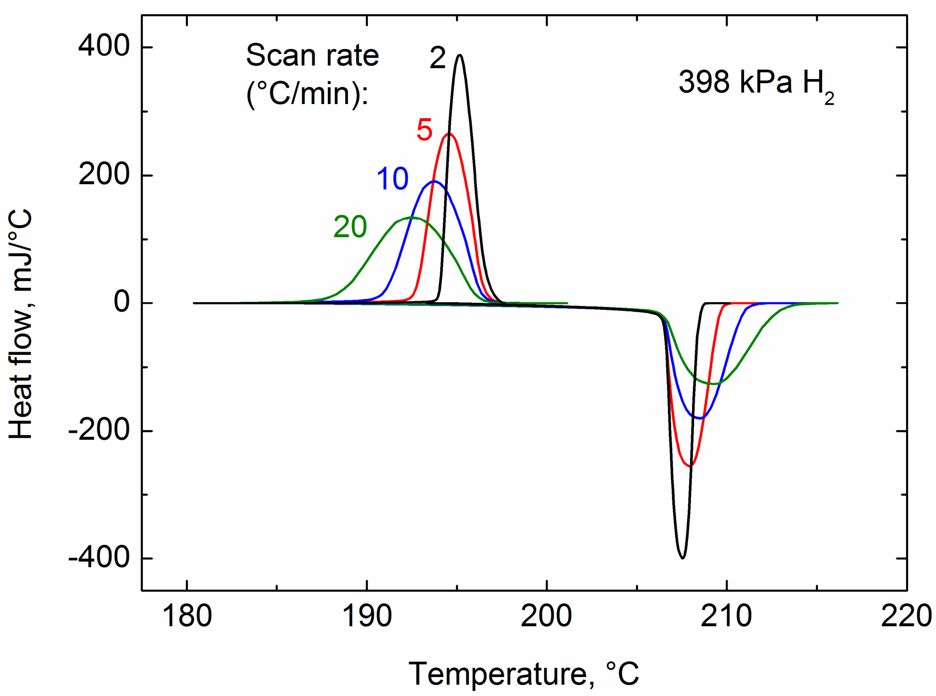
$$He = He_0$$

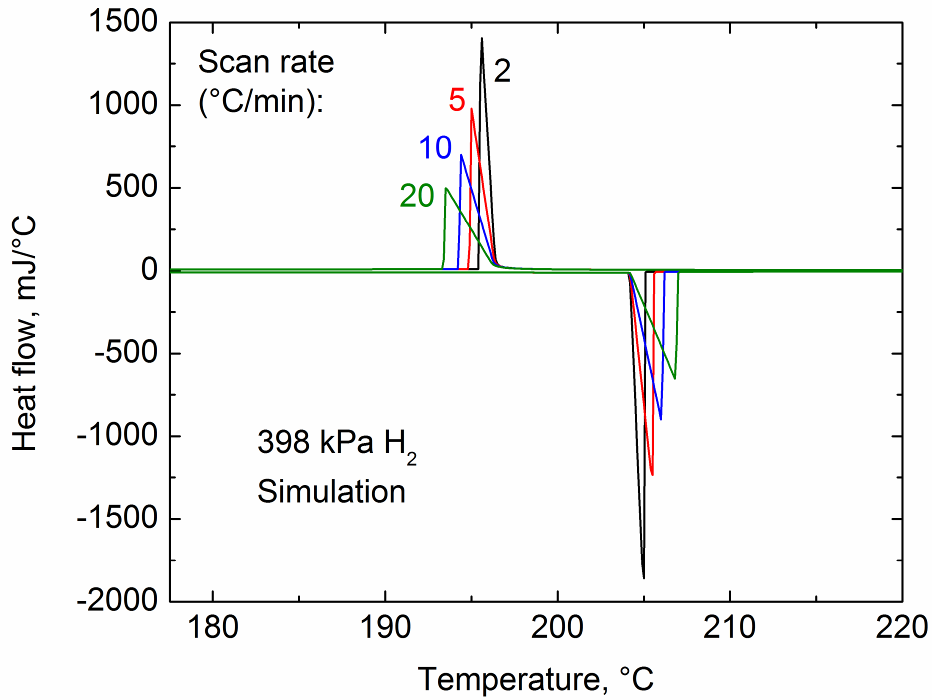
${}^{i}H_s$ in equilibrium with these

V: capsule volume
t: time
r: hole radius
μ: gas viscosity
L: hole length
n: total gas conc.
T: temperature
D: diffusion const.
k: hydride rate const.
m: Pd moles

H_2 scan rate dependence

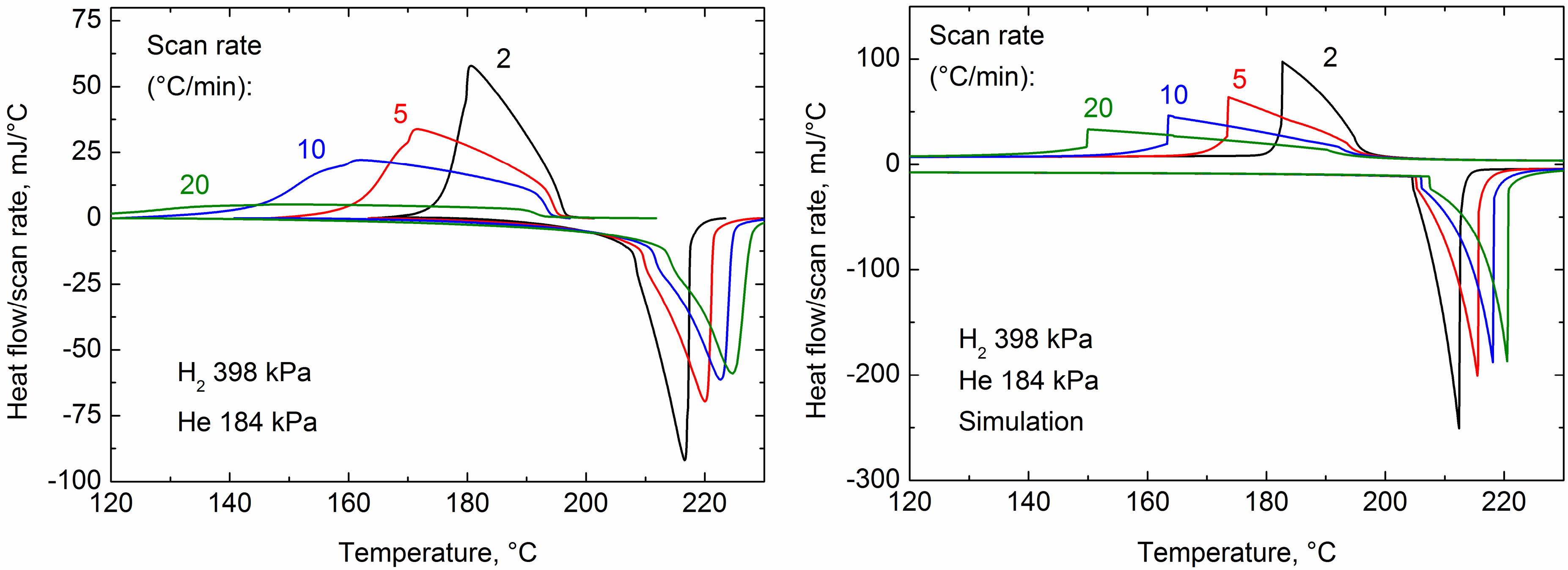
- Modest peak broadening
- Model is too sharp, but captures trend





H_2-He mix: scan rate effect

- Peak smearing is more extreme at higher scan rates
- Increased sensitivity to He (until limited by absorption kinetics)



H_2-D_2 mix: scan rate effect

- Peak broadens with scan rate
  - But not as much as with H_2+He