

*Exceptional service in the national interest*



# Compact Determination of Hydrogen Isotopes and Helium

David B. Robinson

11<sup>th</sup> International Conference on Tritium Science and Technology

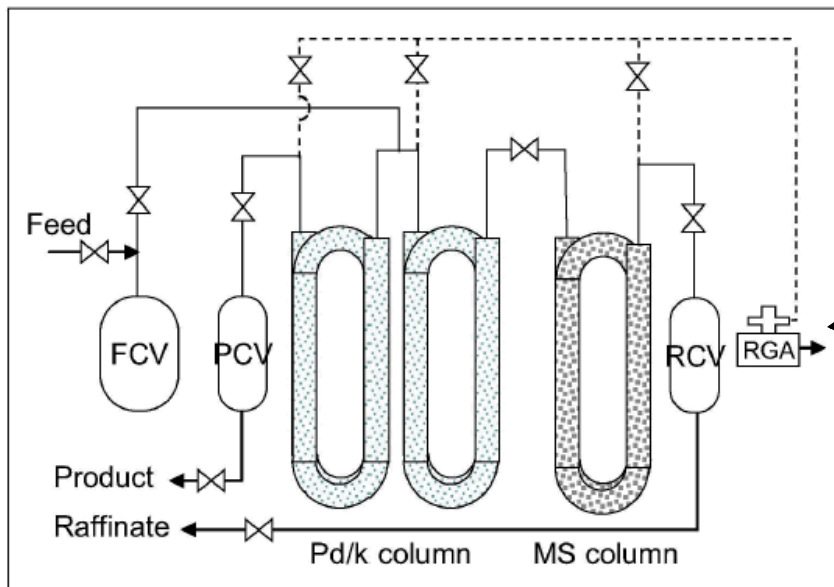
Charleston, SC

# Tritium and helium-3 operations

- $^1\text{H}$ ,  $^2\text{H}$ ,  $^3\text{H}$ ,  $^3\text{He}$ ,  $^4\text{He}$  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

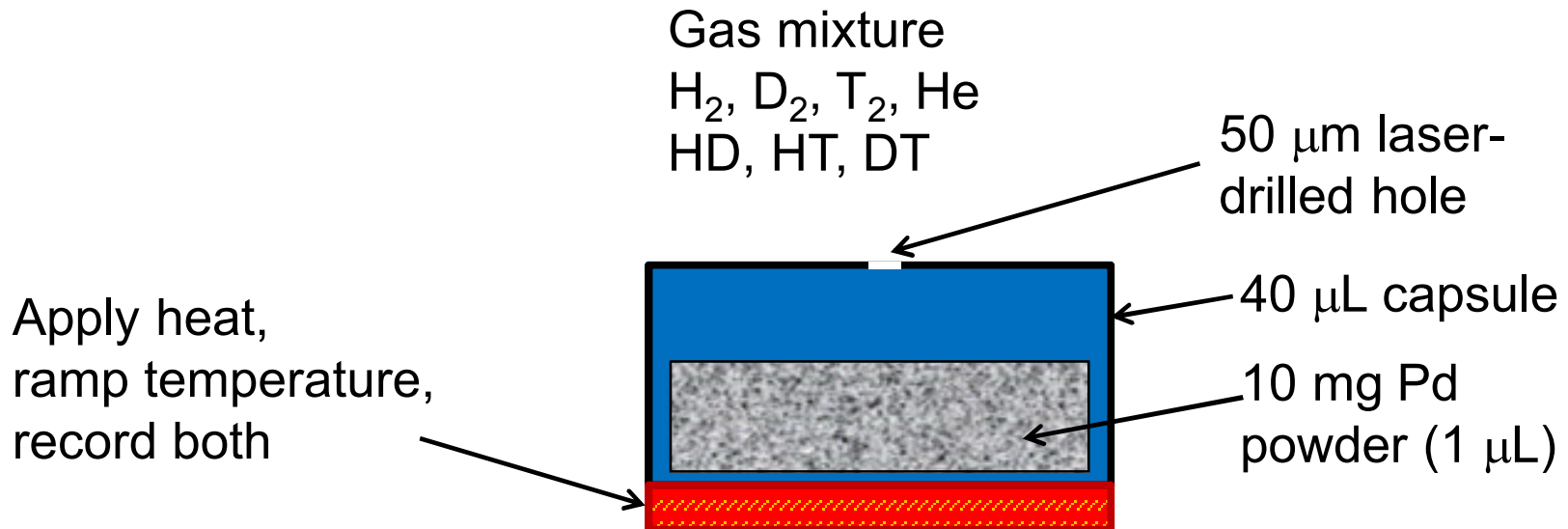
L. K. Heung *et al.*  
Fusion Sci Tech 60 1331 (2011)

# 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: conductivity, sound speed
  - All quite similar among these gases
- Chemical transduction: thermal, electrical
  - significant heat of absorption as metal hydrides

# Detection concept

- Absorption of H, D, T by Pd is temperature, pressure dependent
- 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



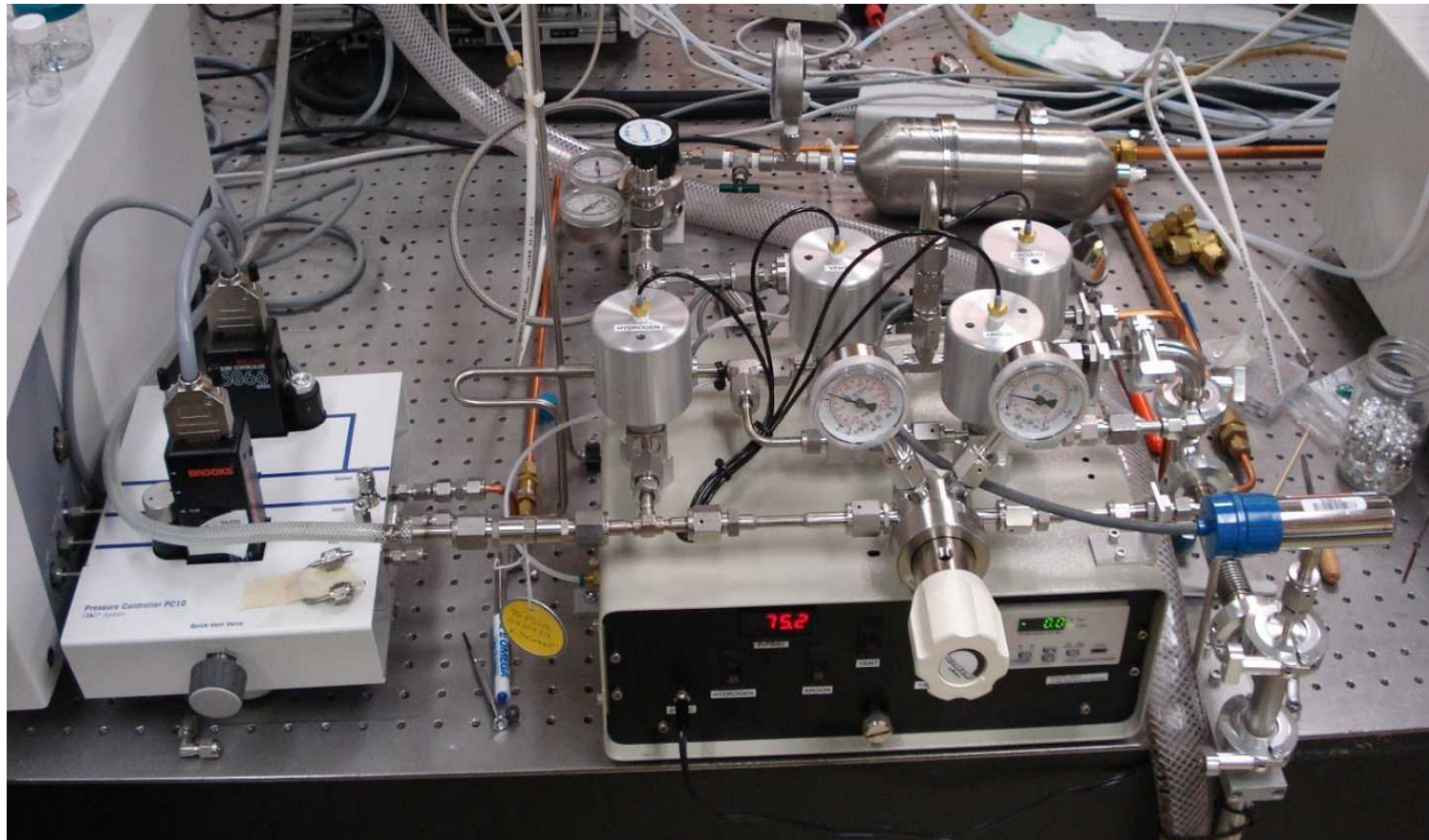
# Virtual lab tour

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



# Virtual lab tour

- H<sub>2</sub>, D<sub>2</sub>, He, Ar, vacuum manifold
- 0-100 psi transducer



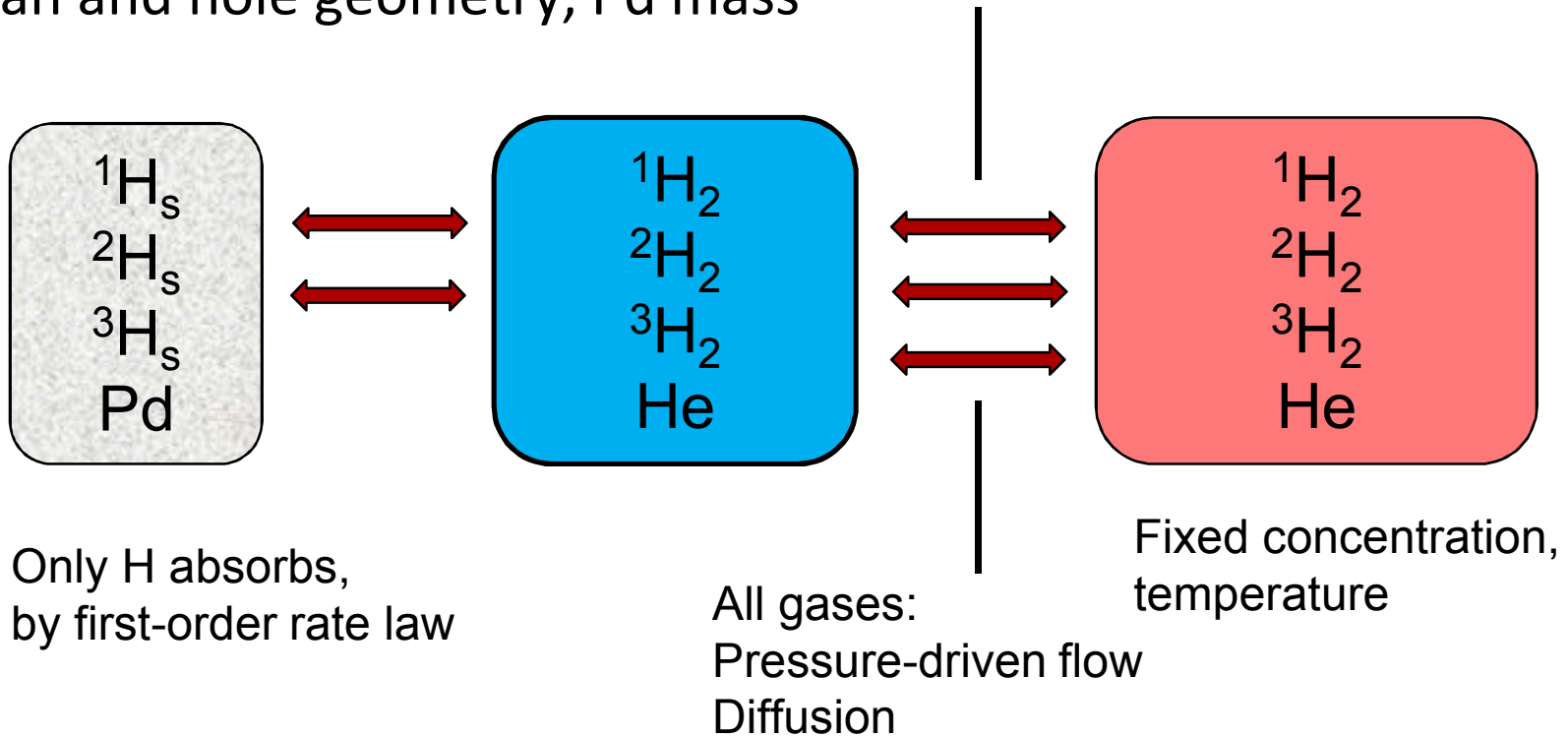
# Inside pressure vessel

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



# Predictive modeling

- 5 variable concentrations, 5 transport equations
- Inputs include outside gas concentration, temperature vs. time, pan and hole geometry, Pd mass



Mixed diatomic isotopologues accounted for implicitly

Account for heat capacities, thermal expansion of gas in pan

# Predictive modeling

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

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

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

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

- Initially:

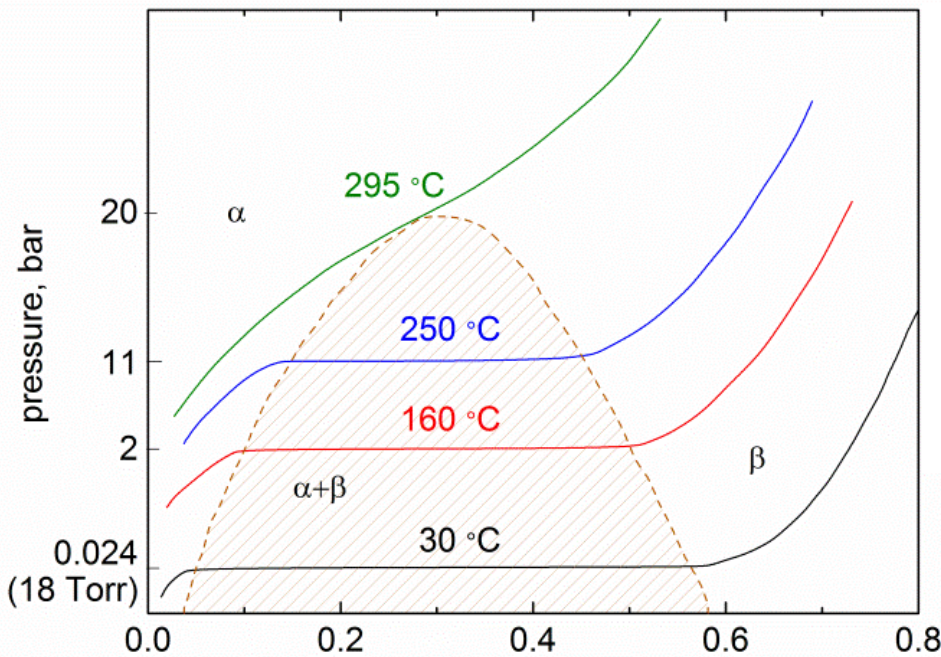
$${}^i H_2 = {}^i H_o$$

$$He = He_o$$

${}^i H_s$  in  
equilibrium  
with these

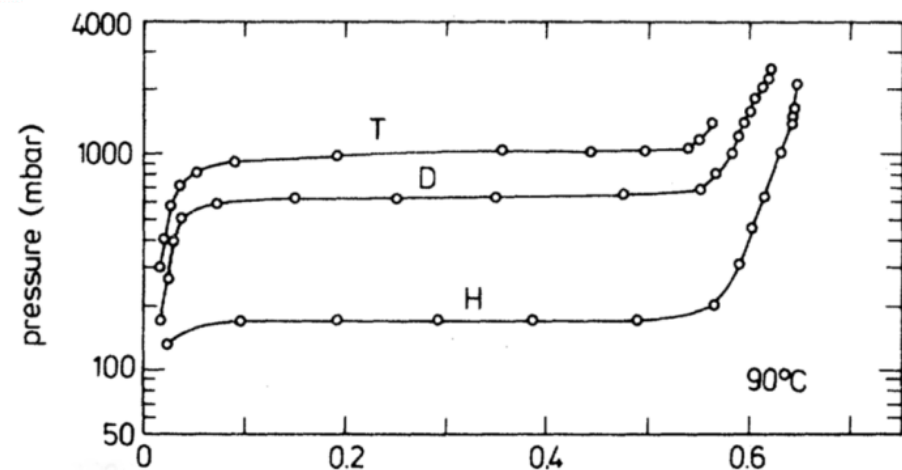
# Prediction of $iH_{eq}$

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



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

Atomic Ratio H:Pd



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  $j = \text{H, D, or T}$ )
- Gas phase: standard state term, ideal pressure-dependent term
  - $\mu^0$  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
  - $\mu^0$  captures absorption enthalpy, vibrational modes
  - “Excess” chemical potential includes elastic, electronic effects
    - Polynomial fit to beta-phase PCT experiments, intersecting at zero

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

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

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

Oates, Lässer, Kuji, Flanagan

J Phys F 15(11) 2273 1985

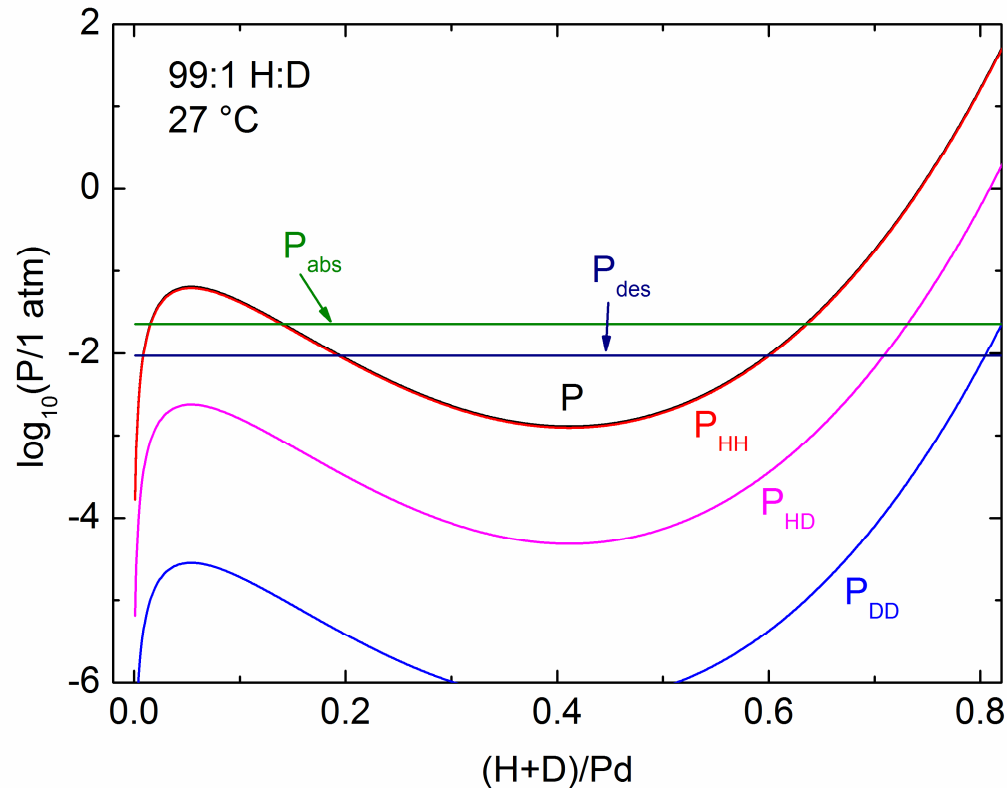
J Phys Chem Solids 47(4) 429 1986

$$x_v = 1 - \sum_i x_i$$

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

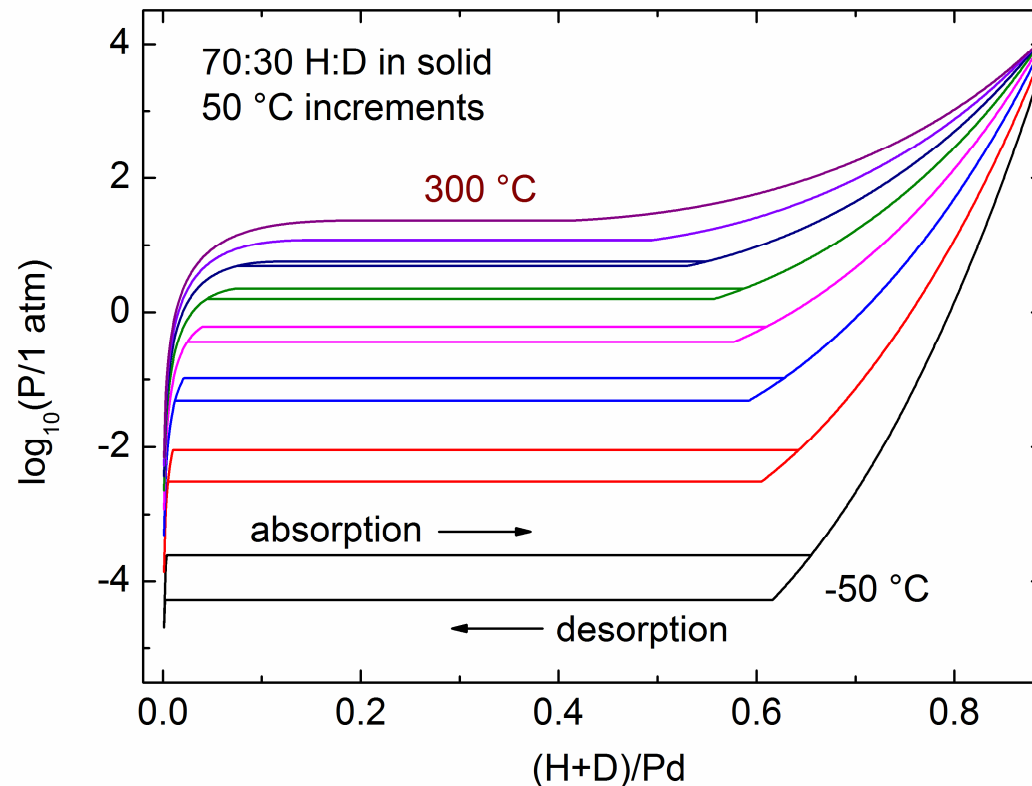
# Plateau pressures

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



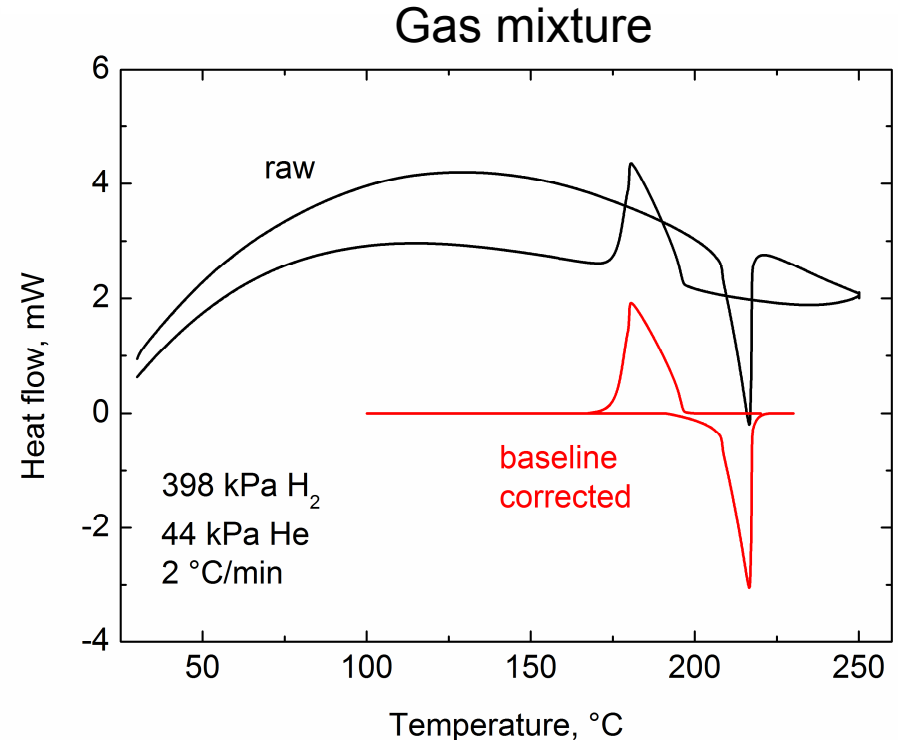
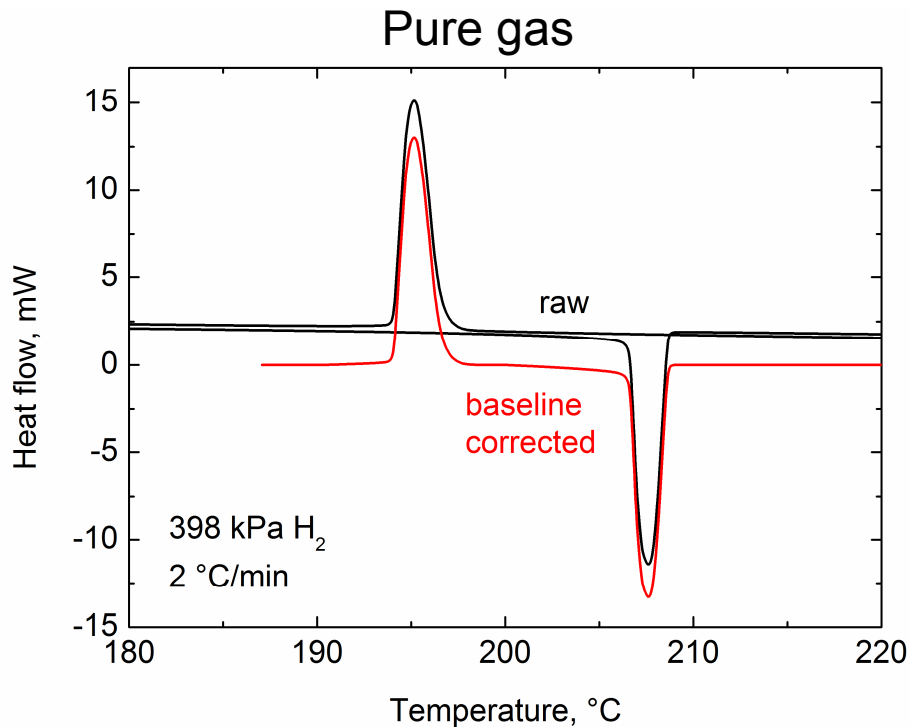
# Mixed-isotope PCT curves

- 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



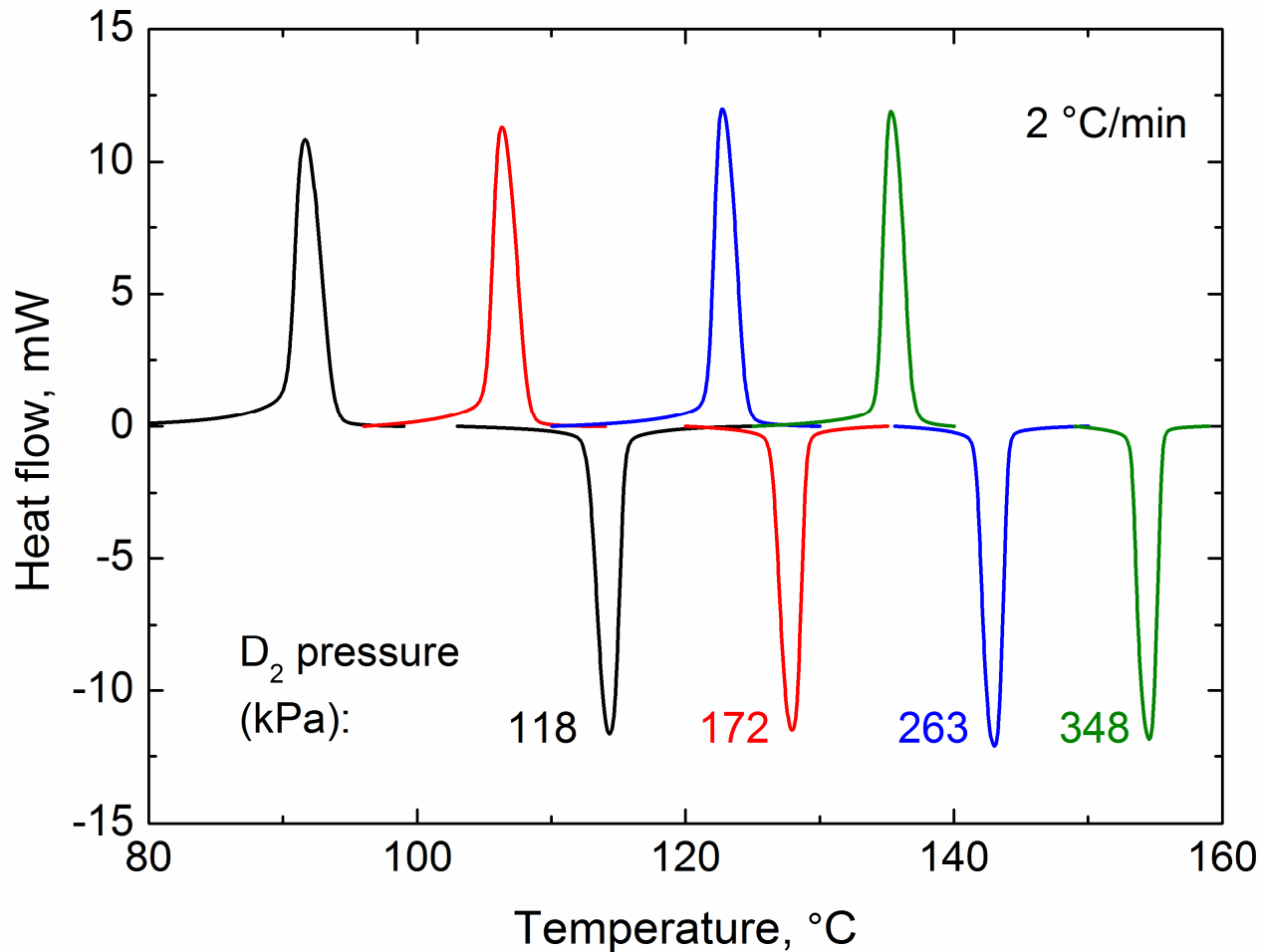
# Processing of calorimetry data

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



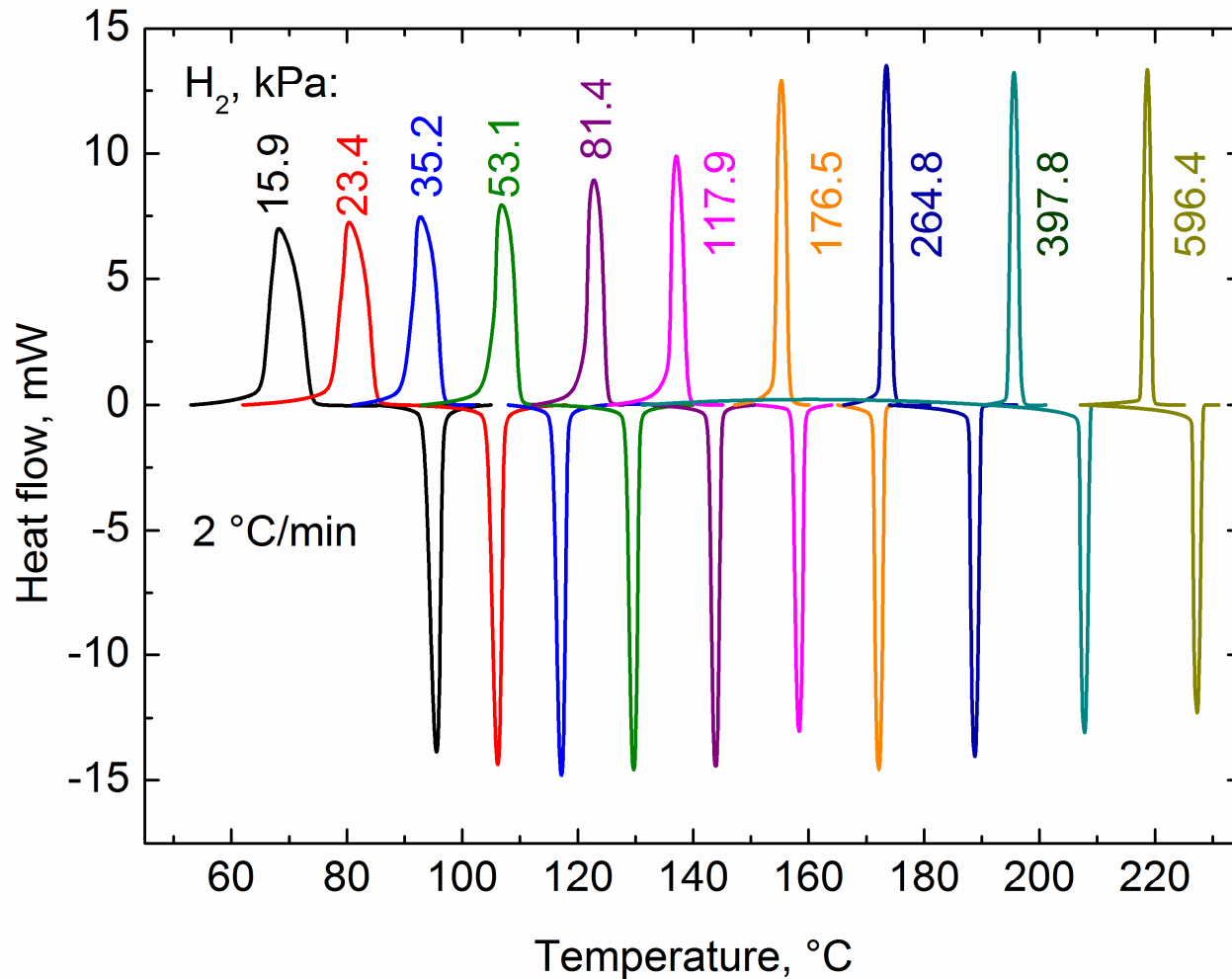
# Calorimetry in pure D<sub>2</sub>

- Peak temperature depends on gas pressure



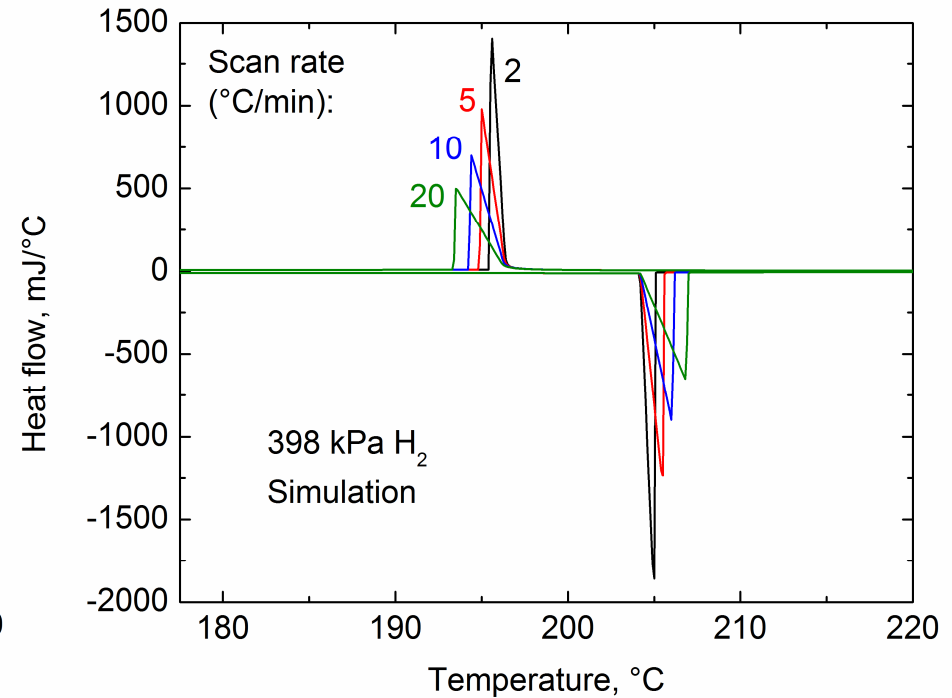
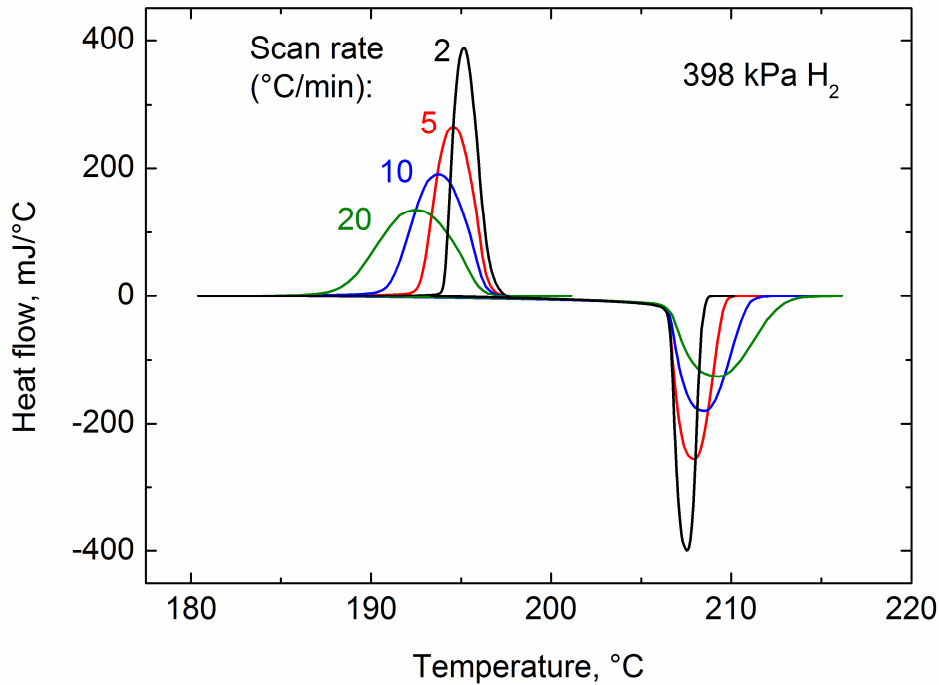
# Calorimetry in pure H<sub>2</sub>

- Absorption is a bit slow at lower temperatures and pressures



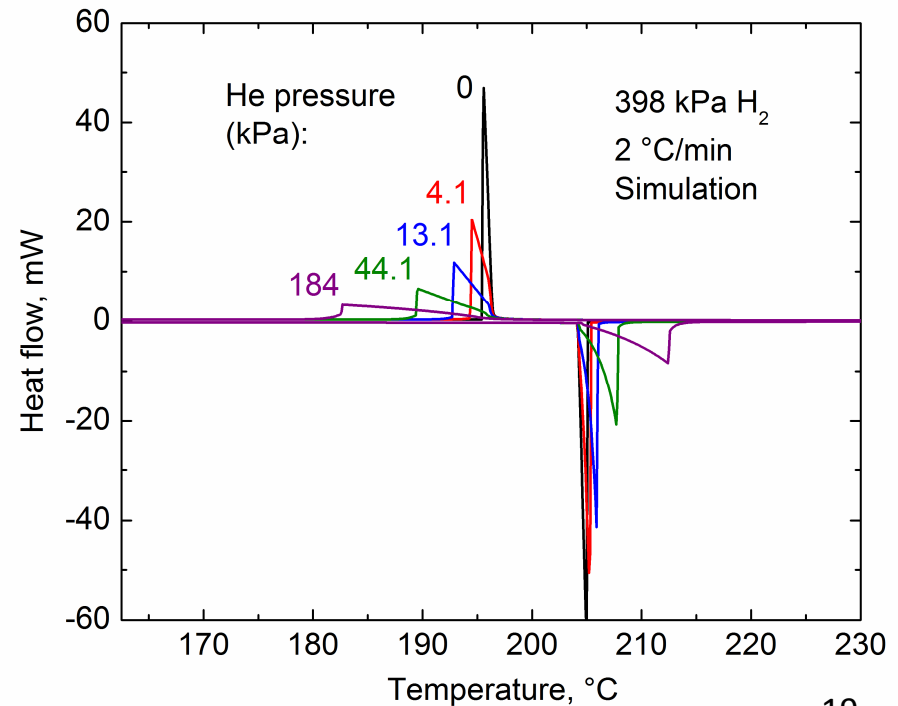
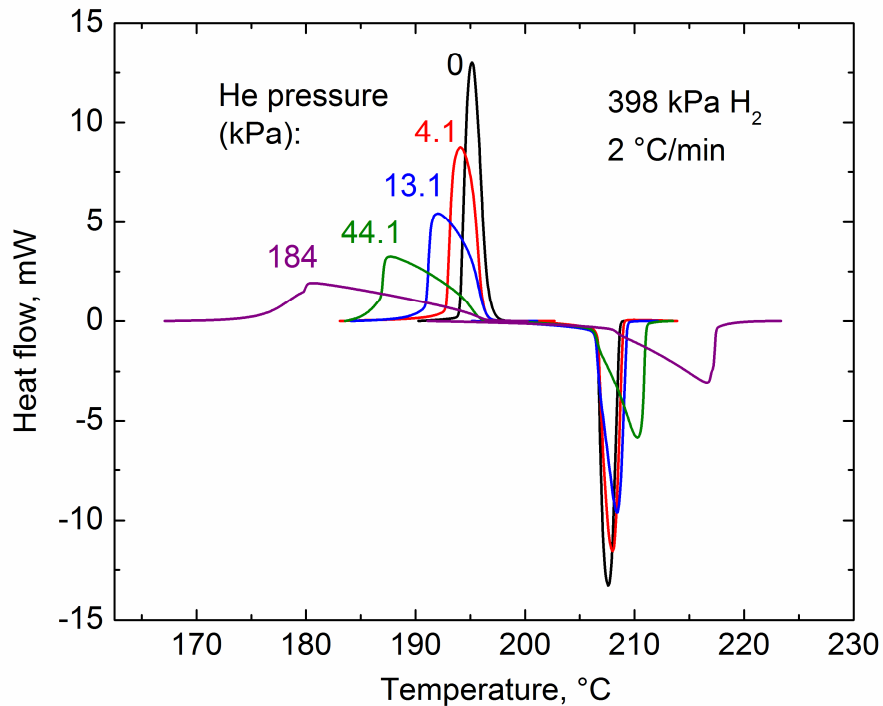
# H<sub>2</sub> scan rate dependence

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



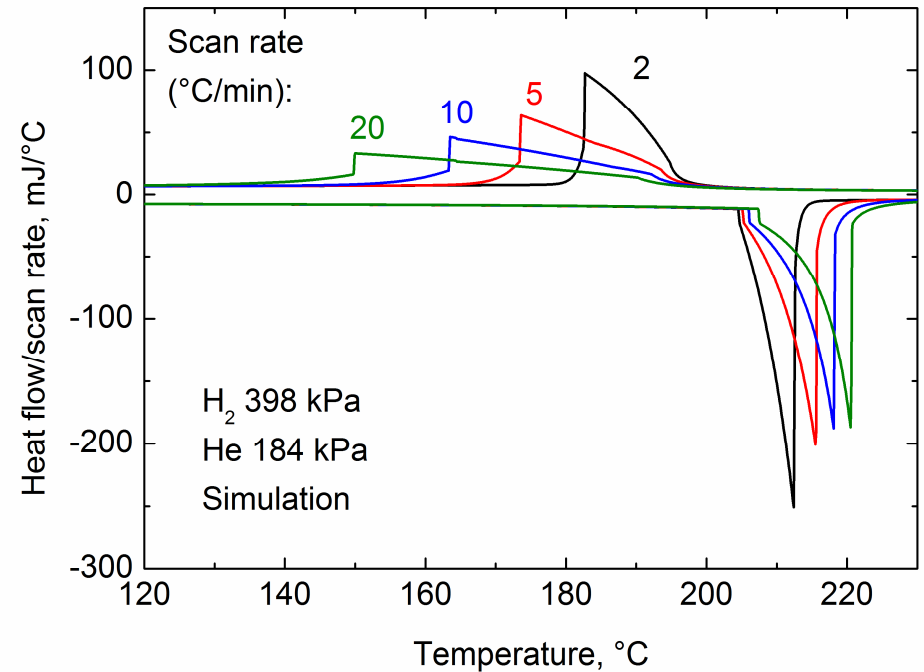
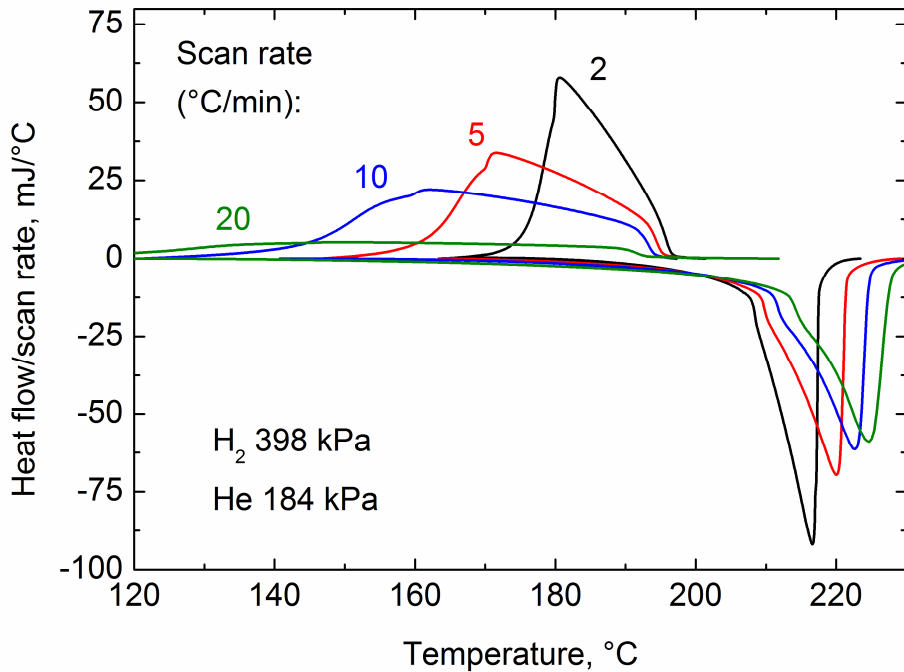
# Helium smears H<sub>2</sub> peaks

- He enters pan along with H<sub>2</sub>, but does not absorb
- He blanket reduces H<sub>2</sub> partial pressure, shifting peak temperature
- With blanket, H<sub>2</sub> transport is diffusion-limited through hole
- H<sub>2</sub> blanket creates opposite effect during desorption



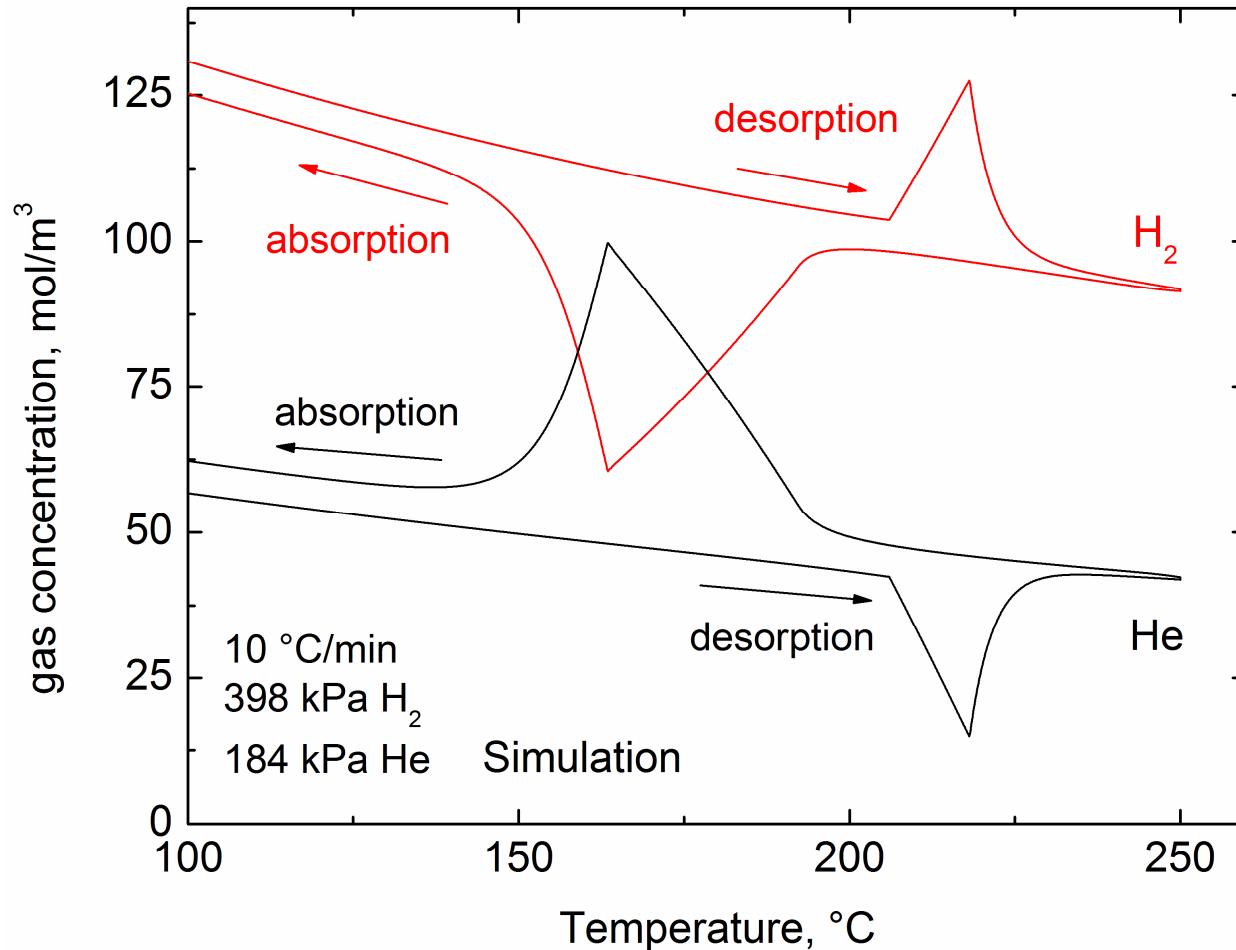
# Scan rate dependence

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



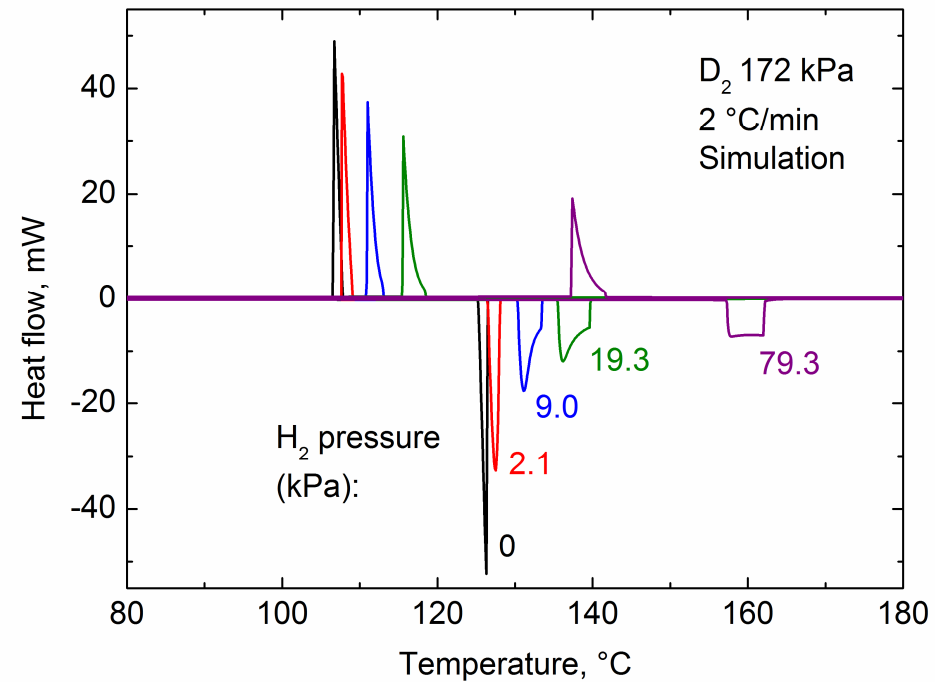
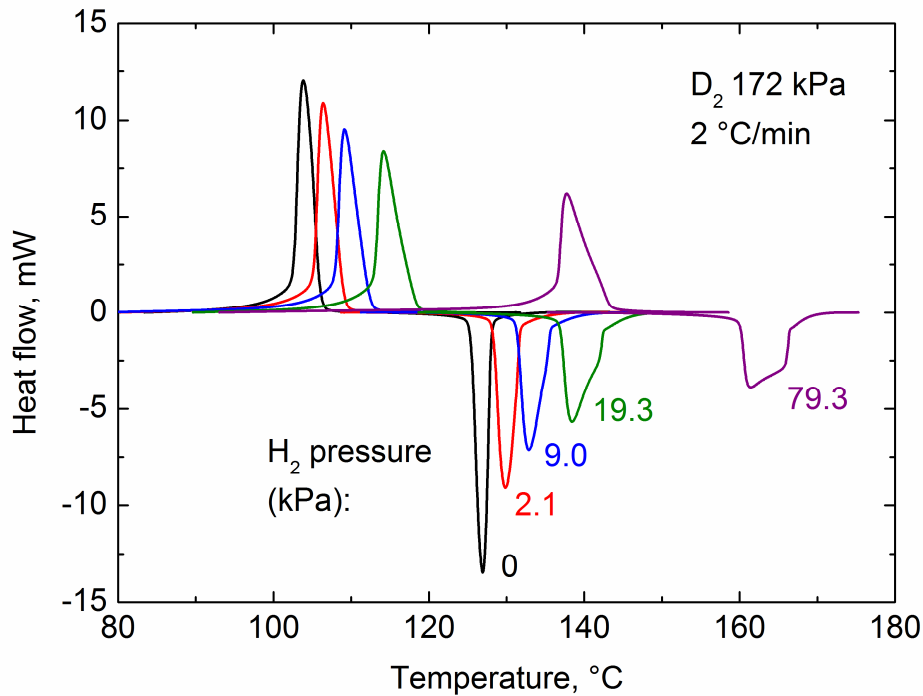
# Modeled He blanketing effect

- He strongly perturbs H<sub>2</sub> concentration



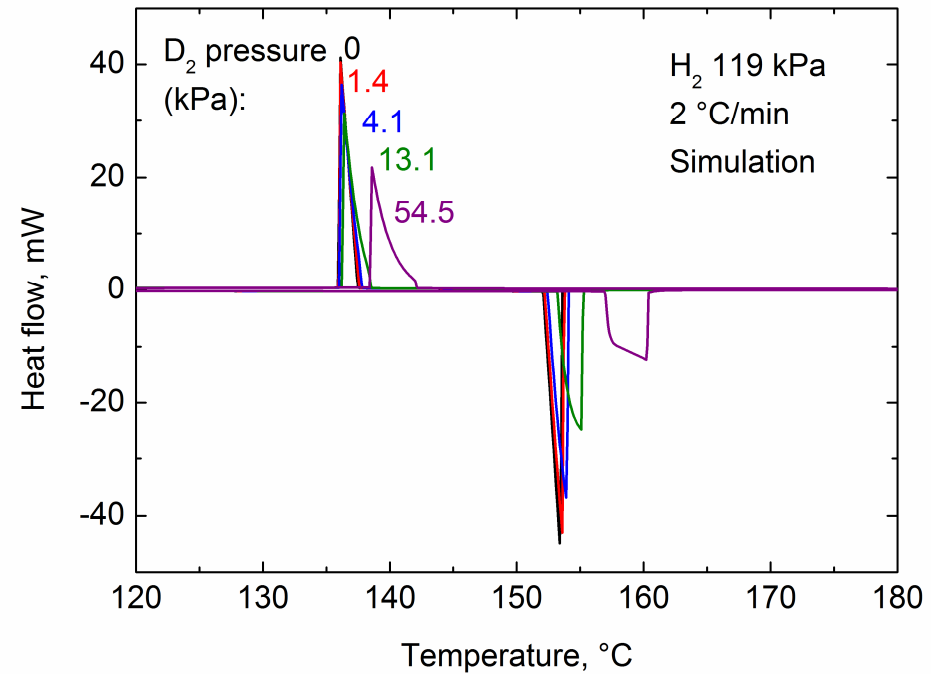
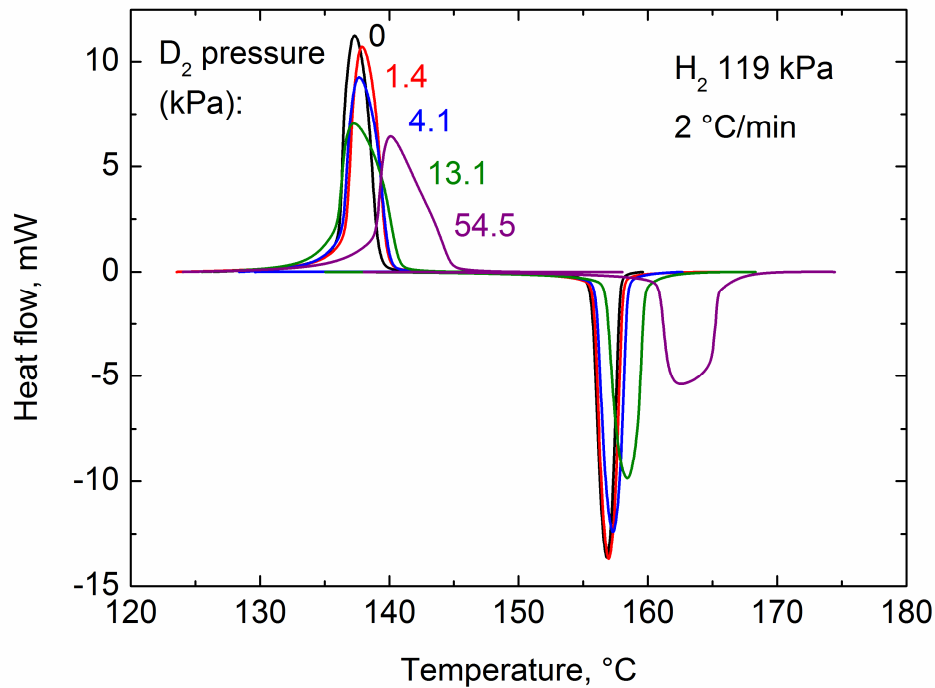
# Adding H<sub>2</sub> to D<sub>2</sub>

- Peak shifts are greater than when adding D<sub>2</sub> to D<sub>2</sub>
- Blanketing causes composition variations that broaden peaks when mole fractions are comparable



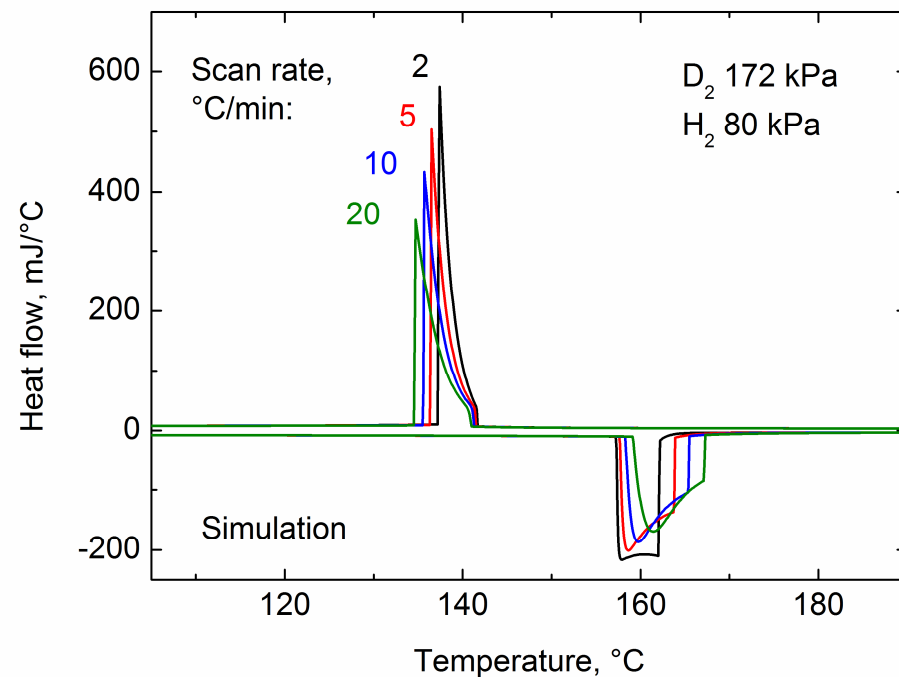
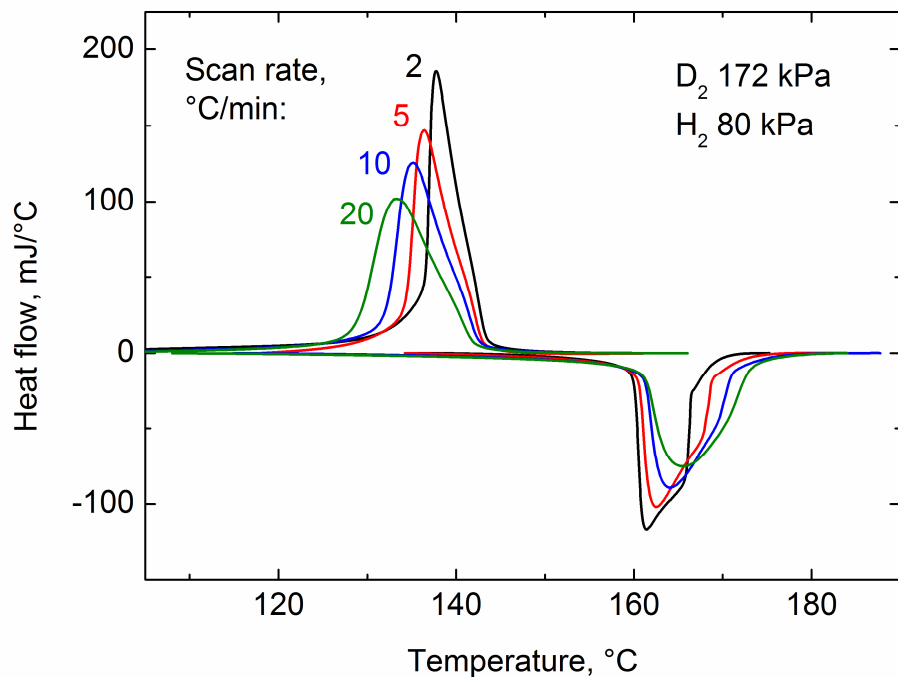
# Adding D<sub>2</sub> to H<sub>2</sub>

- Peak shifts are smaller than when adding H<sub>2</sub> to H<sub>2</sub>
- Blanketing causes composition variations that broaden peaks when mole fractions are comparable



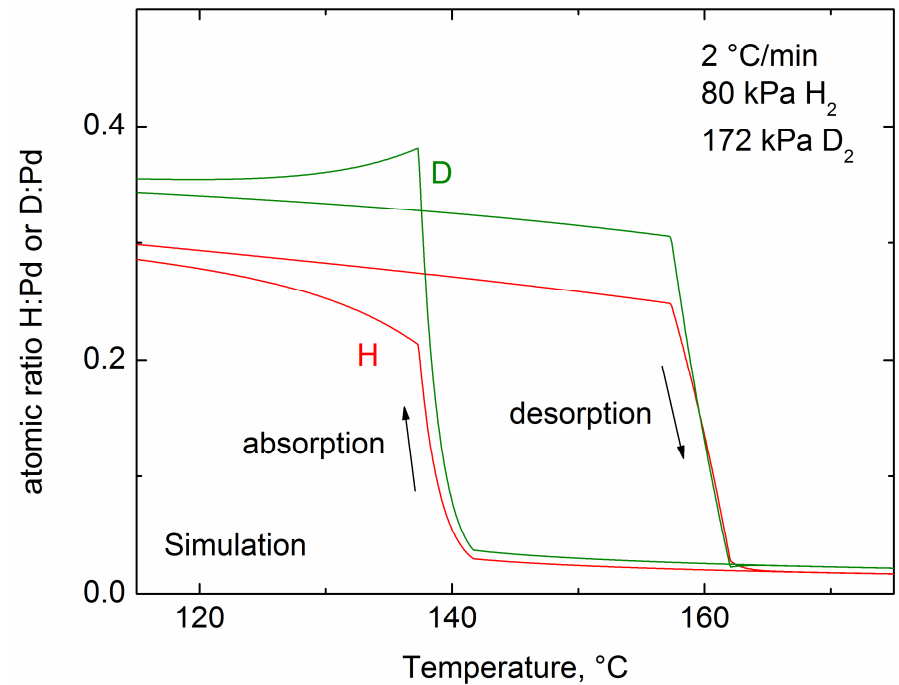
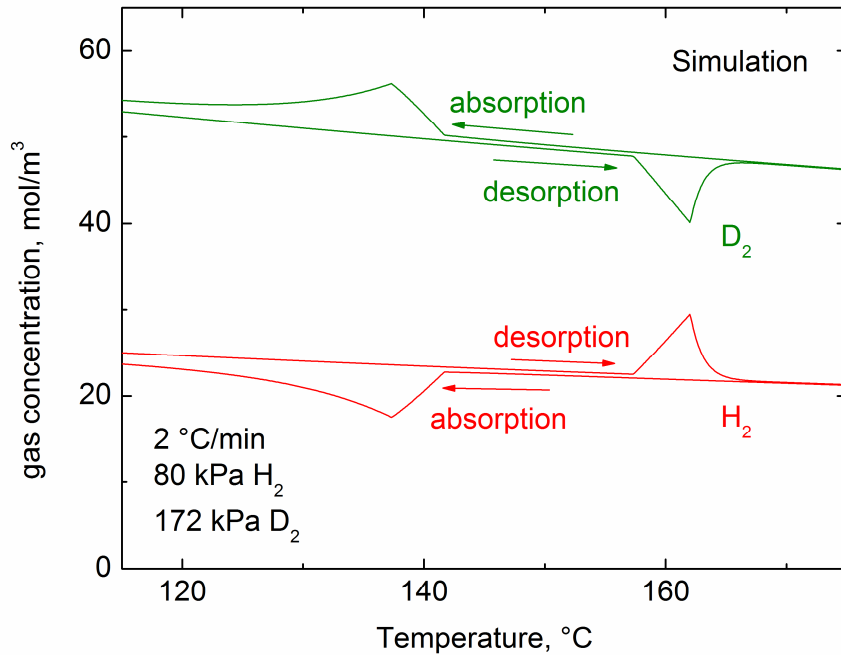
# H<sub>2</sub>-D<sub>2</sub> mix: scan rate effect

- Peak broadens with scan rate
  - But not as much as with H<sub>2</sub>+He



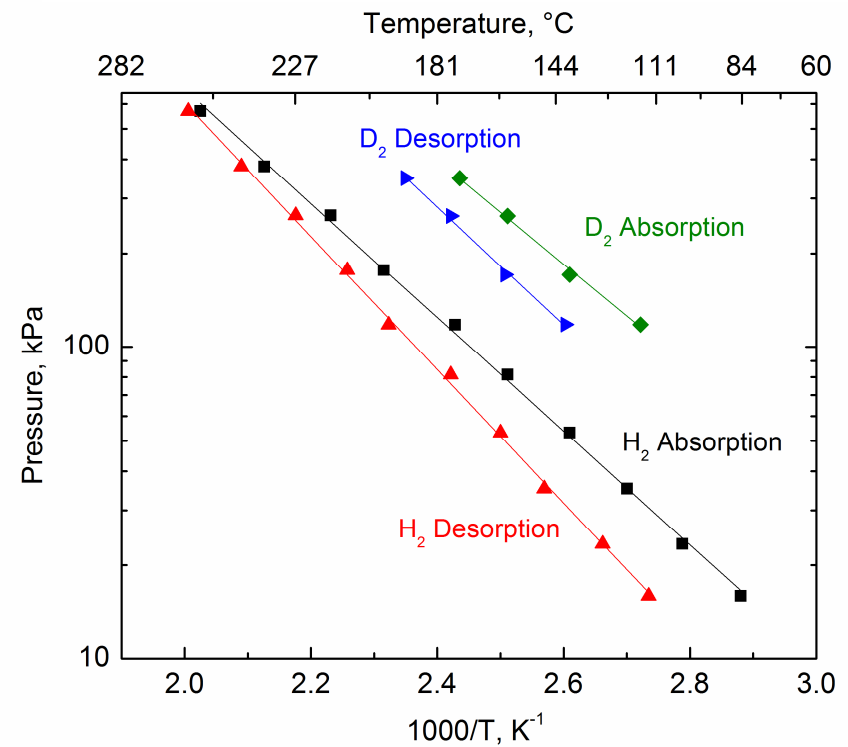
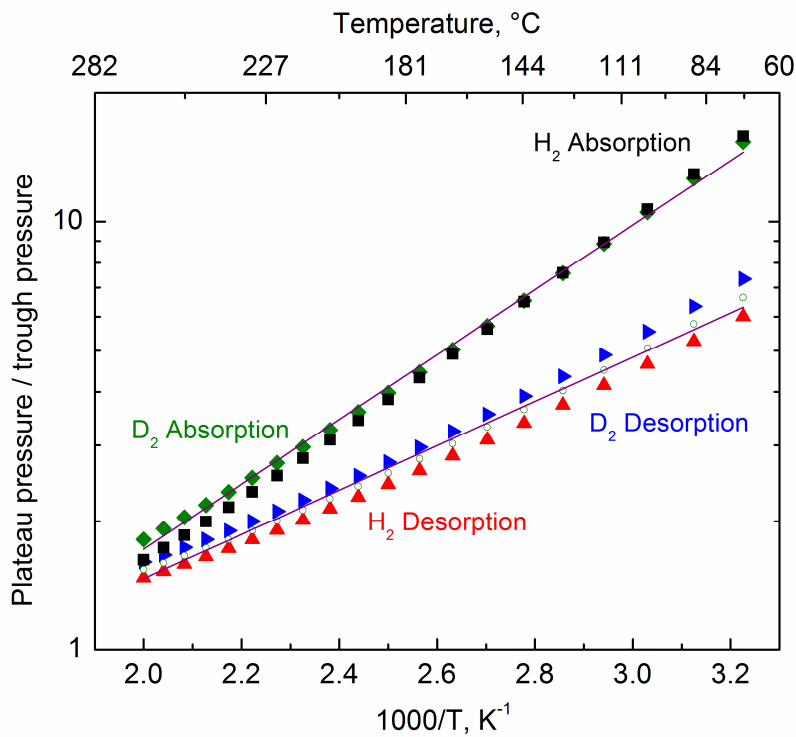
# Concentrations for H<sub>2</sub>-D<sub>2</sub> mix

- H<sub>2</sub>:D<sub>2</sub> balance is perturbed
- solid H:D > gas H<sub>2</sub>:D<sub>2</sub>

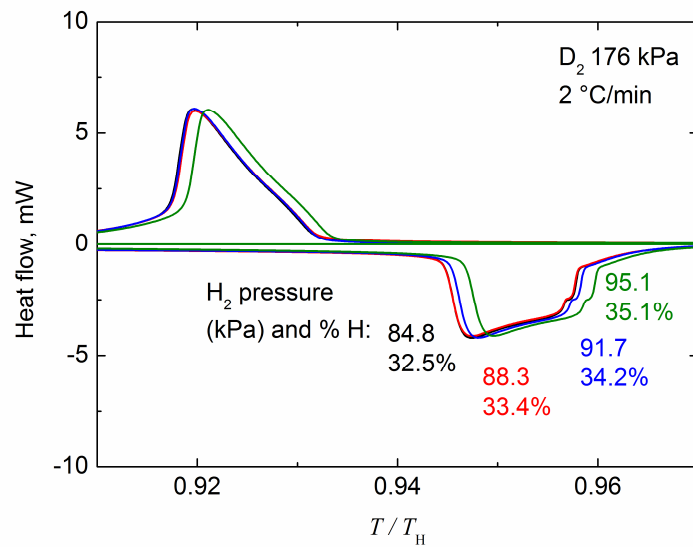
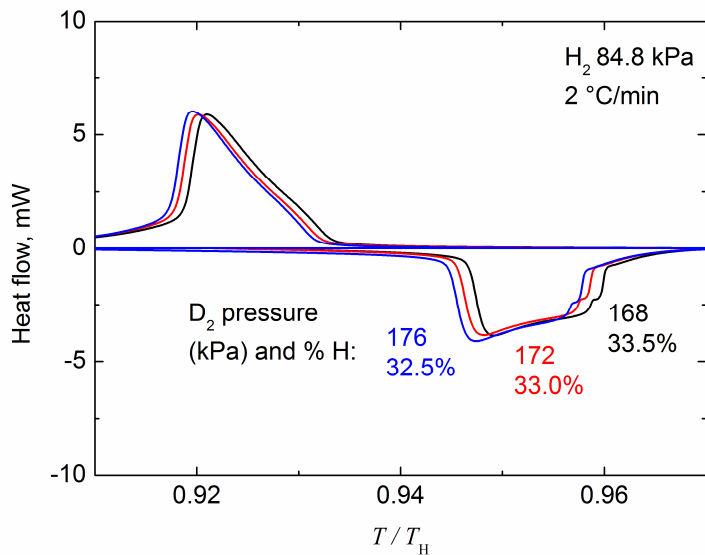
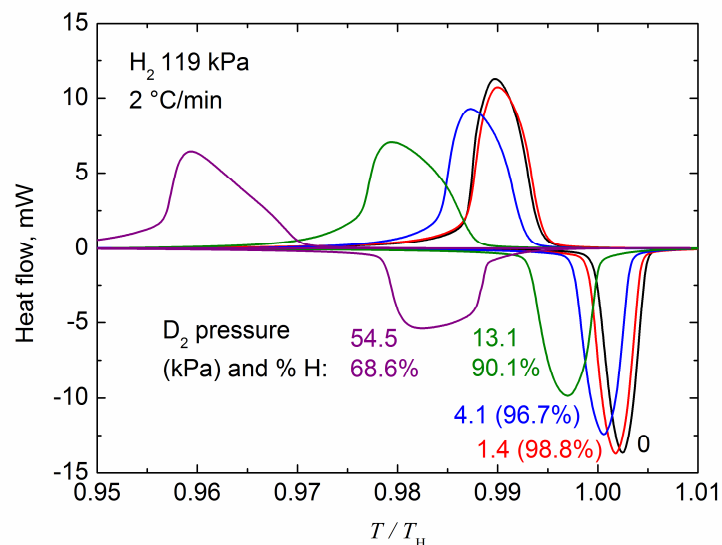
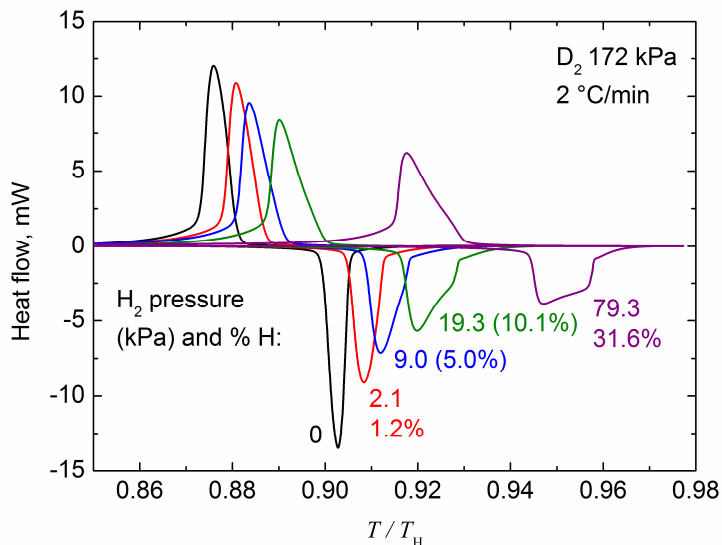


# Empirical fits for plateau pressures

- We compared DSC peak onsets to predicted  $\mu$  troughs

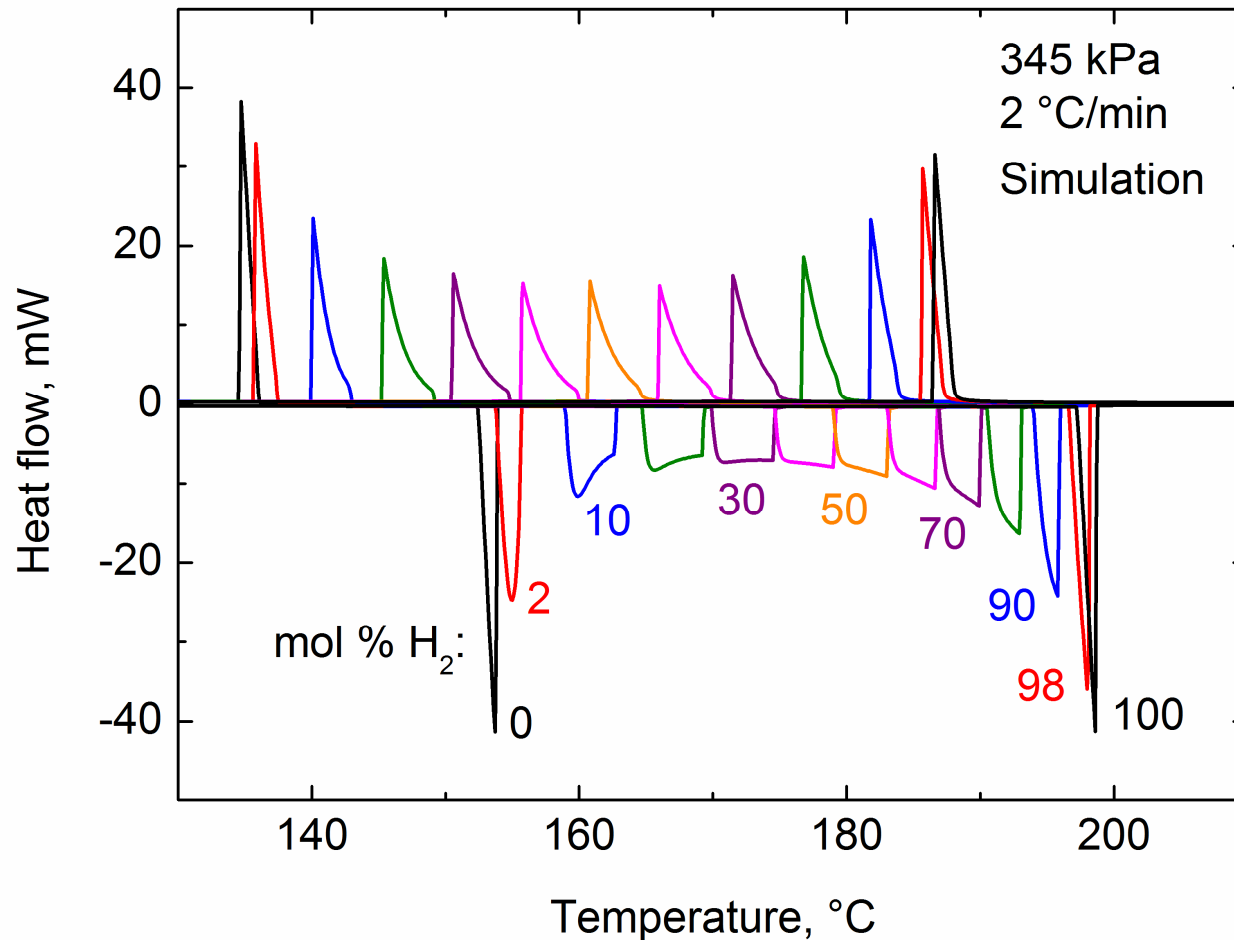


# Sensitivity is about 1% for H vs. D



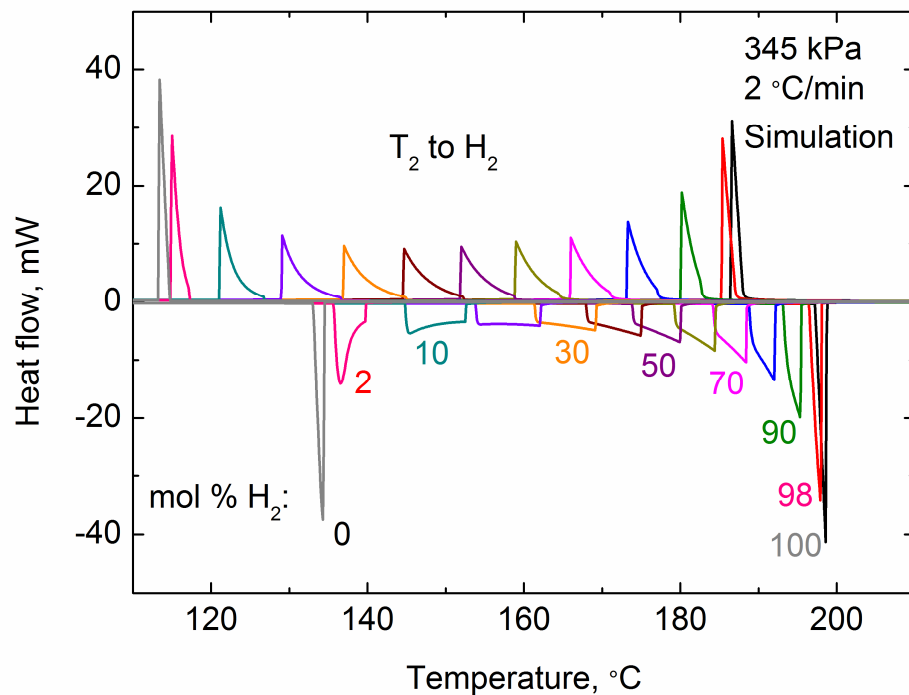
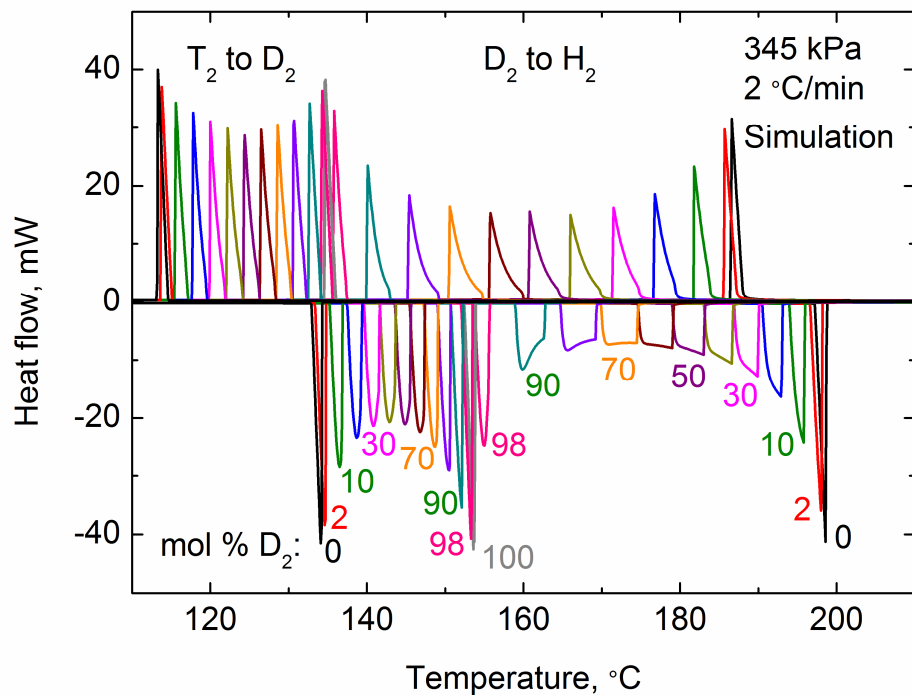
# Constant pressure models

- Inconvenient experiments, but clear composition dependence



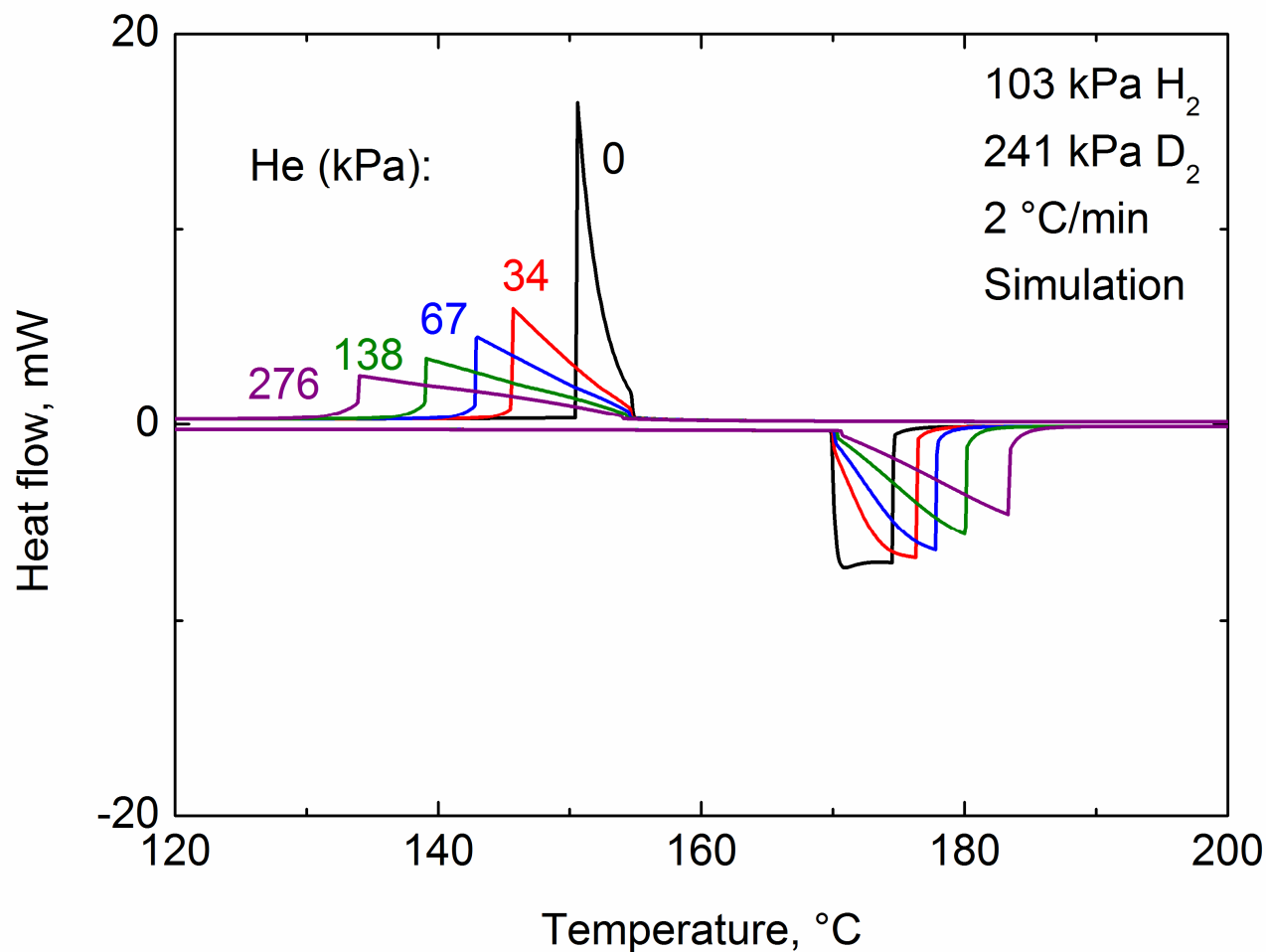
# Constant-P simulations with $T_2$

- More sensitivity with  $H_2$ , less with  $D_2$



# Ternary gas mixture

- Helium blanketing shifts simulated peaks of H-D mixtures



# Conclusions

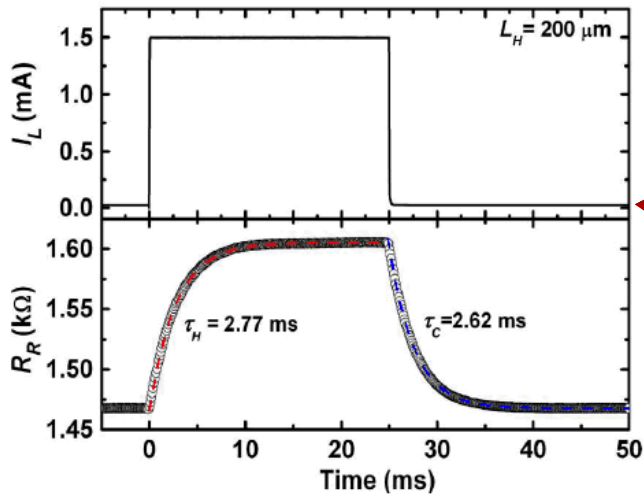
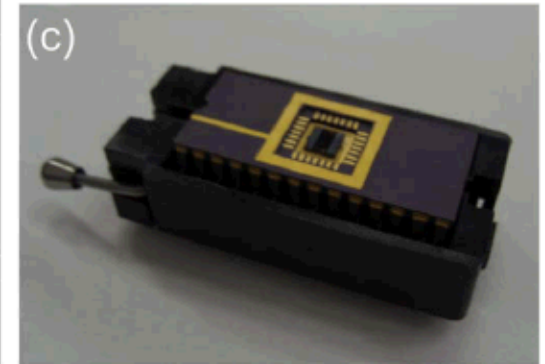
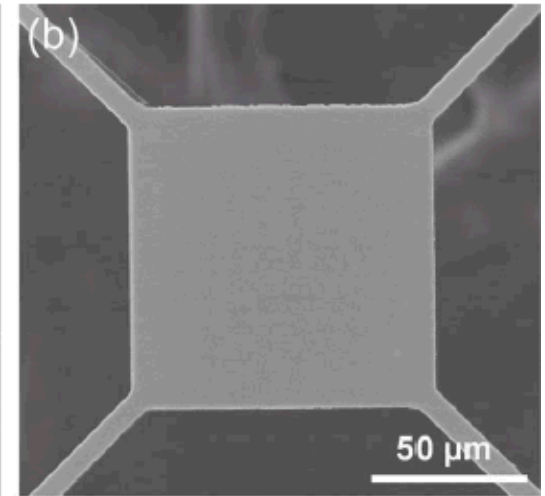
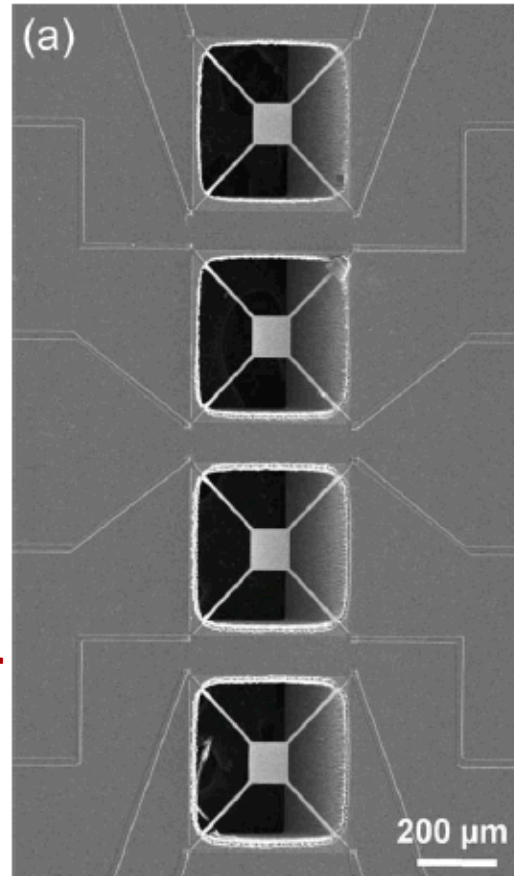
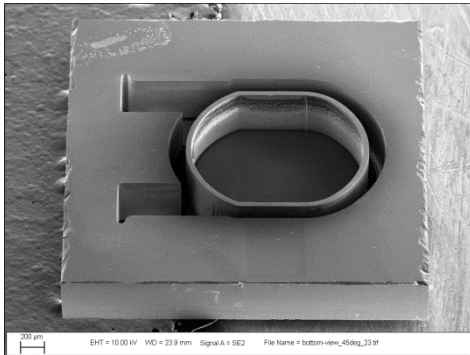
- Distinguishable signals are produced in Pd calorimetry upon variation of  $H_2$ ,  $D_2$ , He partial pressure
- Can detect about:
  - 1% He in  $H_2$  (or presumably  $D_2$ )
  - 1%  $H_2$  vs.  $D_2$
- For temperatures of 30 to 230 C, relevant pressures are:
  - 2-600 kPa  $H_2$
  - 12-1600 kPa  $D_2$
  - 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
- Preliminary investigations have been made to miniaturize the calorimeter

# Microfabricated calorimeter

- Microhotplates fabricated at Sandia and LLNL/UIUC



J. Lee et al., J. MEMS 17 1513 (2008)

# Acknowledgements

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



- Miniaturization: Curt Mowry, Matthew Moorman, Ron Manginell

