

Thermophysical Properties of Carbon Dioxide and CO₂-Rich Mixtures

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Motivation

1. Thermophysical properties of CO₂ for design and optimization of sCO₂ power cycles
2. For Carbon Capture and Sequestration (CCS), need to know phase behavior of water in compressed CO₂ (condensation in pipelines, etc. leads to corrosion)

Outline

1. **CO₂ Thermodynamic Properties (review)**
2. **CO₂ Thermal Conductivity: Measurements and Correlation**
3. **CO₂ Viscosity Correlation**
4. **Dew Point of Water in Compressed CO₂**
5. **Future Possibilities**

Thermodynamic Properties of Pure CO₂

- Compute using Equation of State (EOS) $p(\rho, T)$
[state-of-the-art: Helmholtz energy as $f(\rho, T)$]
- NOTE: EOS also needed for transport correlations [to get $\rho(p, T)$ and for critical enhancement]
- Old engineering EOS (Peng-Robinson, etc.) not accurate enough, especially around critical point.
- For well-measured fluid, can fit substance-specific reference EOS.
- Early standard EOS: Ely et al. (NBS), 1987.
- State of the art: Span and Wagner (1996).

Span-Wagner EOS for CO₂

- Up to 1100 K (1520 °F) and 800 MPa (116,000 psia)
- Extrapolation believed to be good beyond those limits
- Uncertainty similar to that of best data, should be negligible for engineering purposes
- Implemented in NIST REFPROP (and other software)
- Should be the benchmark for work with pure CO₂
- If too slow for an application (CFD), can pre-generate grids for spline interpolation

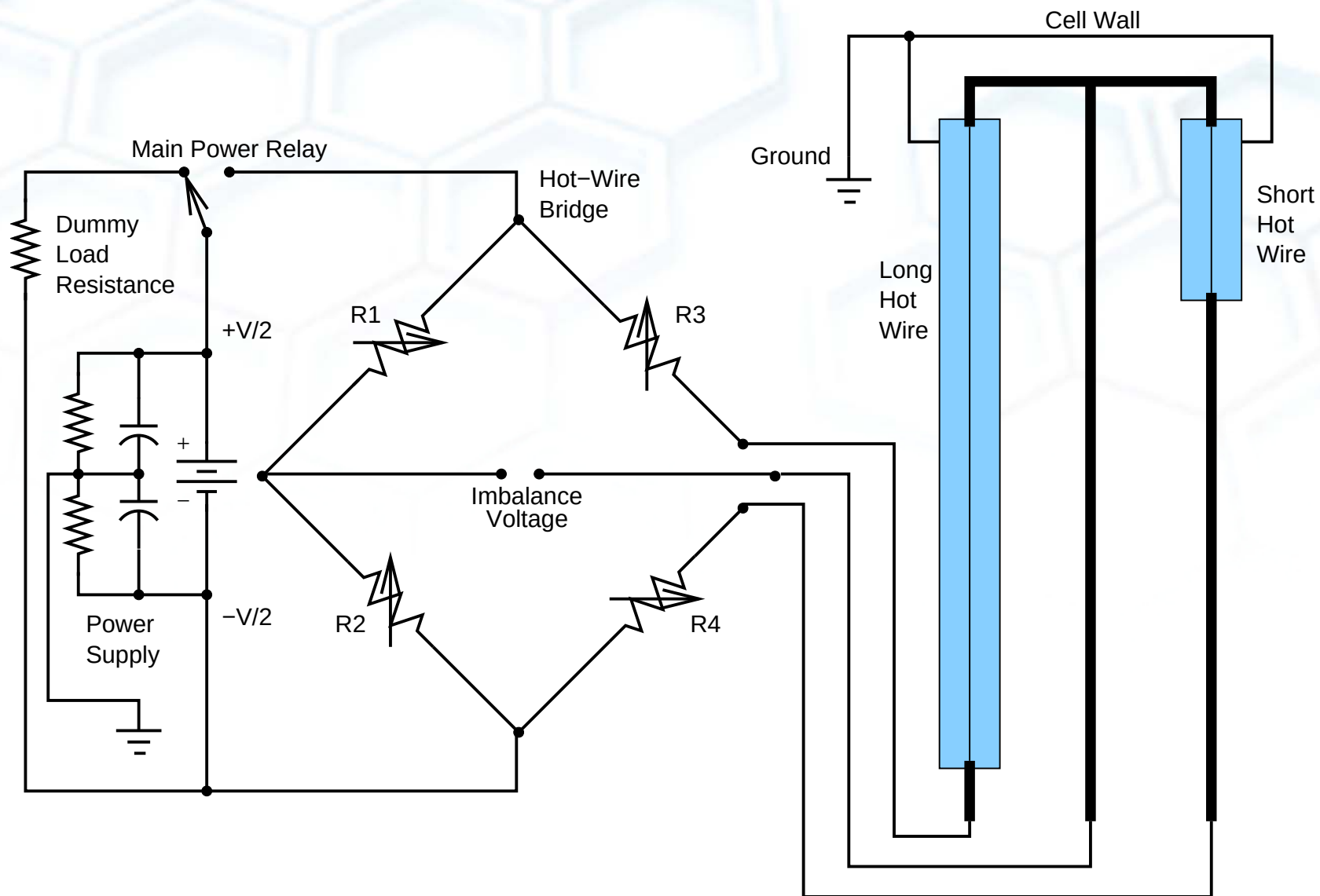
Thermal Conductivity of Pure CO₂

- Current correlation from 1990, based on older data and used older (1987) EOS.
- Uncertainties around 5 % at many conditions (1 % or 2 % in some well-measured regions). Uncertainty due to limitations of existing data, especially at high T and/or P and near the critical point.
- Our plan:
 1. Take new data with lower uncertainty over wide range of conditions (**Done**)
 2. New correlation, using new data, Span-Wagner EOS, and theoretical guidance (**in progress**)

Thermal Conductivity Measurements

- Carbon dioxide sample purity of 99.994 %
- Subcritical thermal conductivity measured for liquid and vapor along 220, 237, 252, 267, 282, and 296 K isotherms
- Supercritical thermal conductivity measured along 310, 314, 324, 340, 370, 404, 453, 503, 553, 603, 652, 702, and 752 K isotherms
- Transient hot-wire measurements for liquid phase and for gas phase at pressures from 0.5 MPa to saturation or 69 MPa
- Steady-state hot-wire measurements for gas phase at pressures below 1 MPa
- Uncertainty is 0.5 % for liquid and compressed gas, increasing to 3 % for gas below 1 MPa and in the critical region

Schematic of Hot-Wire Bridge



Working Equation (transient hot wire)

$$\Delta T_{\text{id}} = \frac{q}{4\pi\lambda} \left[\ln(t) + \ln\left(\frac{4a}{r_0^2 C}\right) \right] = \Delta T_{\text{w}} + \sum_{i=1}^{10} \delta T_i$$

ΔT_{id} = ideal temperature rise (line heat source) (K)

q = applied power per unit length of wire (W/m)

λ = thermal conductivity (W/(m·K))

t = elapsed time (s)

a = thermal diffusivity (m²/s)

r_0 = wire radius (m)

C = exponential of Euler's Constant (1.781...)

ΔT_{w} = measured temperature rise (K)

δT_i = corrections for non-ideal heat transfer (K)

Working Equation (Steady-State Hot Wire)

$$\lambda = \frac{q}{2\pi(T_1 - T_2)} \left[\ln \left(\frac{r_2}{r_1} \right) \right]$$

λ = thermal conductivity (W/(m·K))

q = applied power per unit length of wire (W/m)

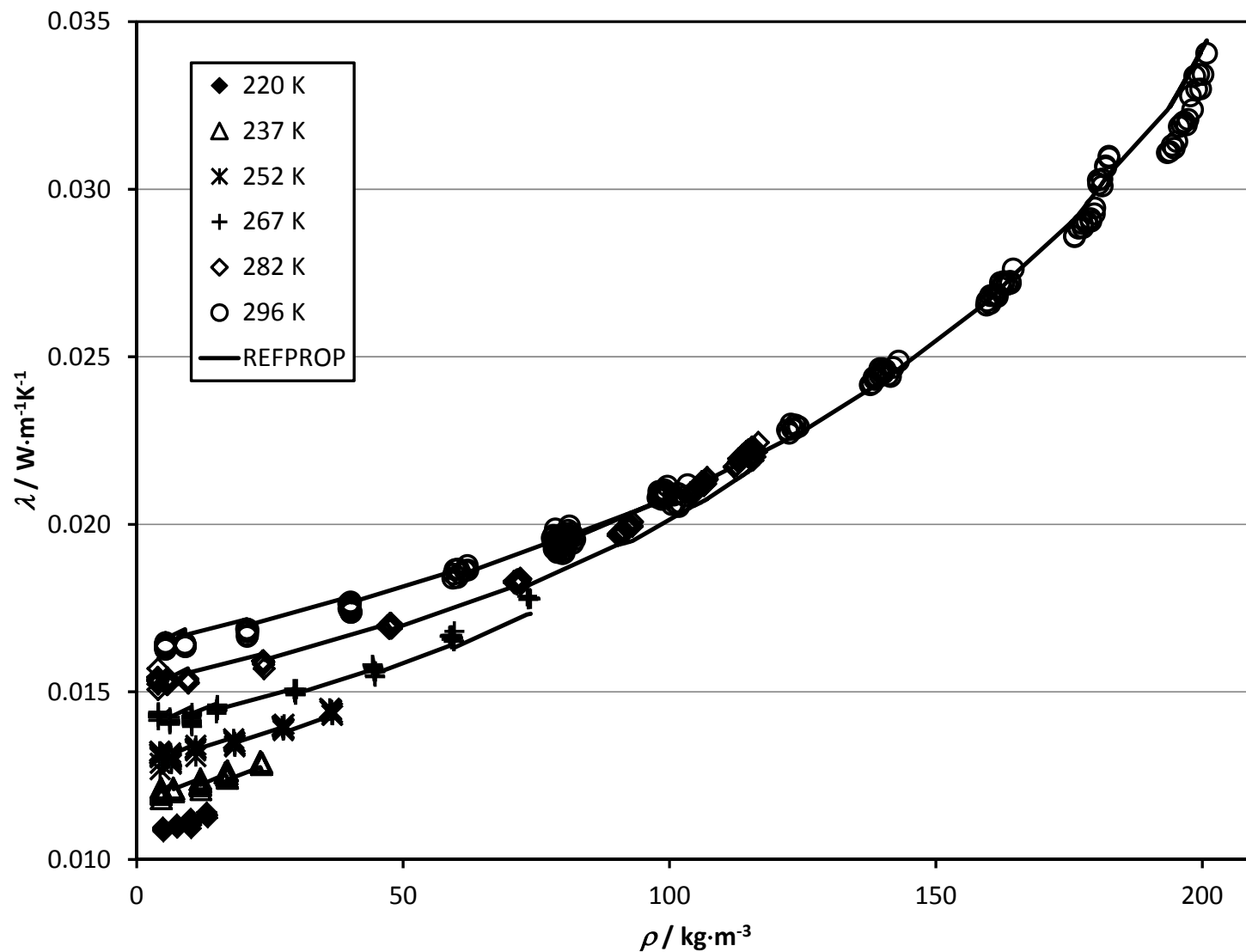
r_1 = wire radius (m)

r_2 = concentric cavity radius (m)

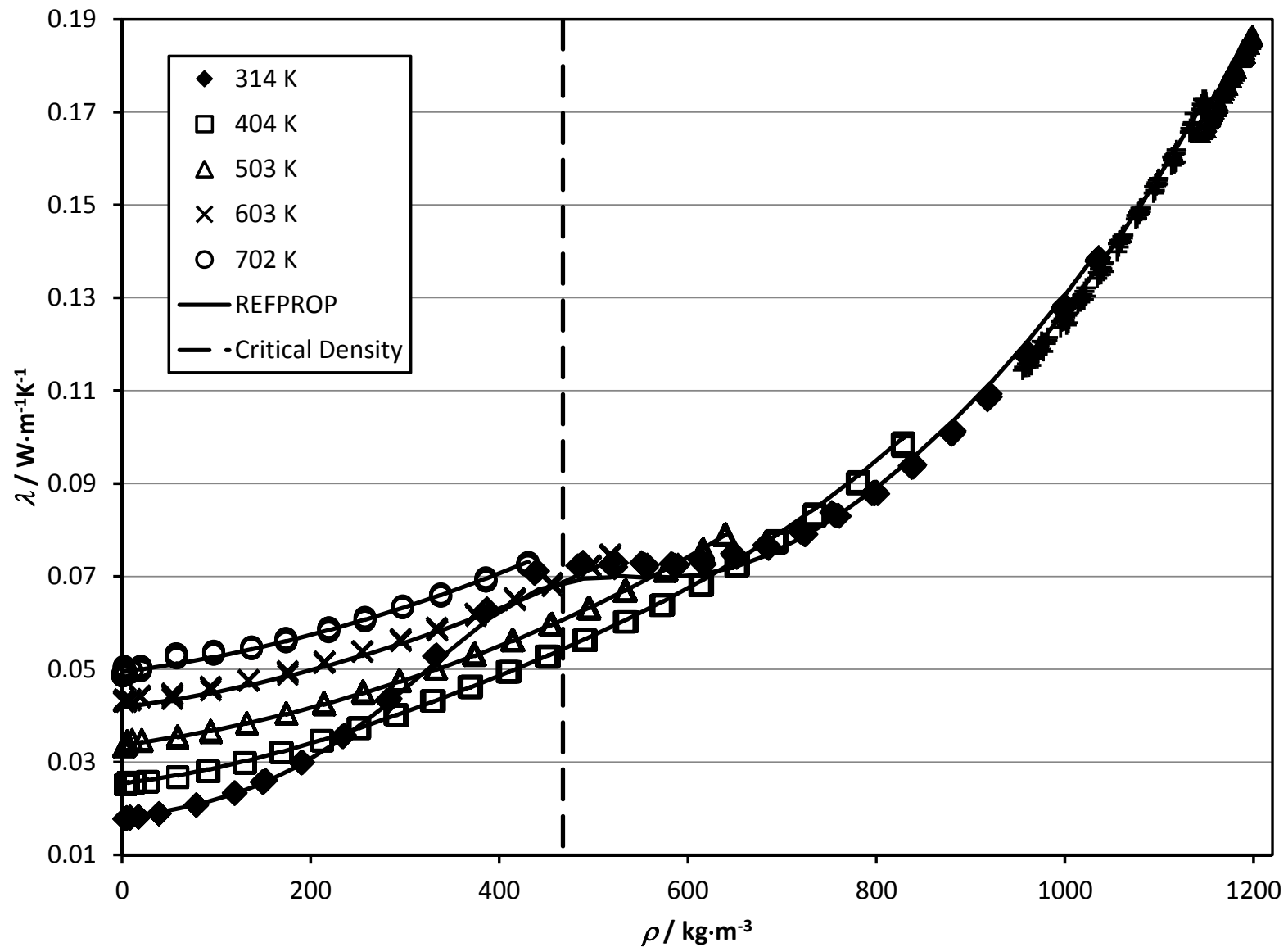
T_1 = measured wire temperature (K)

T_2 = cell temperature (K)

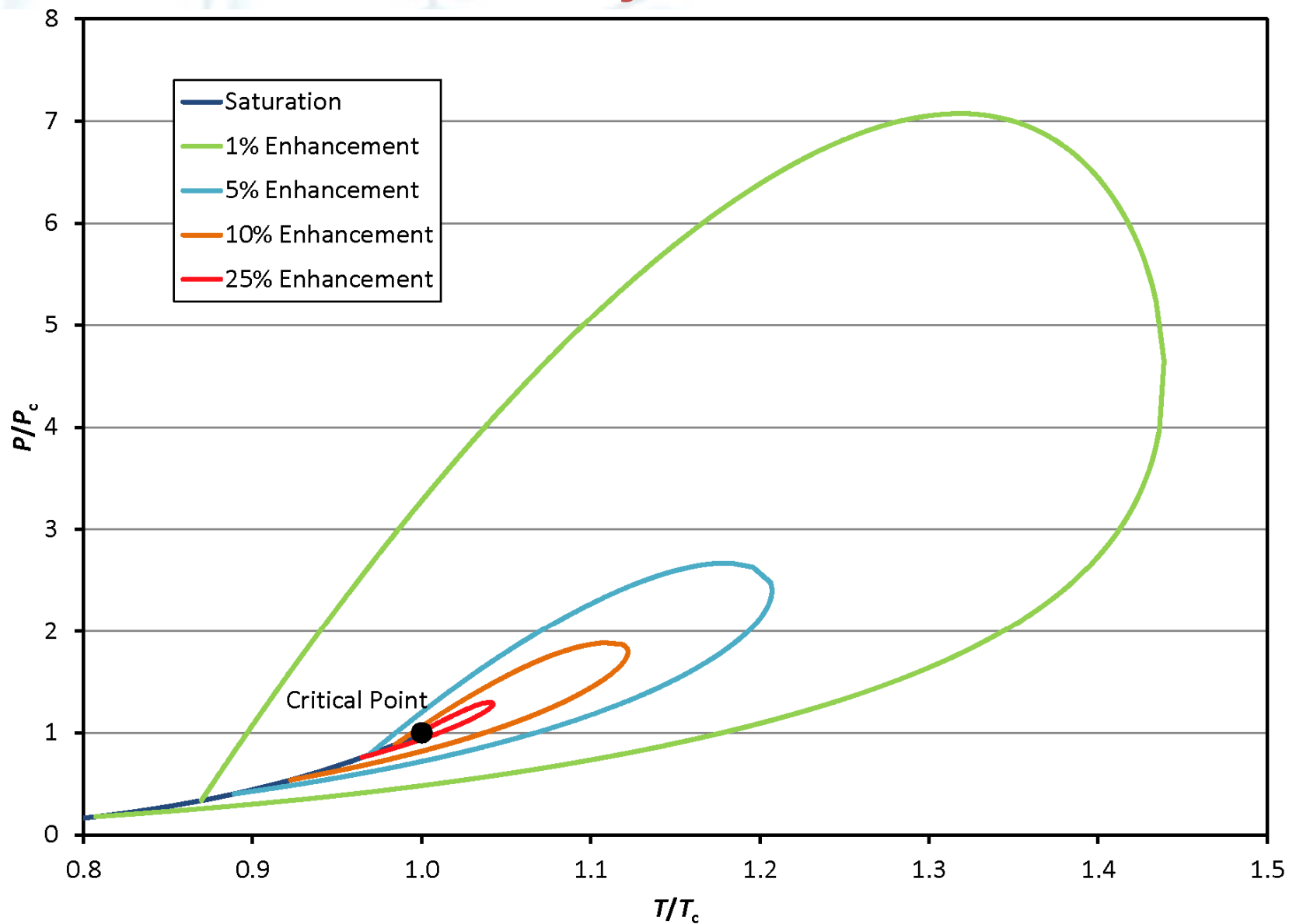
Thermal Conductivity (Subcritical Vapor)



Thermal Conductivity: Liquid & Supercritical Phases



Thermal Conductivity Critical Enhancement



Thermal Conductivity Correlation

- Thermal conductivity expressed as sum of 3 contributions

$$\lambda(\rho, T) = \lambda_0(T) + \lambda_1(\rho, T) + \lambda_2(\rho, T)$$

Zero-Density contribution

Residual contribution

Critical enhancement

Zero-Density Limit

- Experimental data at density $< 50 \text{ kg/m}^3$ considered for regression
- Data sorted into “bins” of $\sim 3 \text{ K}$; thermal conductivity corrected to nominal temperature

$$\lambda_{\text{corr}}(T_{\text{nom}}, \rho) = \lambda_{\text{exp}}(T_{\text{exp}}, \rho) + [\lambda(T_{\text{nom}}, \rho) - \lambda(T_{\text{exp}}, \rho)]_{\text{calc}}$$

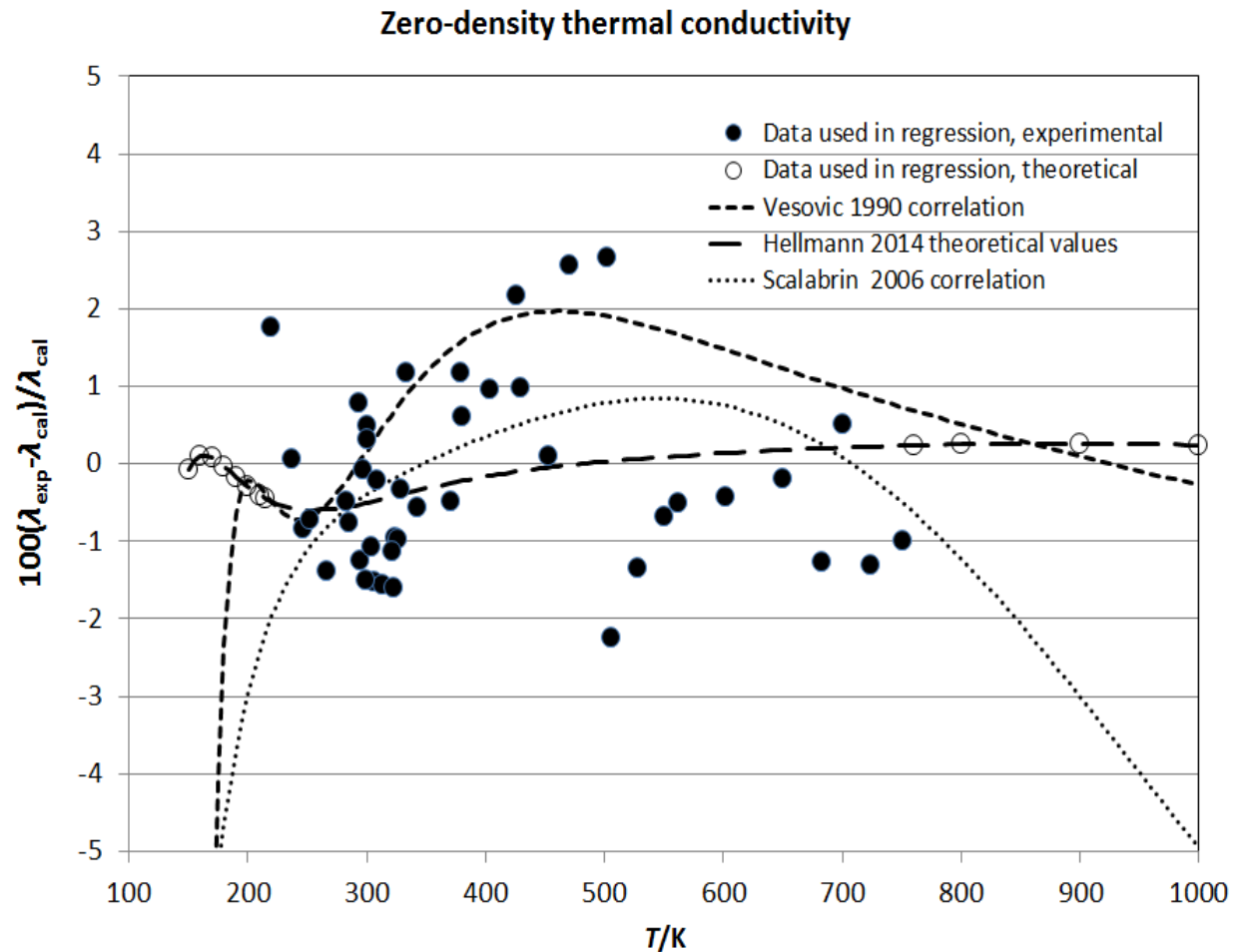
- Weighted linear least squares regression used to extrapolate to zero density resulting in set of experimental $\lambda_0(T_r)$
 - o Results: 47 isotherms from 219 K to 751 K
- Experimental data supplemented by selected theoretical results from the work of Hellmann (2014)
 - o Uncertainty of 1 % for $300 \text{ K} < T < 700 \text{ K}$, increasing to 2 % at 150 K and 2000 K.
 - o Added 8 points between 150 K and 215 K, 14 points between 760 K and 2000 K

Zero-Density Limit, continued

- Zero-density values fit to functional form:

$$\lambda_0(T_r) = \frac{\sqrt{T_r}}{\sum_{k=0}^J \frac{L_k}{T_r^k}}$$

$$T_r = T/T_c$$



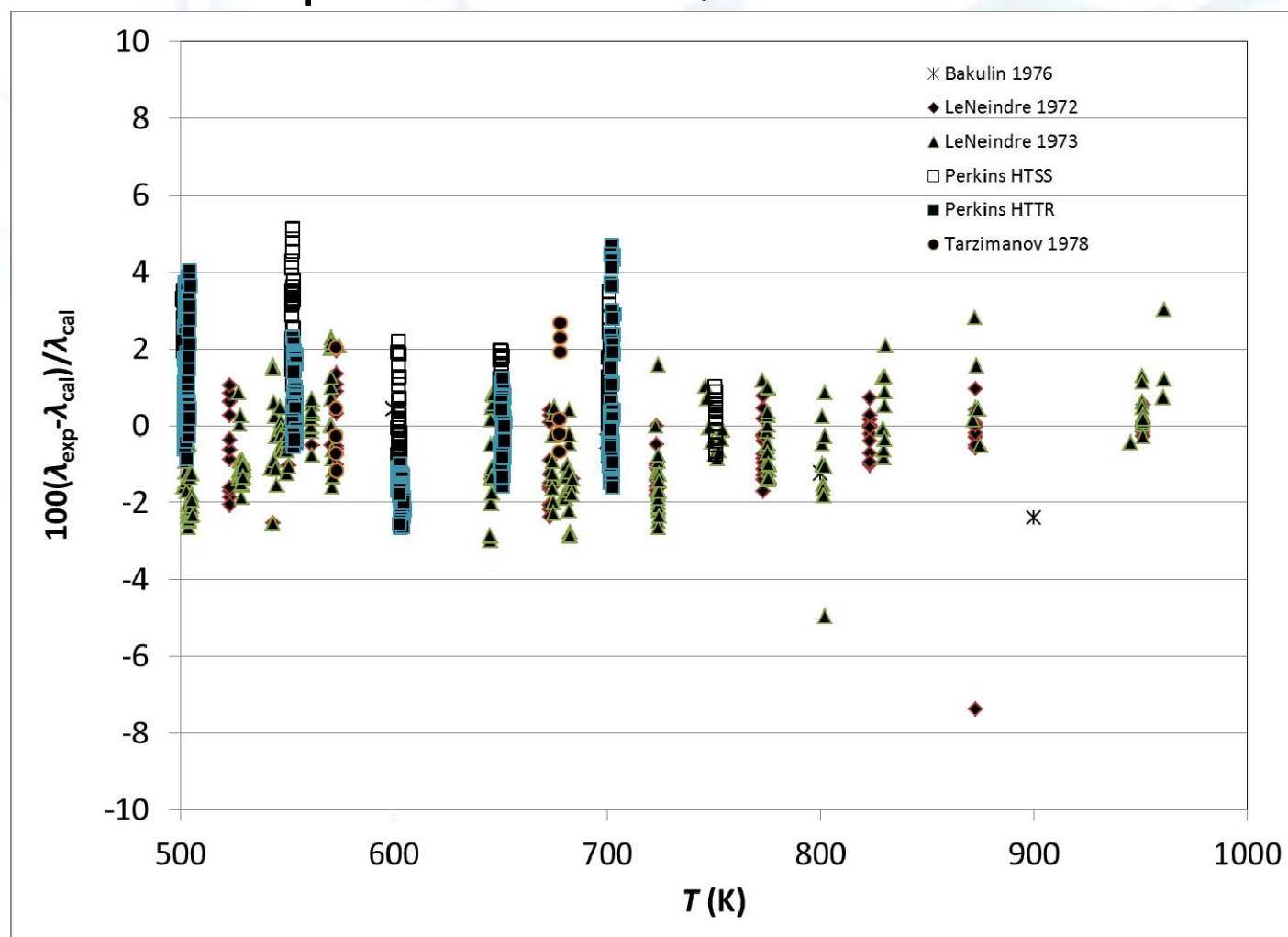
Residual Contribution

- Identify primary data set and assess their uncertainties
- Fit primary experimental data *simultaneously* for residual and critical enhancement terms.
- Use equation of state of Span and Wagner to provide density and thermodynamic properties required in enhancement term
- Theoretical guidance *not* available for the residual contribution
- Use empirical form

$$\lambda_1(T_r, \rho_r) = \sum_{j=1}^m (B_{1,j} + B_{2,j} T_r) \rho_r^j$$

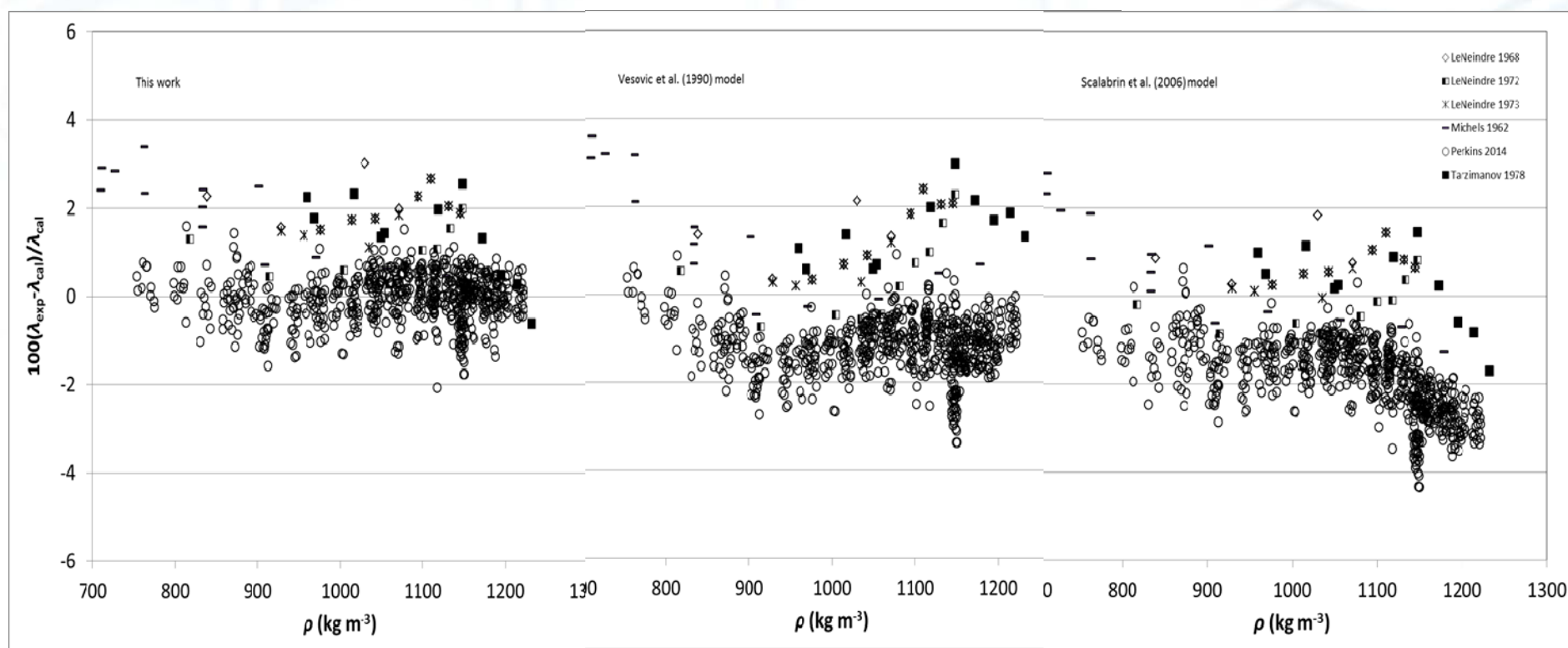
Selected (preliminary) Results

Supercritical Fluid, $T > 500$ K



Selected (preliminary) Results

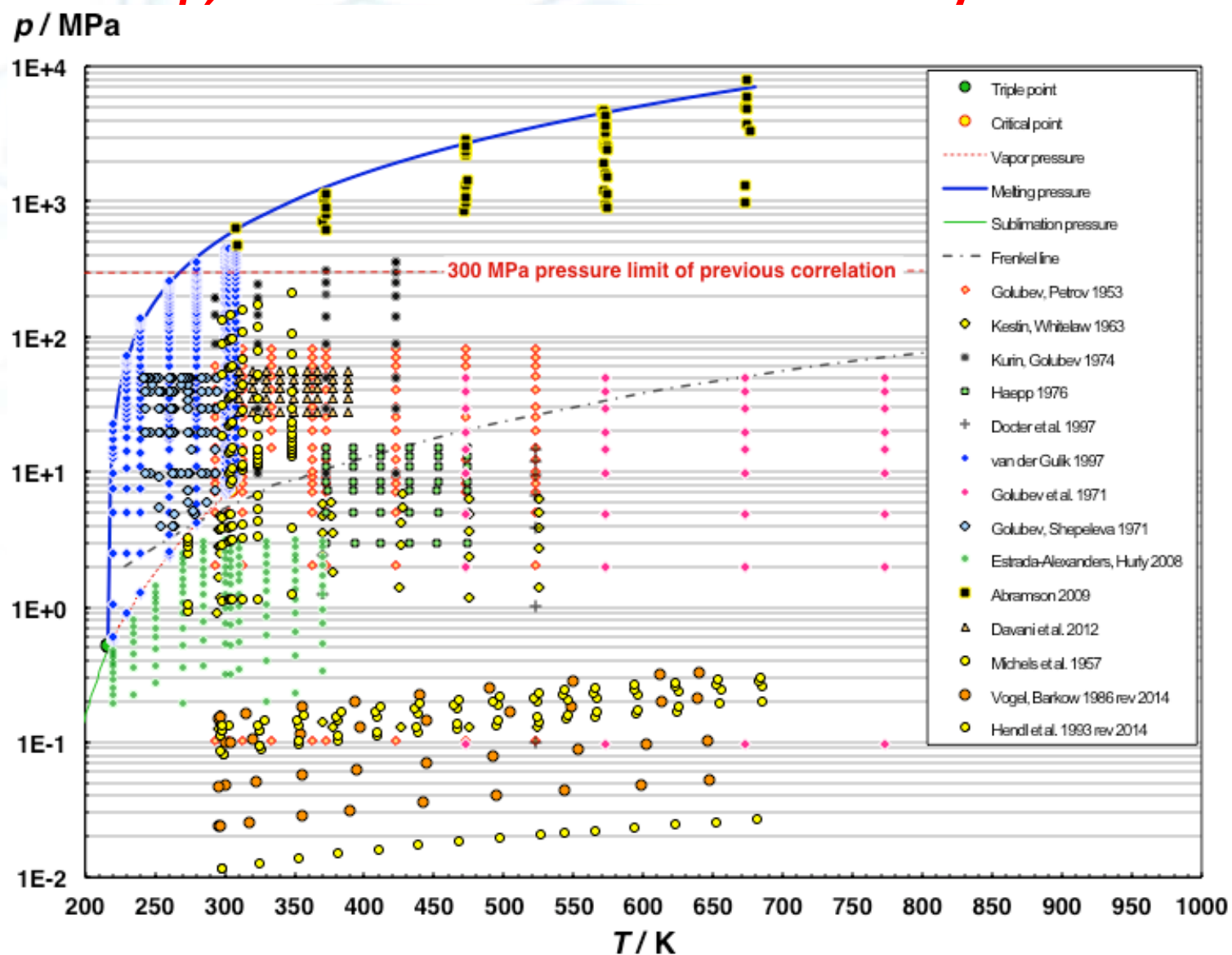
Significant improvements in representation of liquid phase
Our new data represented to ~1%



Viscosity of Pure CO₂

- Current correlation from 1990, slight revision in 1998 for better data in one high-pressure region. Uses old (1987) equation of state.
- Uncertainties 4-5 % at many conditions (1 % or 2 % in some well-measured regions)
- Since 1998, some new data available, and better theoretical understanding (esp. for dilute gas)
- Our plan: New correlation, using new data, Span-Wagner EOS, and theoretical guidance

p, T -Distribution of Selected Viscosity Data



Viscosity Formulation

$$\eta(T, \rho) = \underbrace{\eta_0(T)}_{\text{Visc(Temp,Dens)}} + \underbrace{\Delta\eta(T, \rho)}_{\rho \rightarrow 0} + \underbrace{\Delta\eta_c(T, \rho)}_{\text{residual}} + \underbrace{\Delta\eta_c(T, \rho)}_{\text{critical enhancement (small)}}$$

Correlation for $\rho \rightarrow 0$ by Bock et al. (2002)

$$\eta_0(T) = 0.021357 \sqrt{(MT)} / \sigma^2 \exp \left[\sum_{i=0}^4 a_i (\ln T^*)^i \right]$$

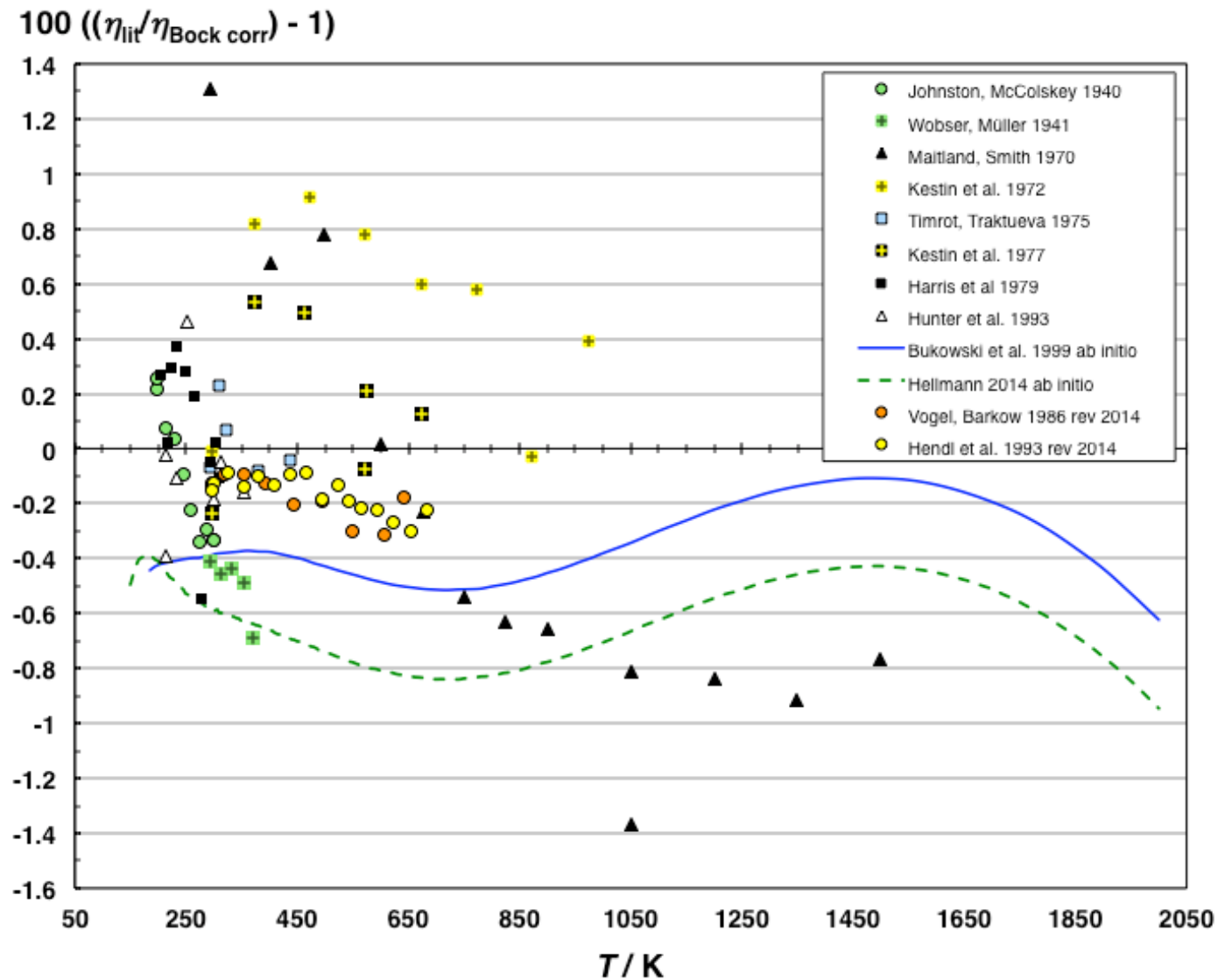
with $T^* = T / (\varepsilon / k_B)$

Residual part, Symbolic regression (preliminary)

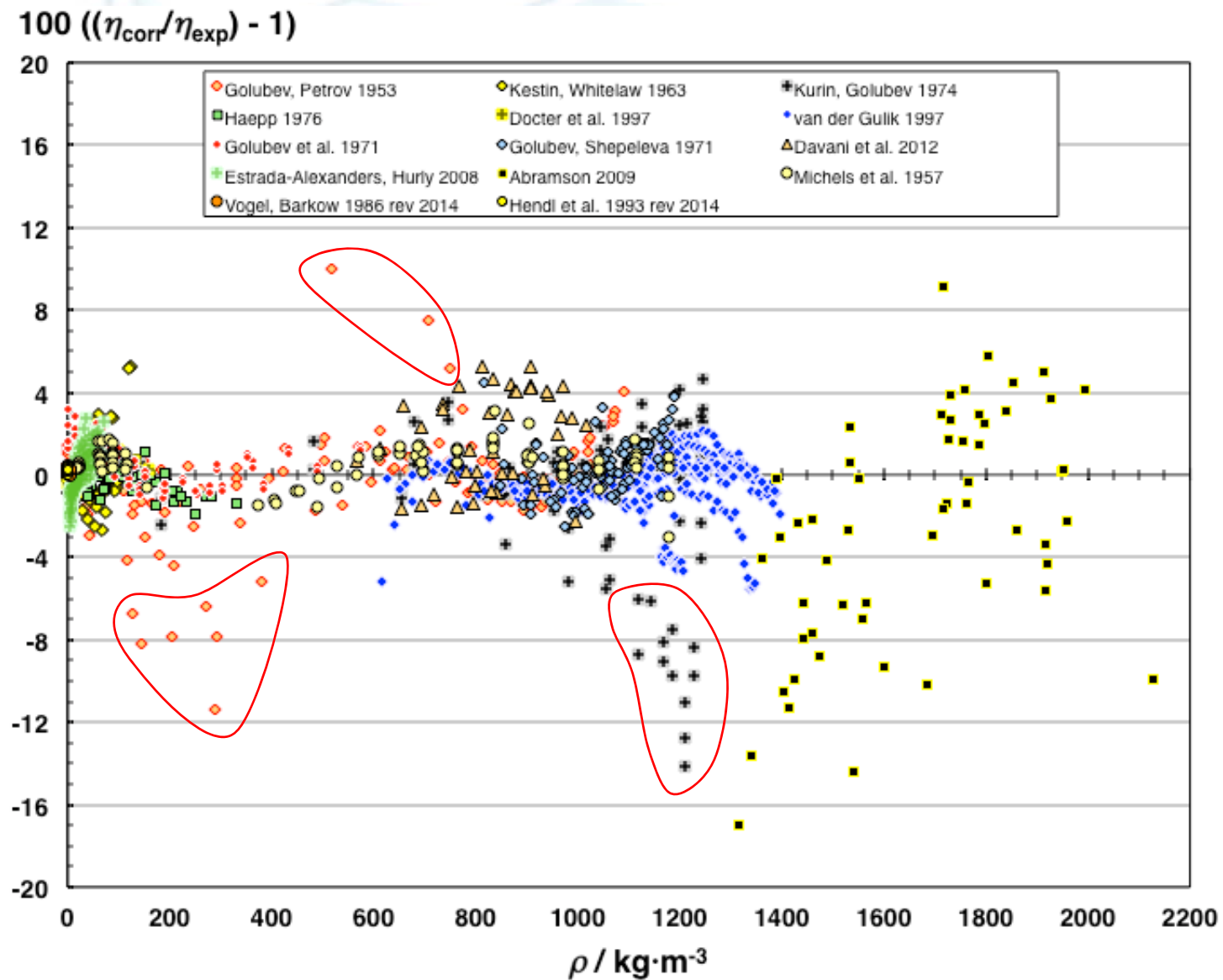
$$\Delta\eta(T, \rho) = \eta_{tL} \left[a_1 \rho_r + a_2 \rho_r^{a_3} + (a_4 \rho_r)^{a_5} / T_r \right]$$

$$\eta_{tL} = \frac{\rho_{tL}^{2/3} \sqrt{R T_t}}{M^{1/6} N_A^{1/3}}$$

Viscosity Data and Correlation for $\rho \rightarrow 0$



Data Representation by Preliminary Correlation



Dew Points in CCS

- For carbon capture and sequestration (CCS), compressed CO_2 in pipelines will contain some H_2O .
- Condensation of H_2O undesirable (corrosion).
- Need to be able to predict dew point temperature as a function of pressure and H_2O concentration (calculate how much drying of CO_2 needed).
- Thermodynamically, this mainly depends on the deviation of the mixture from ideal-gas behavior.

Thermodynamics: Virial Expansion

[Heike Kamerlingh Onnes (1901)]

$$p / (\rho RT) = 1 + B(T)\rho + C(T)\rho^2 + \dots$$

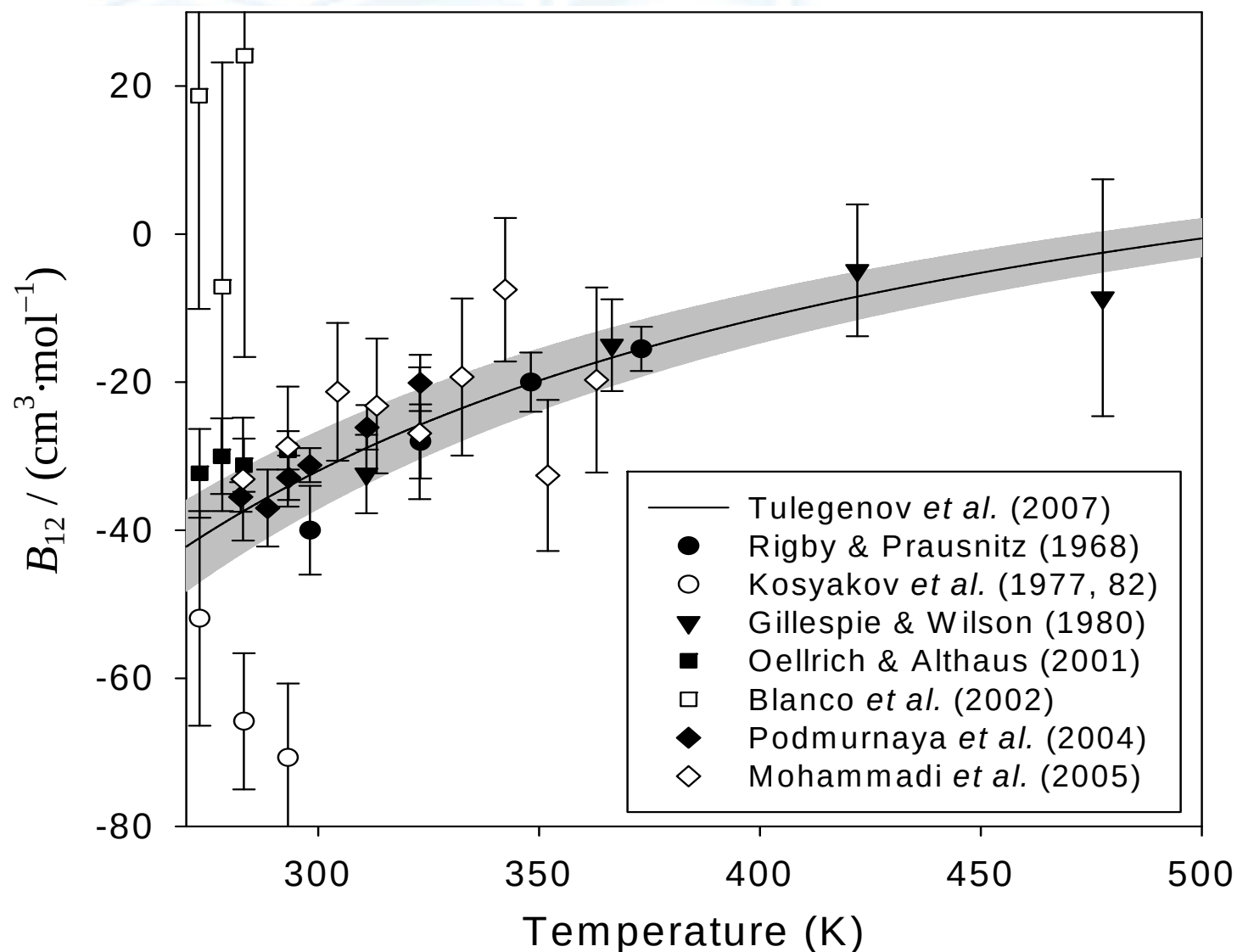
$$B(T) = \sum_i \sum_j x_i x_j B_{ij}(T)$$

- B_{ij} (second virial coefficient) rigorously related to pair potential, C_{ijk} adds 3-body effects, etc.
- Can calculate all thermodynamic properties (if density low enough); use as EOS boundary condition.

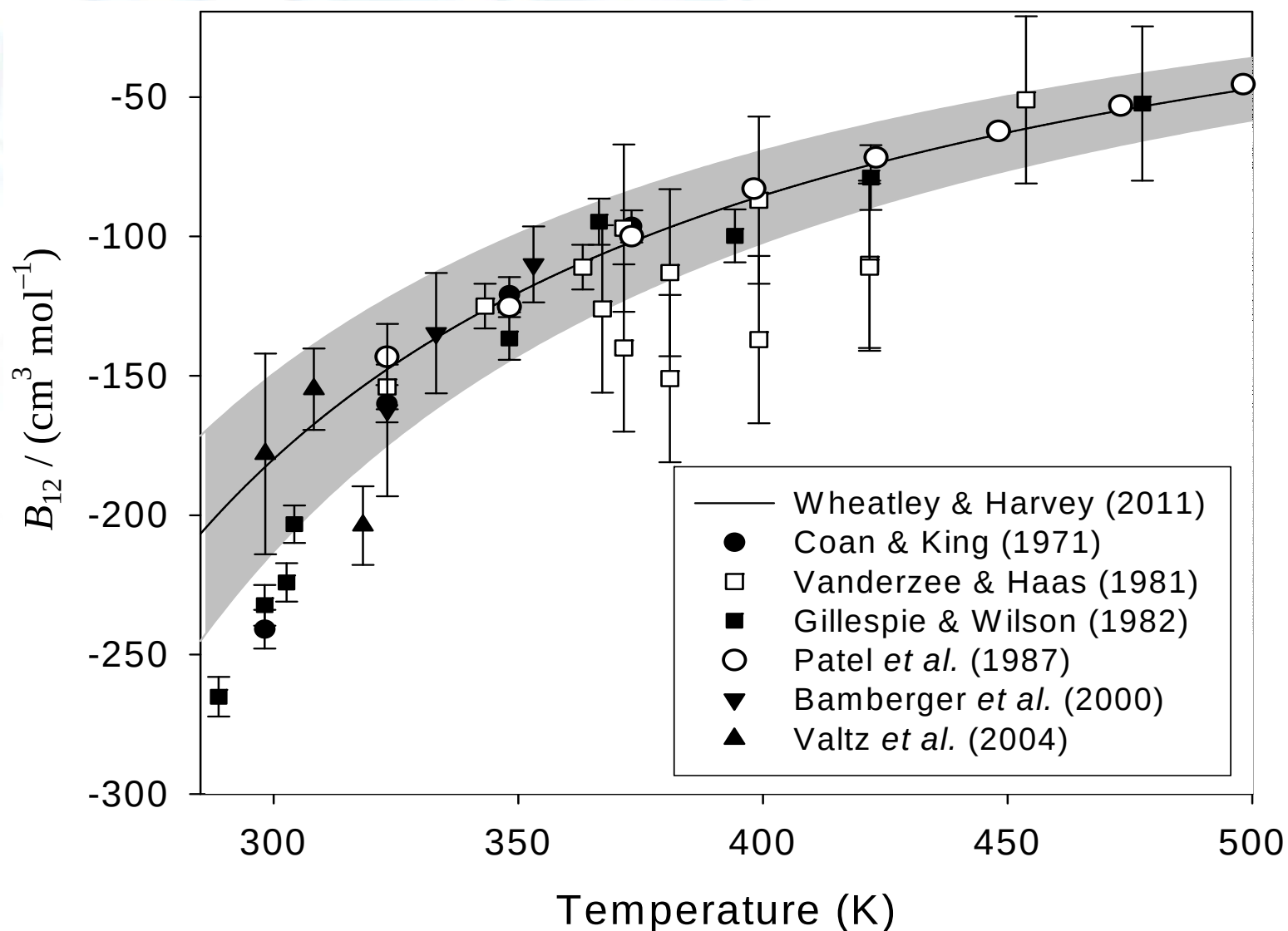
Gas/H₂O Second Virial Coefficient

- Experiments are difficult (high-T PVT data, or measure (small!) solubility of water or ice in carrier gas at low T).
- Theory (collaboration with Richard Wheatley, U. of Nottingham): *ab initio* quantum mechanics → quantitatively accurate potential for pairs of small molecules, then calculate B_{12} rigorously (uncertainties from unc. in potential).

Water-Nitrogen $B_{12}(T)$ from theory



Water-CO₂ $B_{12}(T)$ from theory



Dew-Point Data

- **Problem:** Uncertainties from theory are larger than desired, reducing uncertainty with more computations not currently feasible. Also, theory loses accuracy at higher pressures.
- **Solution:** Better measurements in key temperature range, using NIST dew-point apparatus developed for humidity standards.

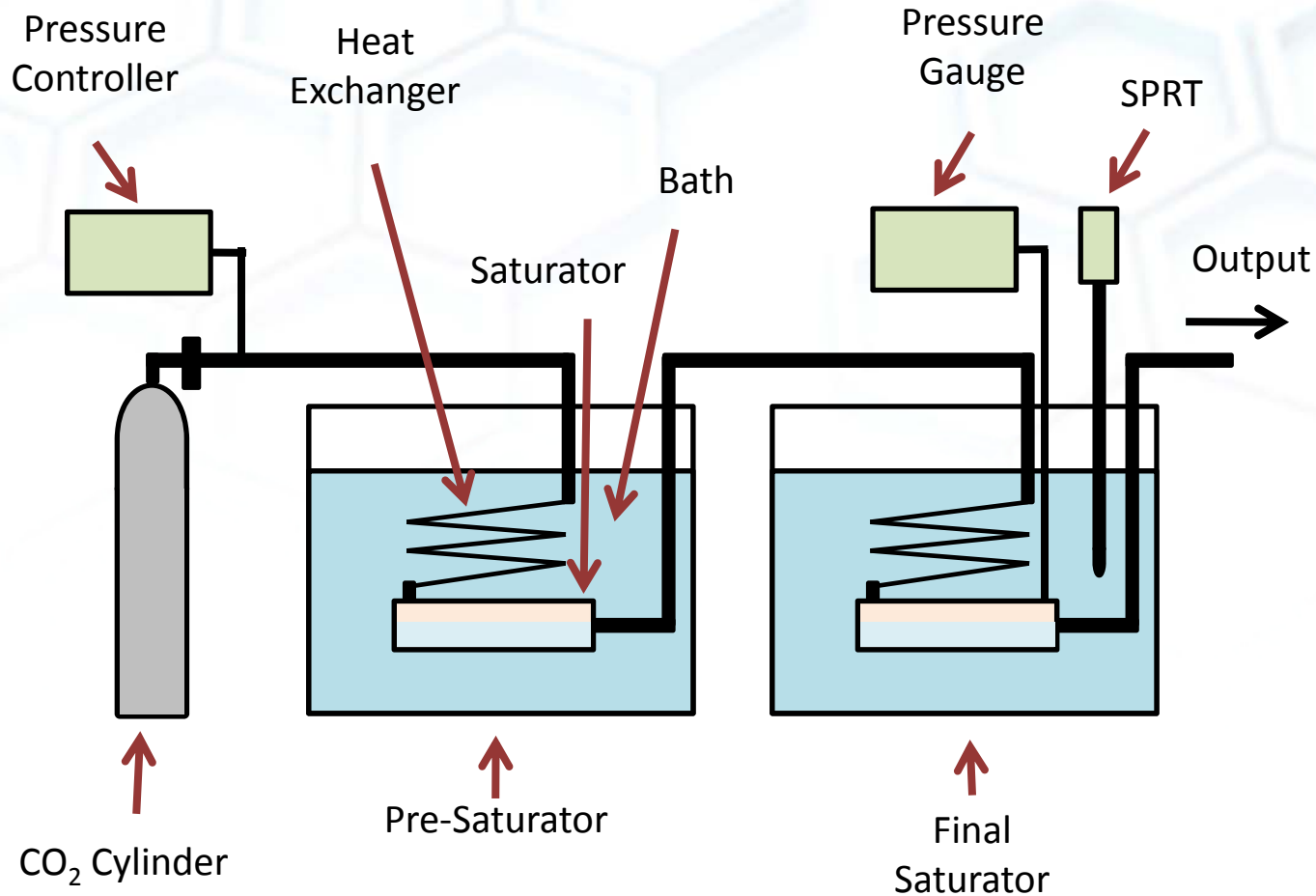
Dew-Point Experiments

1. Saturation system for compressed CO₂ (generates saturated gas at P and T_{DP})
2. Gravimetric hygrometer (designed for humidity standards) measures amounts of H₂O and CO₂ in saturated gas

NIST has only working metrology-class gravimetric hygrometer in the world [C.W. Meyer *et al.*, *Metrologia* 47, 192 (2010)].

Expected uncertainty for $T_{DP}(x,P)$: 0.05 °C.

Saturation System (for p to 5 MPa)



NIST Gravimetric Hygrometer

$$r = \frac{m_w}{m_g}$$

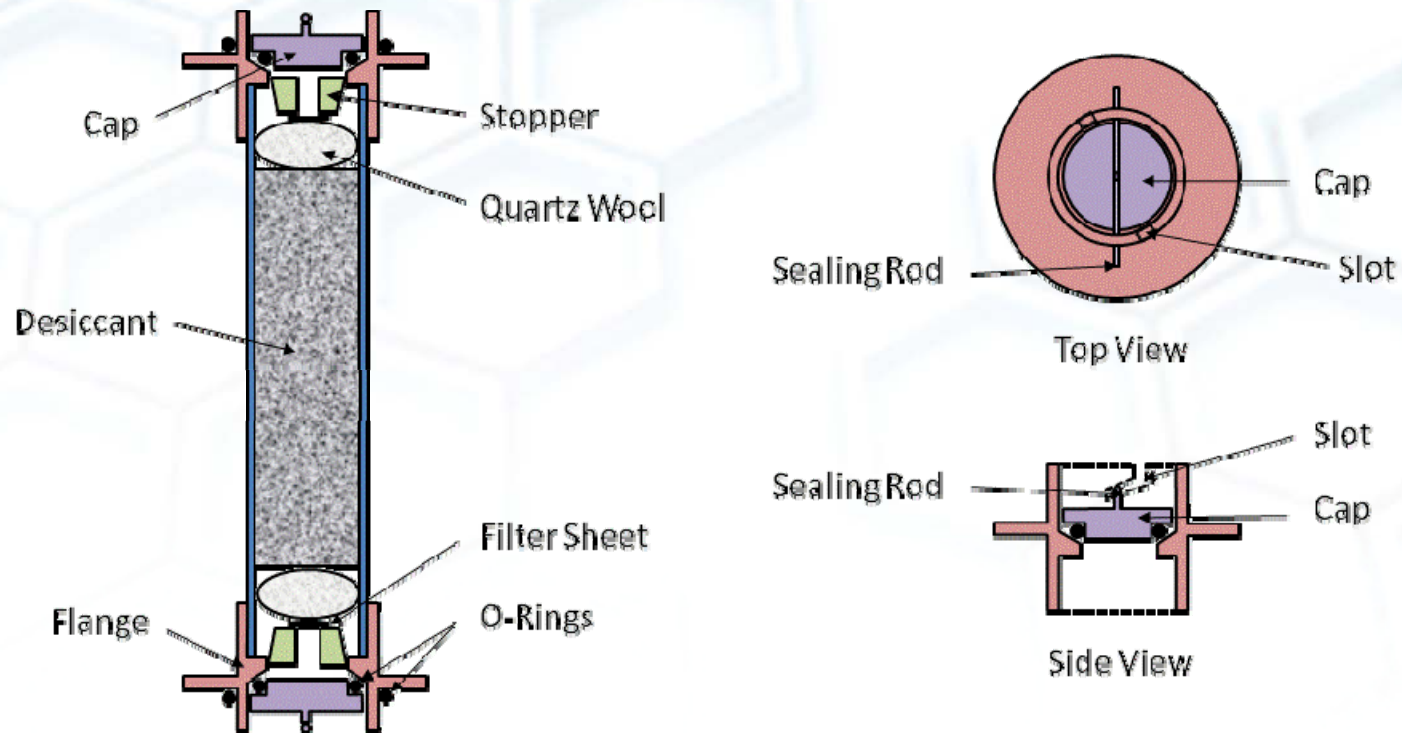
m_w : mass of water vapor

m_g : mass of carrier gas



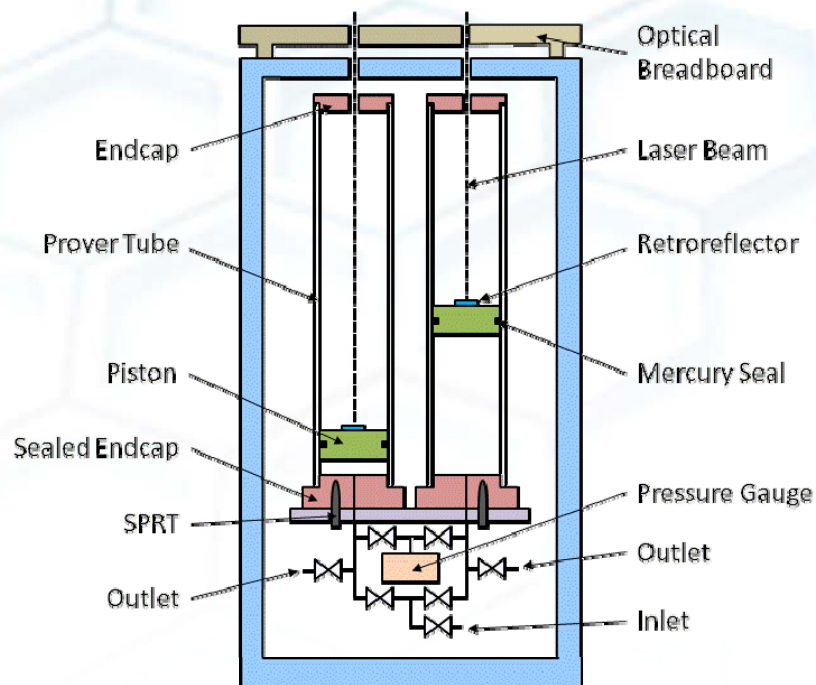
- 1) Separate moisture from dry gas (using desiccants)
- 2) Determine m_w by measuring increase in mass of water collection system
- 3) Determine m_g from volume, temperature and pressure measurements by use of pure-component EOS

Water Collection Tubes



- Desiccant used: Magnesium Perchlorate
- Mass measurements ($10\ \mu\text{g}$ resolution) made before and after water collection. $\sim 70\ \mu\text{g}$ uncertainty in water mass measurement.

Prover Tube Gas Collection System



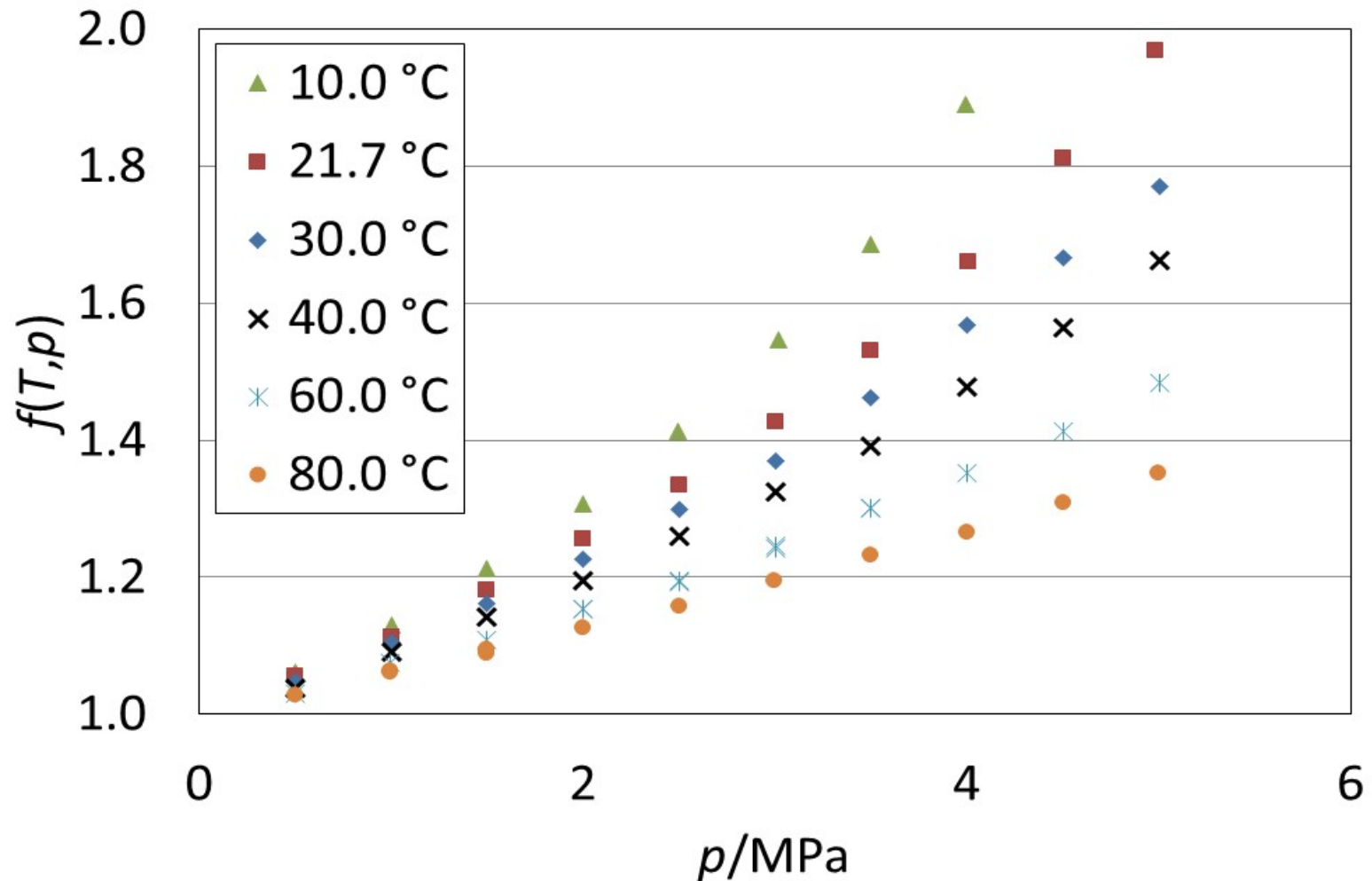
- Pressure and temperature measurements determine gas density (CO_2 equation of state well known)
- Laser interferometer measures piston displacement to determine gas volume, therefore total moles of gas
- Alternating pistons allow continuous gas flow

Experimental Program

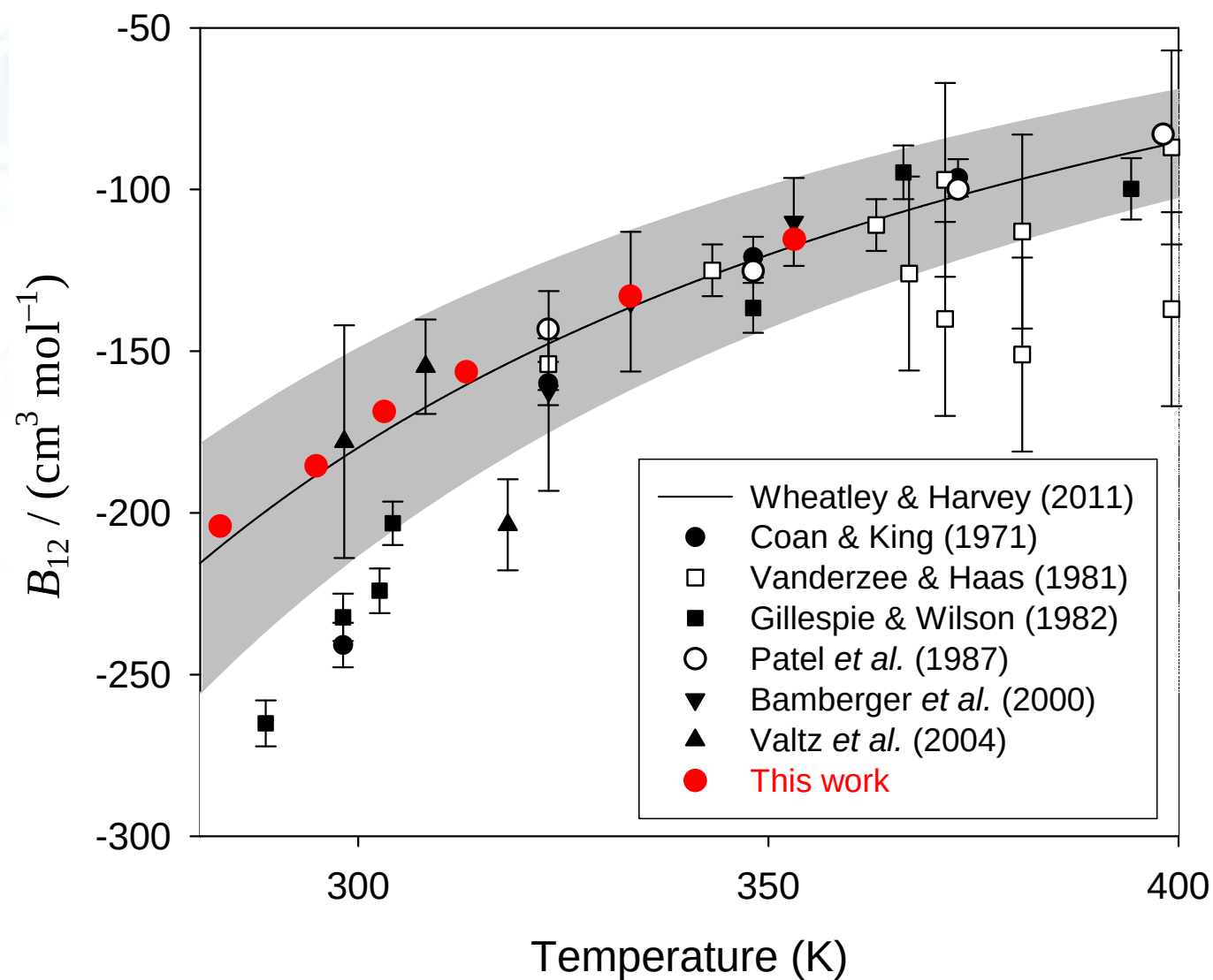
- Report saturated vapor composition (dew point) and enhancement factor (ratio of H_2O partial pressure in vapor phase to pure H_2O vapor pressure)
- 6 Temperatures from 10 °C to 80 °C
- Pressures up to 5 MPa (higher-pressure saturator could be built in the future)
- Avoid conditions where gas hydrates form (low T , high p)
- Use data to fit mixture EOS, also back out B_{12} with good precision and rough estimates for C_{122}

Preliminary Results

Water Vapor Enhancement Factor in CO₂



Preliminary Results for B_{12}



Summary of Dew-Point Results

- H_2O dew point in CO_2 measured more accurately than previous data.
- Preliminary results agree very well with theory for B_{12} (Wheatley & Harvey, 2011), but have smaller uncertainty.
- Data should be useful for optimizing mixture models for design of CCS processes.

Possible Future Work

- Thermophysical properties of mixed working fluids for supercritical CO₂ power cycles.
- Extension of dew-point experiments to higher pressures.
- Materials compatibility for CO₂-rich fluids (for pipelines and power cycles).