Thermophysical Properties of Carbon Dioxide and CO_2-Rich Mixtures

Allan H. Harvey, Marcia L. Huber, Arno Laesecke,
Chris D. Muzny, Richard A. Perkins
Applied Chemicals and Materials Division
National Institute of Standards and Technology
325 Broadway, Boulder, CO 80305, USA

Christopher W. Meyer
Sensor Science Division
National Institute of Standards and Technology
100 Bureau Drive, Gaithersburg, MD 20899, USA

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Motivation

1. Thermophysical properties of CO_2 for design and optimization of sCO2 power cycles
2. For Carbon Capture and Sequestration (CCS), need to know phase behavior of water in compressed CO_2 (condensation in pipelines, etc. leads to corrosion)

Outline

1. CO_2 Thermodynamic Properties (review)
2. CO_2 Thermal Conductivity: Measurements and Correlation
3. CO_2 Viscosity Correlation
4. Dew Point of Water in Compressed CO_2
5. Future Possibilities

Thermodynamic Properties of Pure CO_2

- **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 CO_2

- 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 CO_2
- If too slow for an application (CFD), can pre-generate grids for spline interpolation

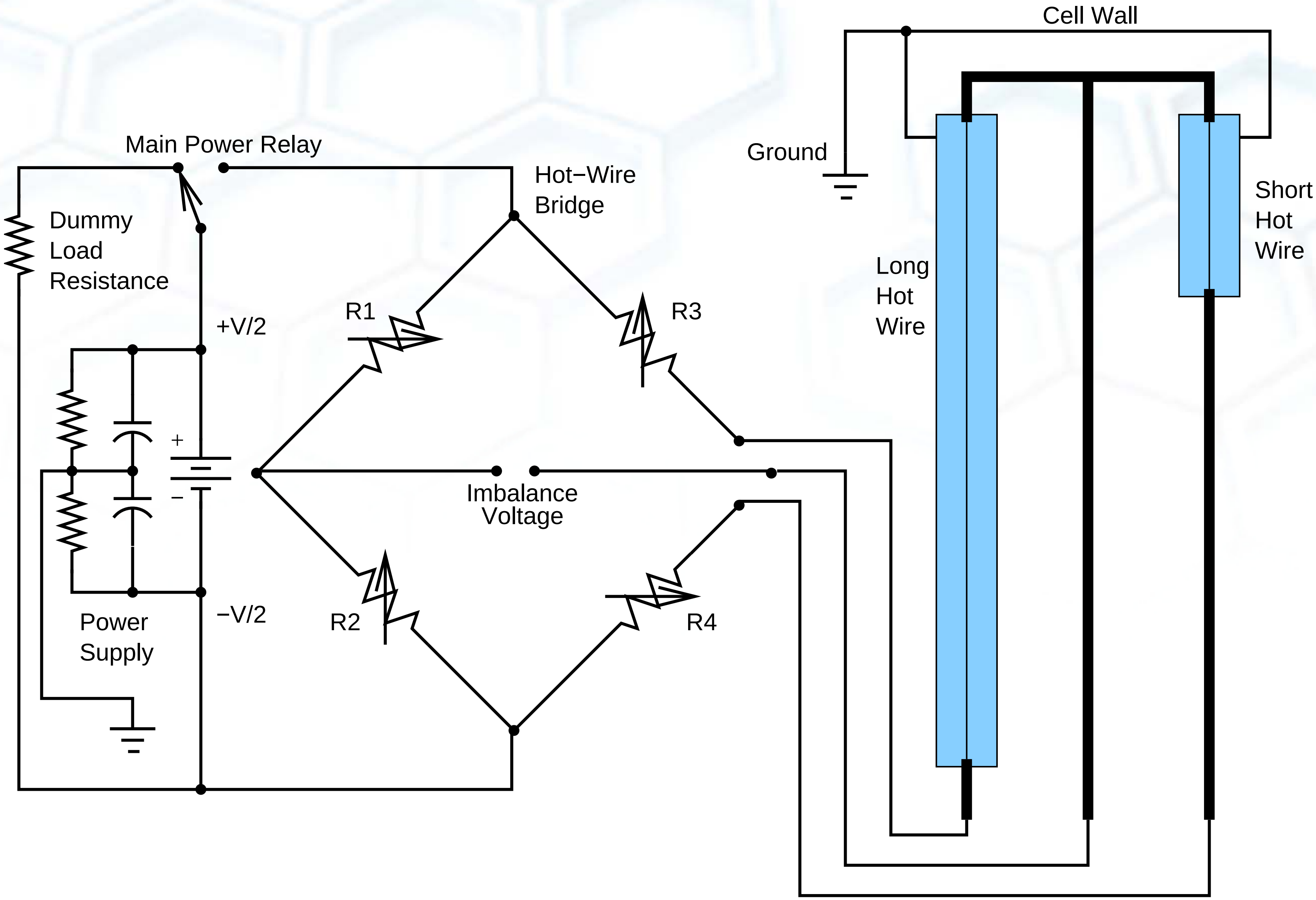
Thermal Conductivity of Pure CO_2

- 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)

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

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)

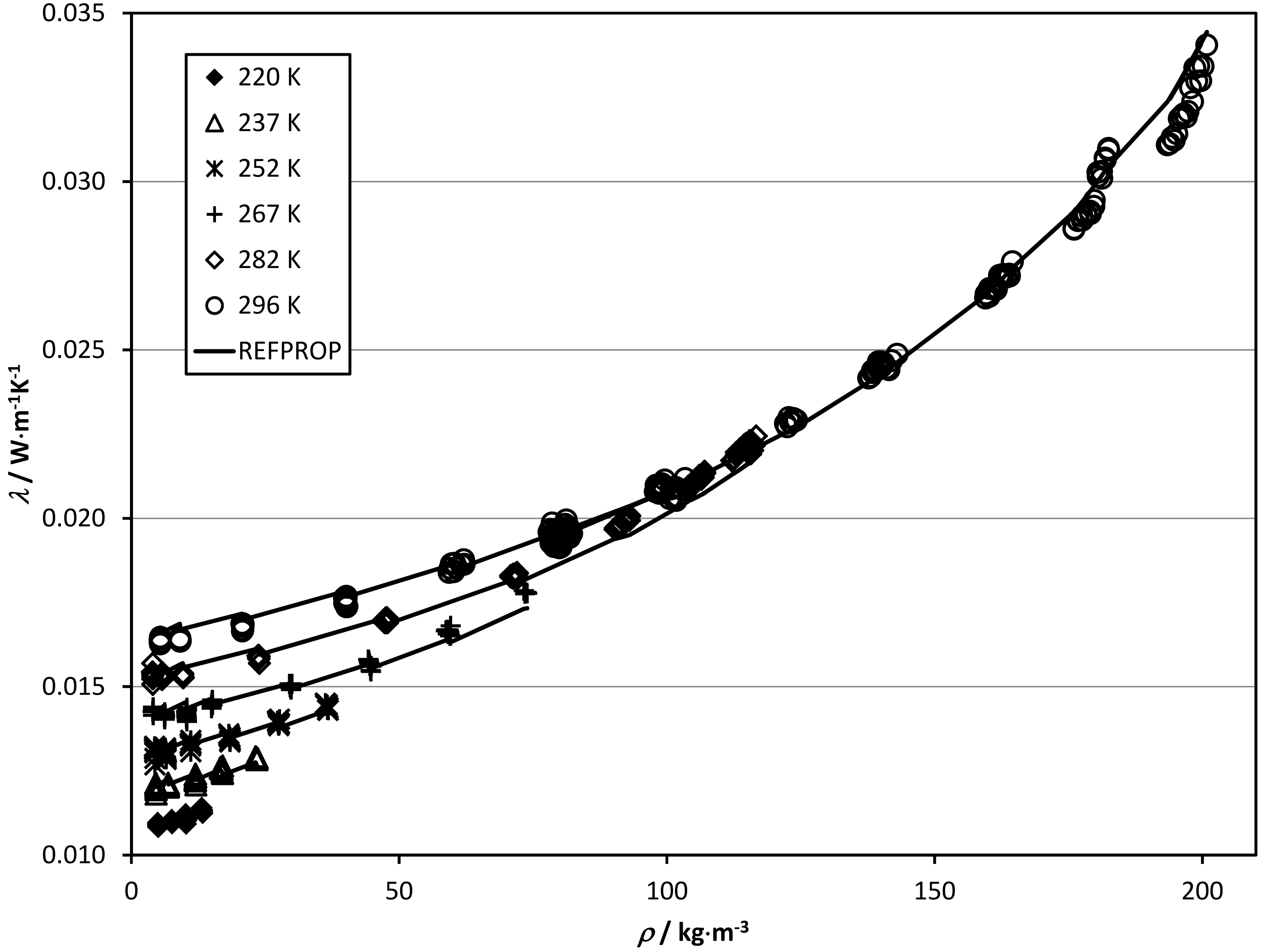
r_1 = wire radius (m)

r_2 = concentric cavity radius (m)

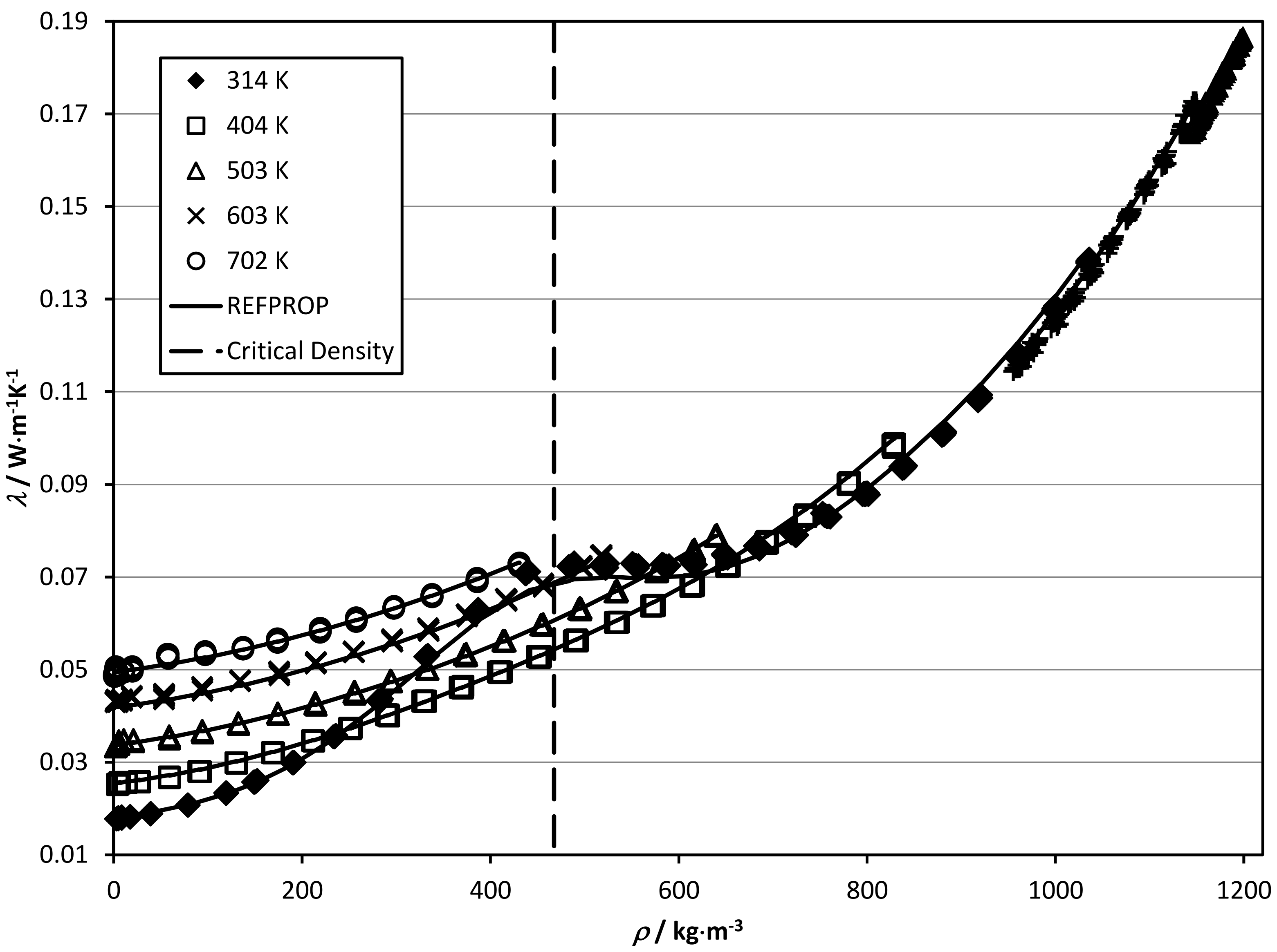
T_1 = measured wire temperature (K)

T_2 = cell temperature (K)

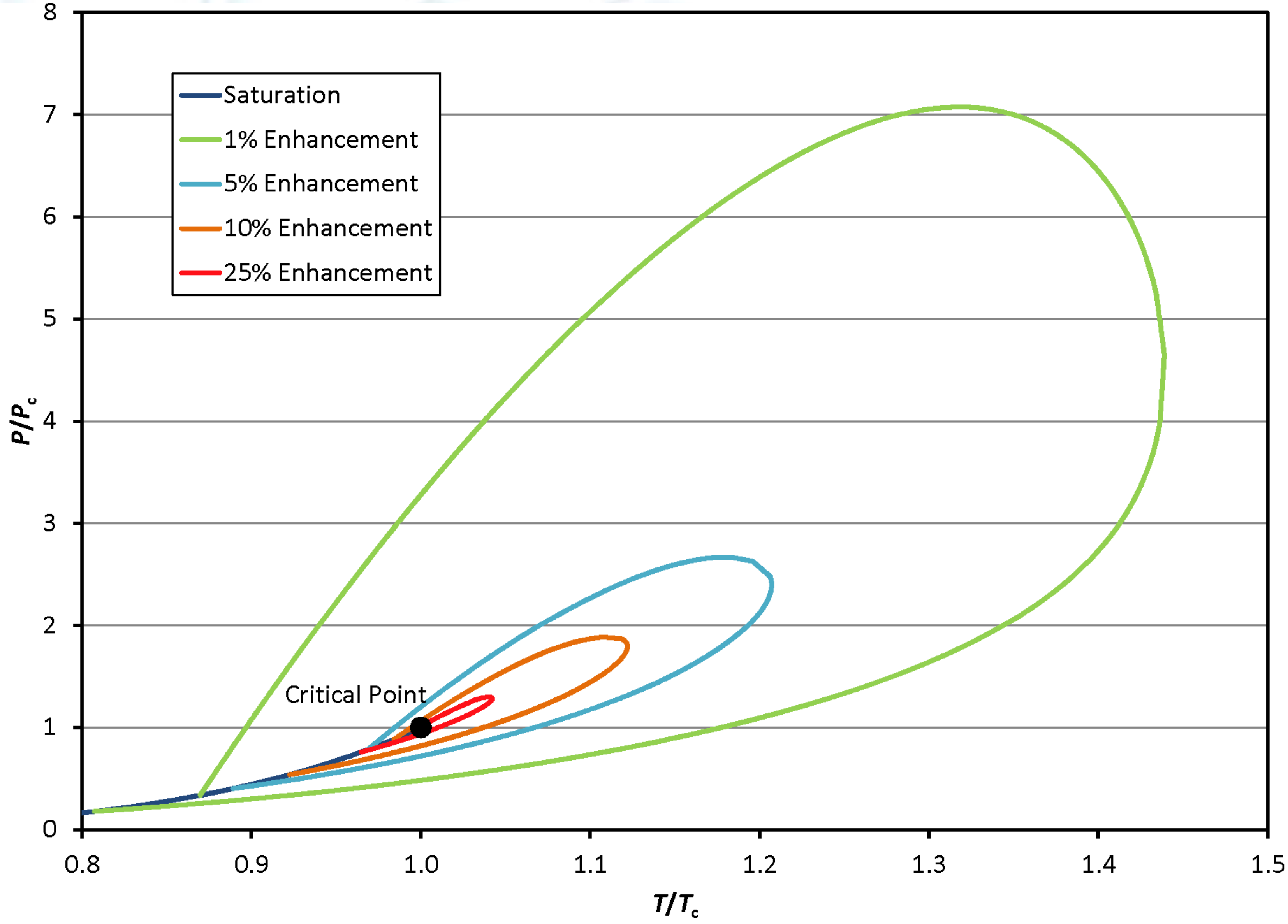
Thermal Conductivity (Subcritical Vapor)



Thermal Conductivity: Liquid & Supercritical Phases



Thermal Conductivity Critical Enhancement



Thermal Conductivity Correlation

- Thermal conductivity expressed as sum of 3 contributions

$$\underbrace{\lambda(\rho,T)=\lambda_0(T)}_{\text{Zero-Density contribution}}+\underbrace{\lambda_1(\rho,T)}_{\text{Residual contribution}}+\underbrace{\lambda_2(\rho,T)}_{\text{Critical enhancement}}$$

Zero-Density Limit

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

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

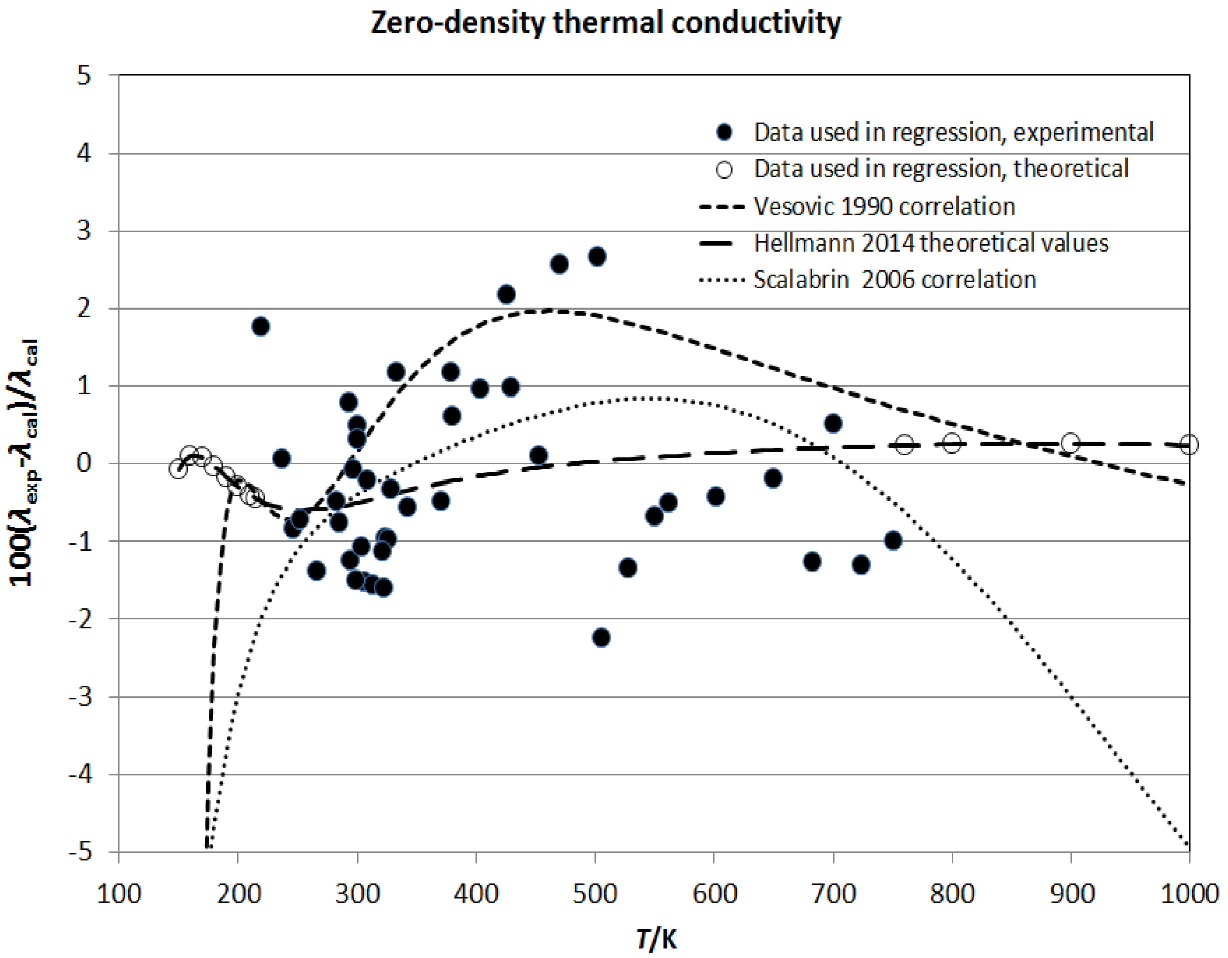
- Weighted linear least squares regression used to extrapolate to zero density resulting in set of experimental $\lambda_0(T_r)$
  - Results: 47 isotherms from 219 K to 751 K
- Experimental data supplemented by selected theoretical results from the work of Hellmann (2014)
  - Uncertainty of 1 % for 300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

$$\lambda_0(T_\mathrm{r}) = \frac{\sqrt{T_\mathrm{r}}}{\displaystyle\sum_{k=0}^{J} \frac{L_k}{T_\mathrm{r}^{\,k}}}$$

$$T_\mathrm{r} = T/T_\mathrm{c}$$



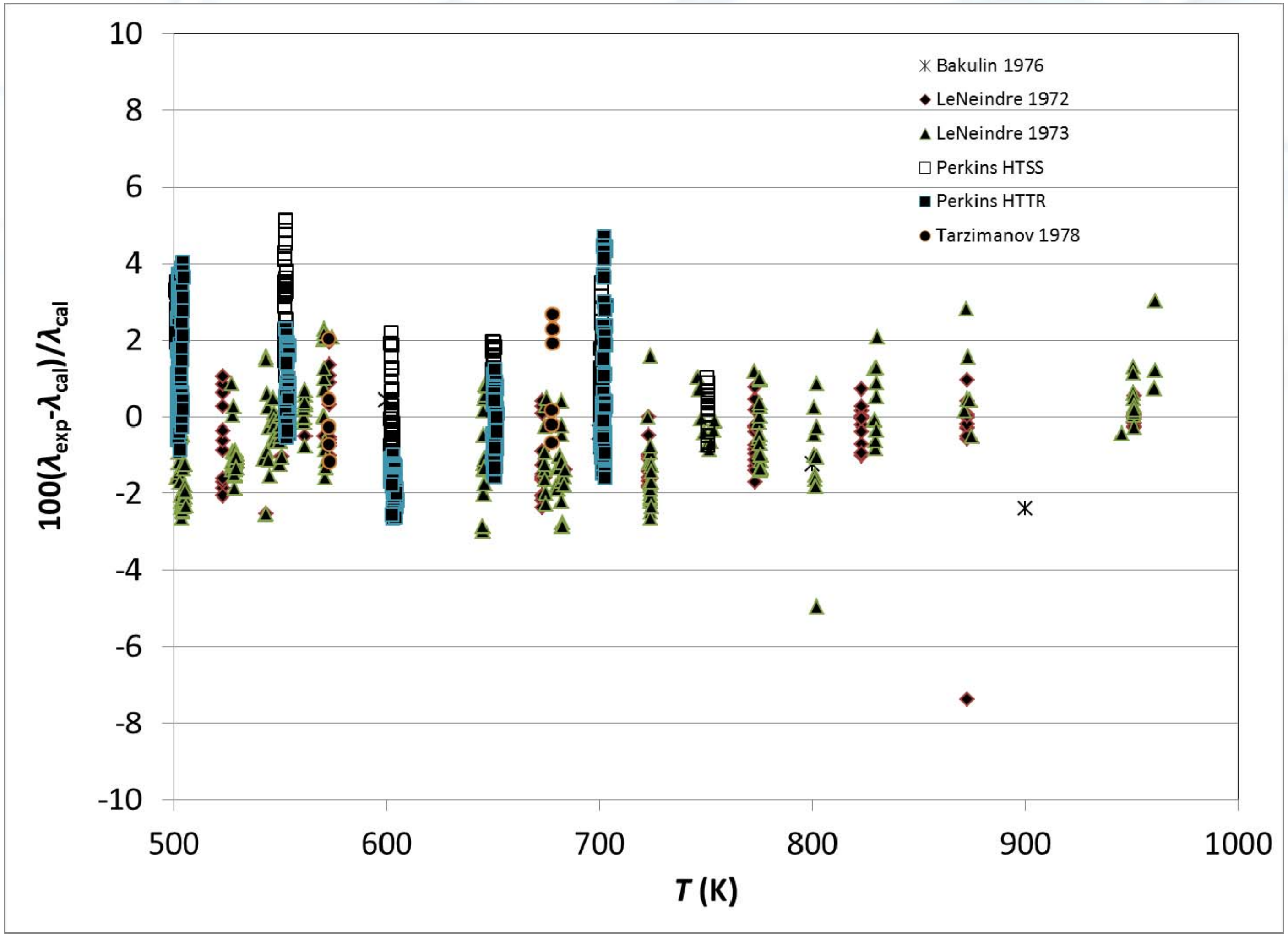
Residual Contribution

- 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

$$\lambda_1(T_\mathrm{r},\rho_\mathrm{r}) = \sum_{j=1}^{m}(B_{1,j} + B_{2,j}T_\mathrm{r})\rho_\mathrm{r}^{j}$$

Selected (preliminary) Results

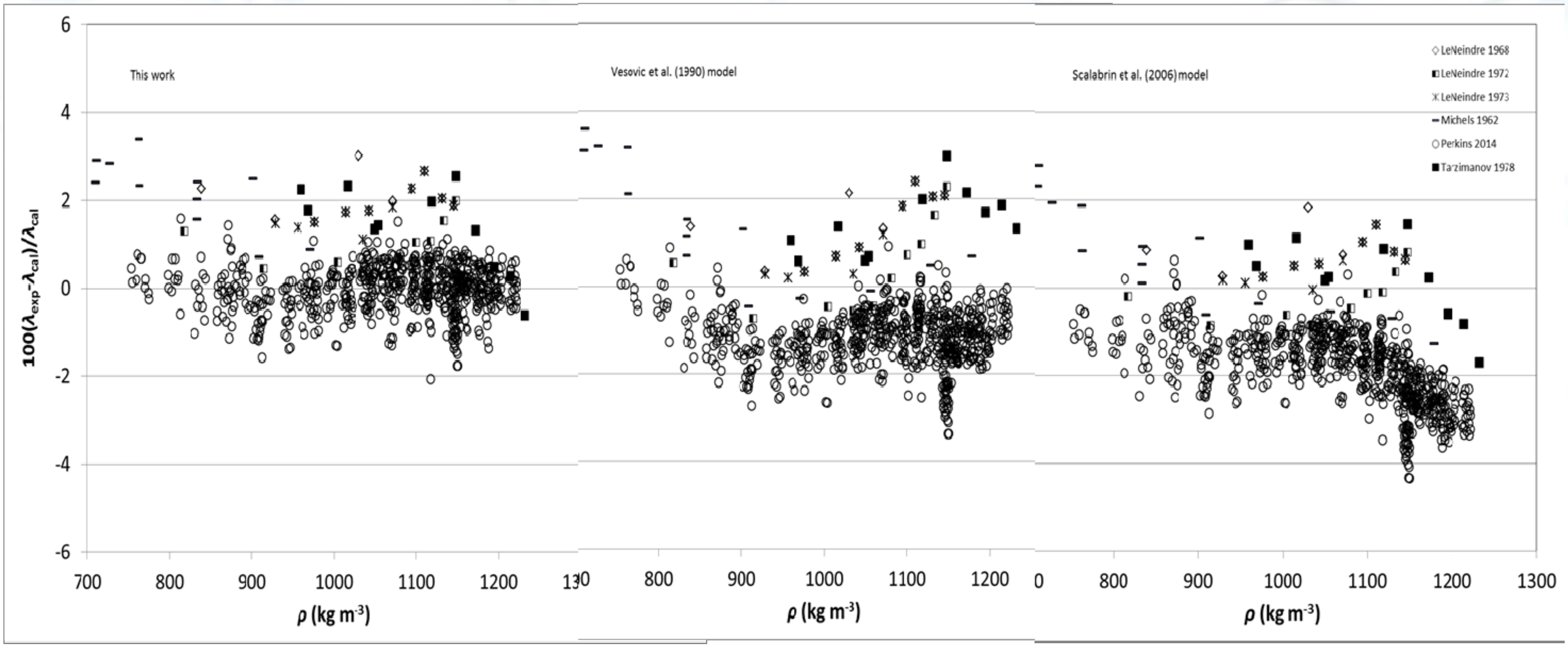
Supercritical Fluid, T > 500 K



Selected (preliminary) Results

Significant improvements in representation of liquid phase

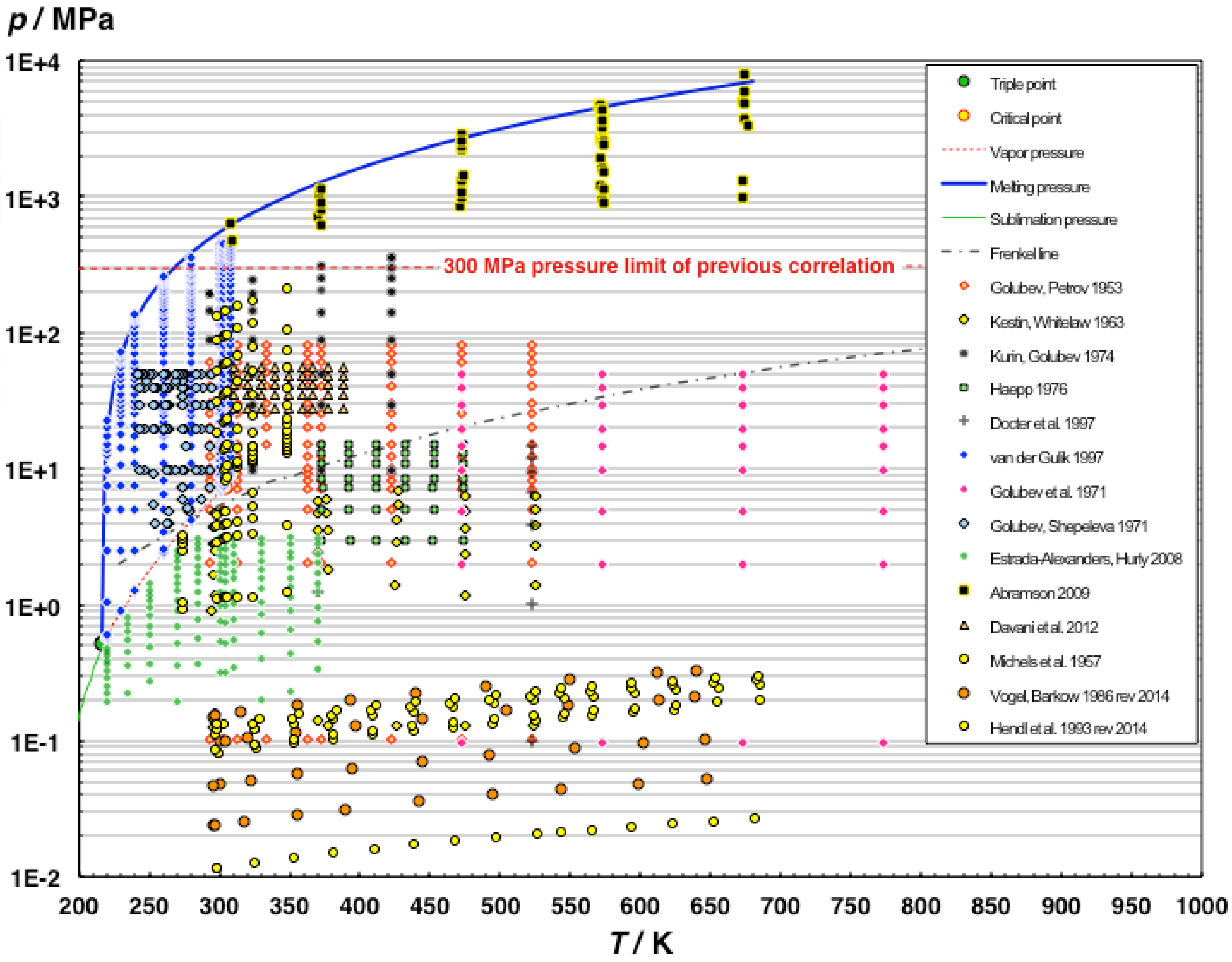
Our new data represented to ~1%



Viscosity of Pure CO_2

- 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

$$\eta(T,\rho) = \eta_0(T) \; + \; \Delta\eta(T,\rho) \; + \; \Delta\eta_c(T,\rho)$$

Visc(Temp,Dens) $\rho \to 0$ residual critical enhancement (small)

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

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

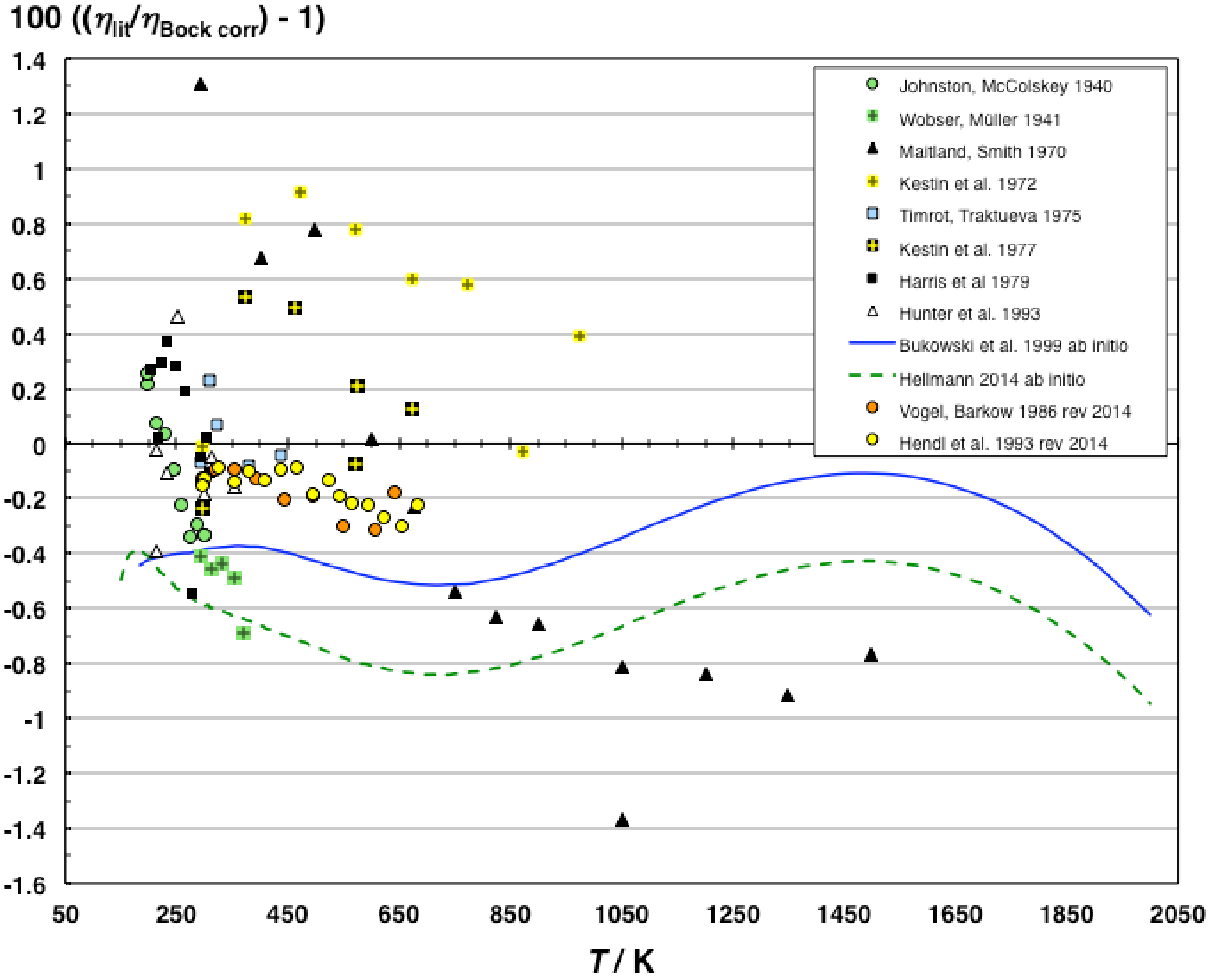
with $T^* = T/(\varepsilon/k_B)$

Residual part, Symbolic regression (preliminary)

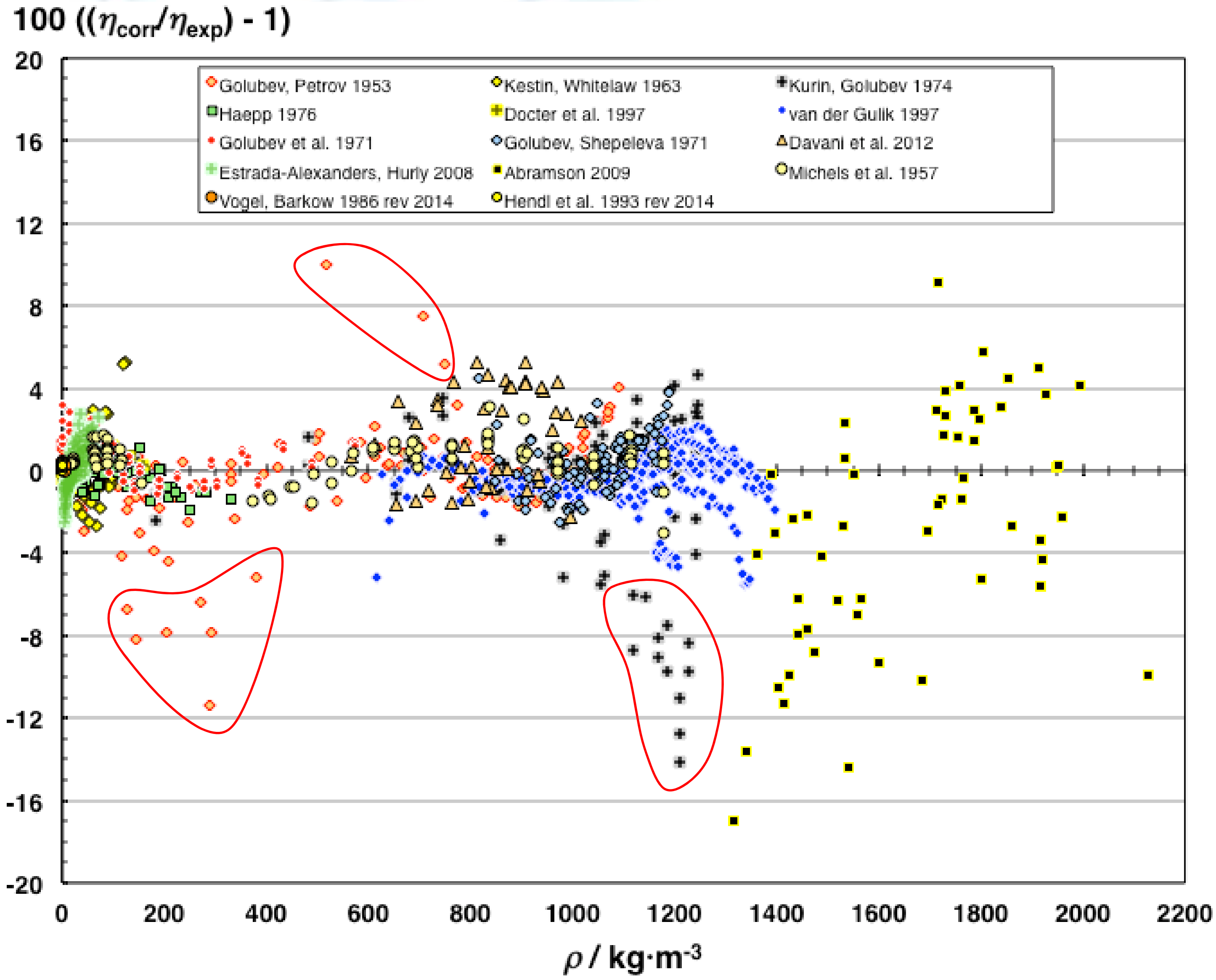
$$\Delta\eta(T,\rho) = \eta_{tL}\left[a_1\rho_r + a_2\rho_r^{a_3} + (a_4\rho_r)^{a_5}/T_r\right]$$

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

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)]

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

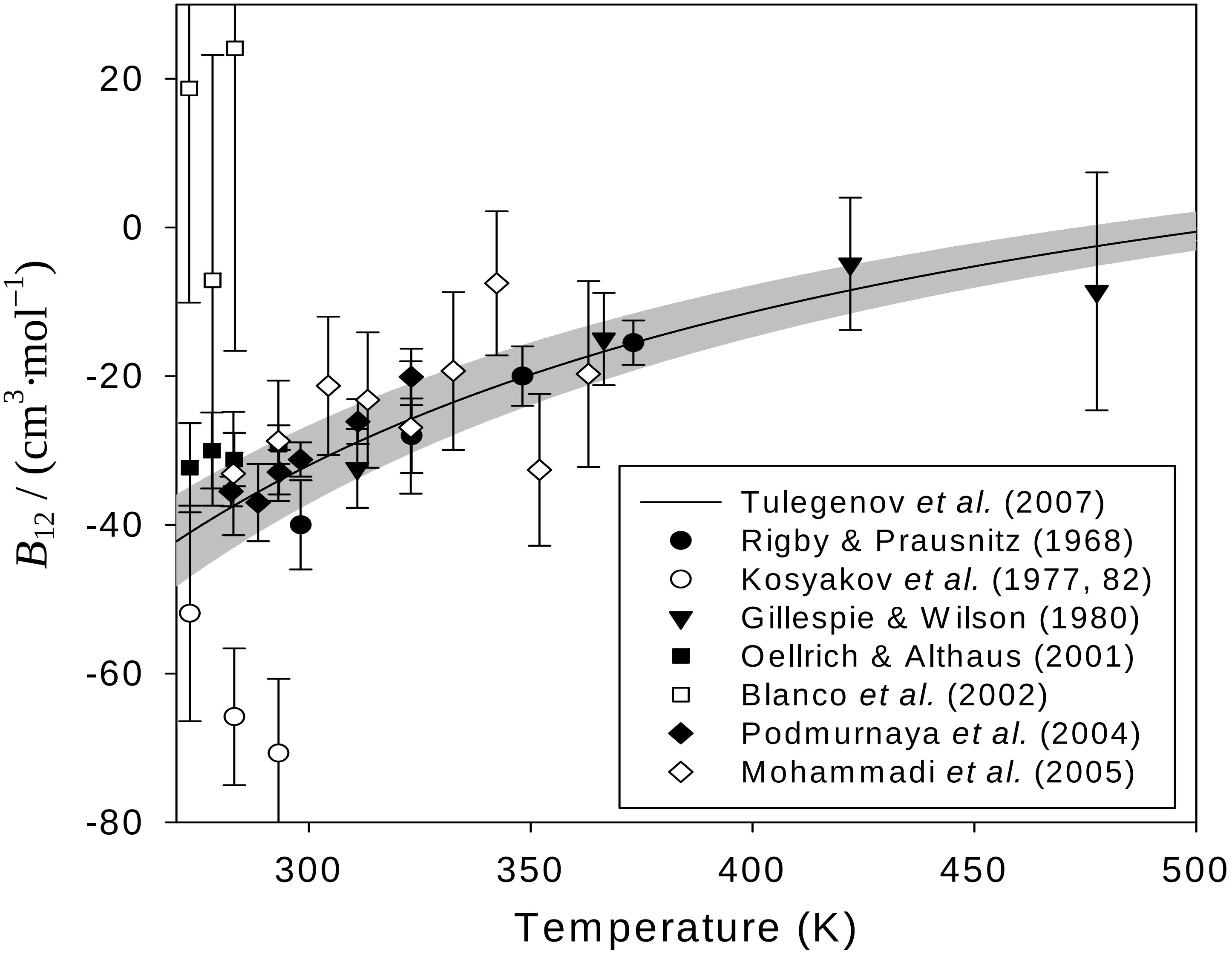
$$B(T) = \sum_i \sum_j x_i x_j B_{ij}(T)$$

- 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.

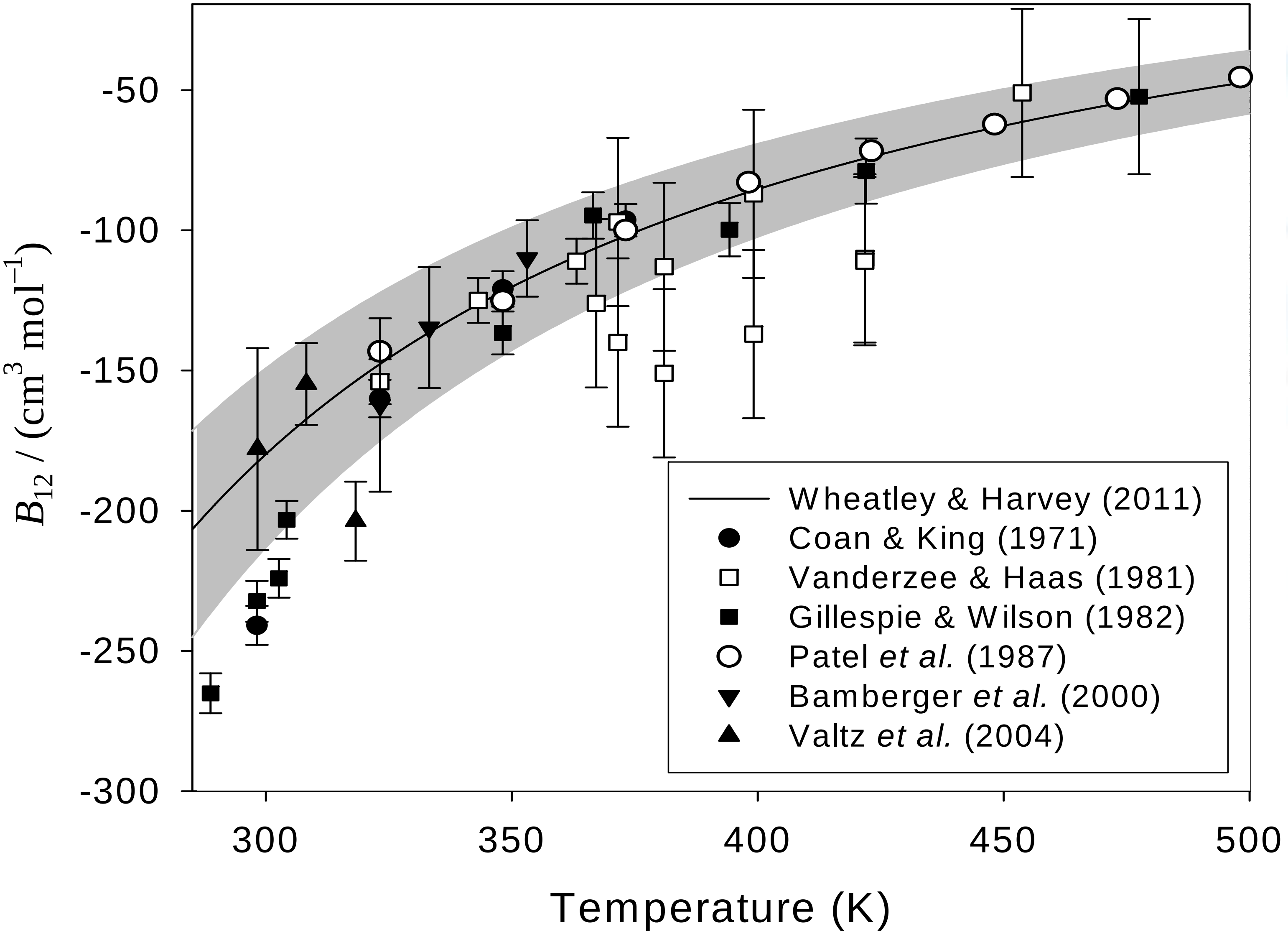
Gas/H_2O Second Virial Coefficient

- 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-CO_2 $B_{12}(T)$ 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.

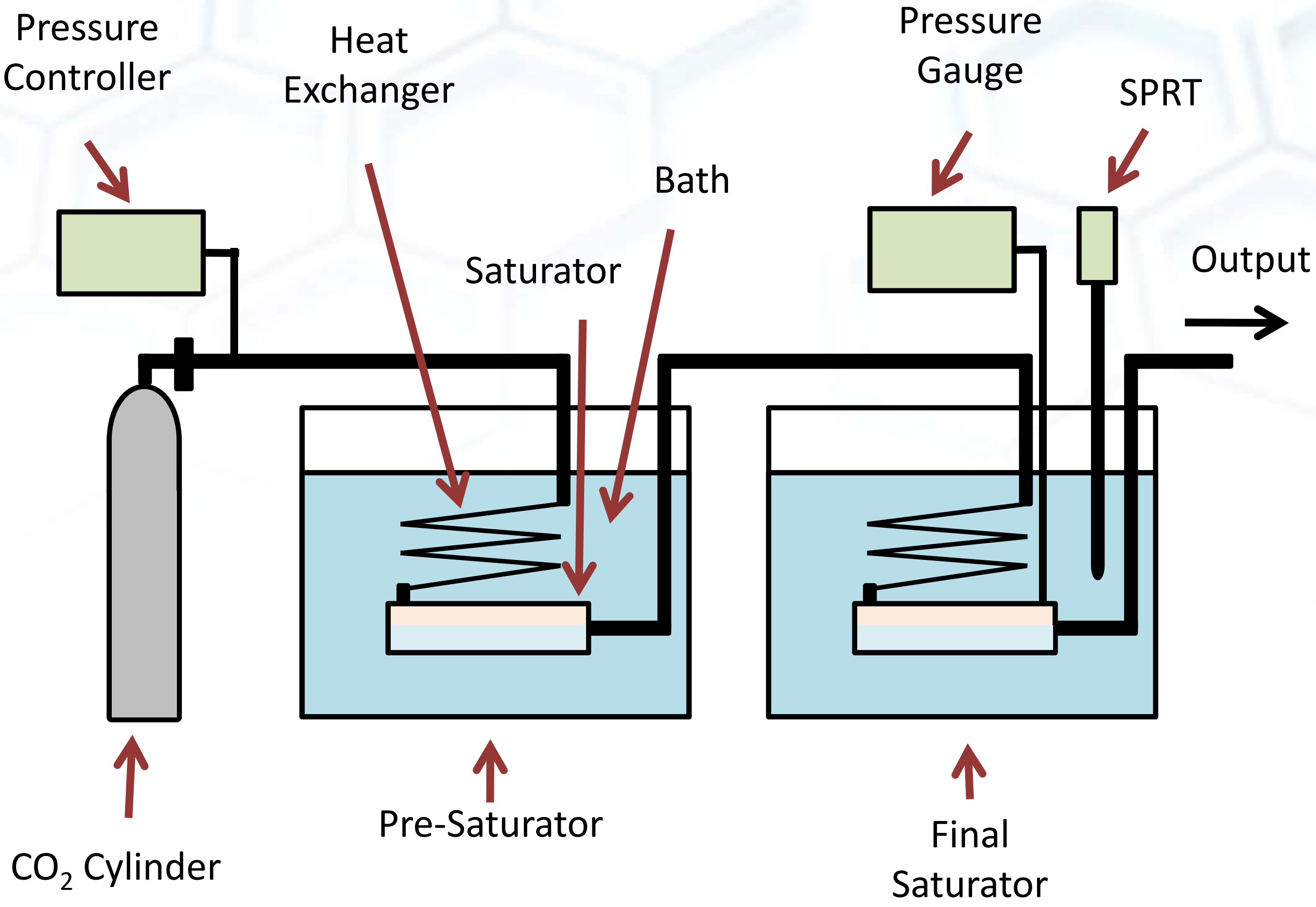
Dew-Point Experiments

1. **Saturation system for compressed CO_2 (generates saturated gas at P and T_{DP})**
2. **Gravimetric hygrometer (designed for humidity standards) measures amounts of H_2O and CO_2 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

$$r = \frac{m_\mathrm{w}}{m_\mathrm{g}}$$

m_w: mass of water vapor

m_g: mass of carrier gas

Incoming Humid Gas

Water Trap (used only for $r > 15$ mg/g)

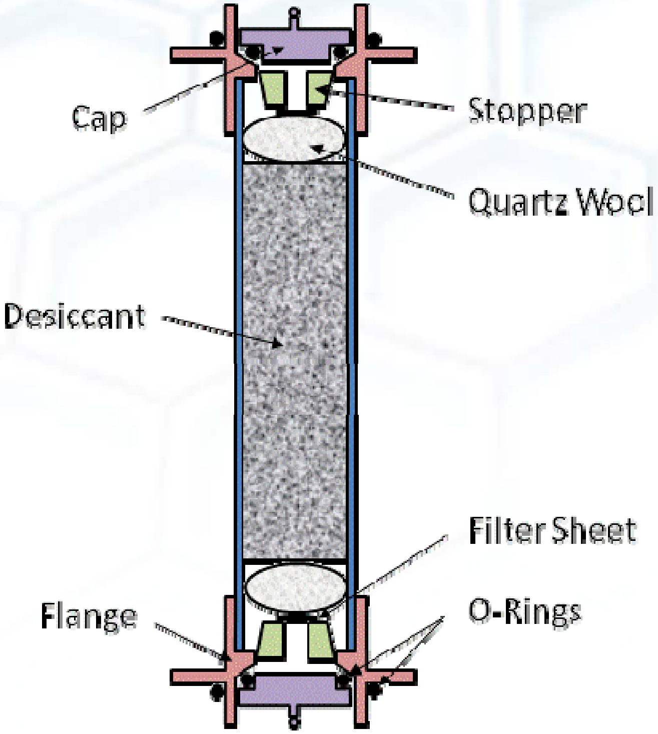
Water Collection Tubes

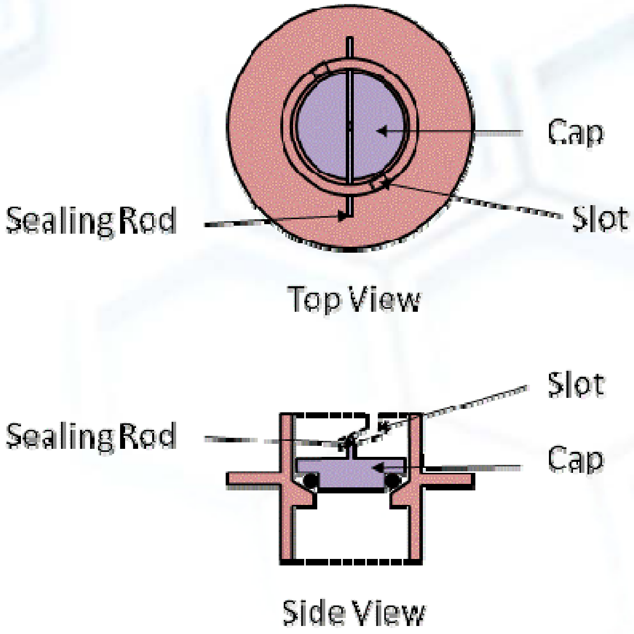
Gas Mass Determination System

Outgoing Dry 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

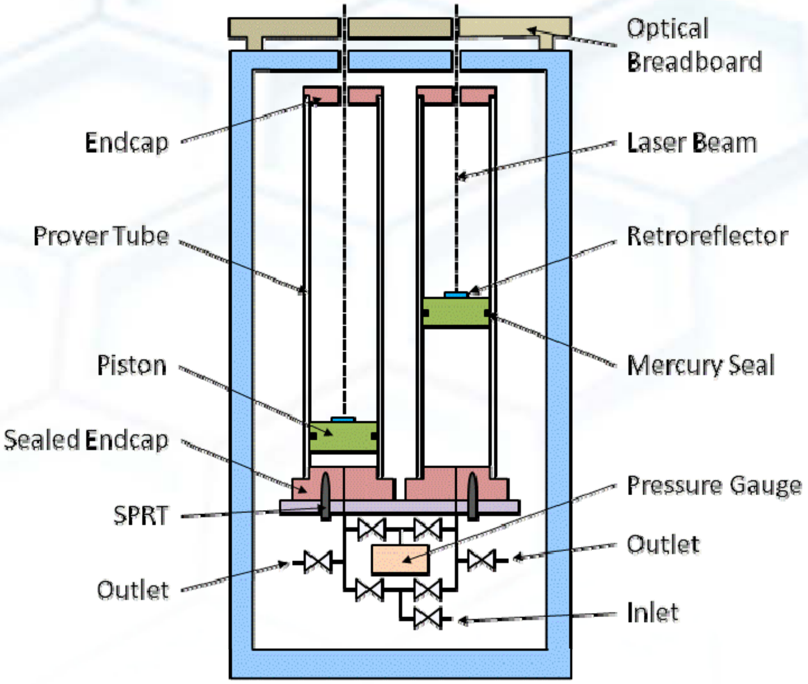
Water Collection Tubes





- Desiccant used: Magnesium Perchlorate
- Mass measurements (10 µg resolution) made before and after water collection. ~70 µg uncertainty in water mass measurement.

Prover Tube Gas Collection System



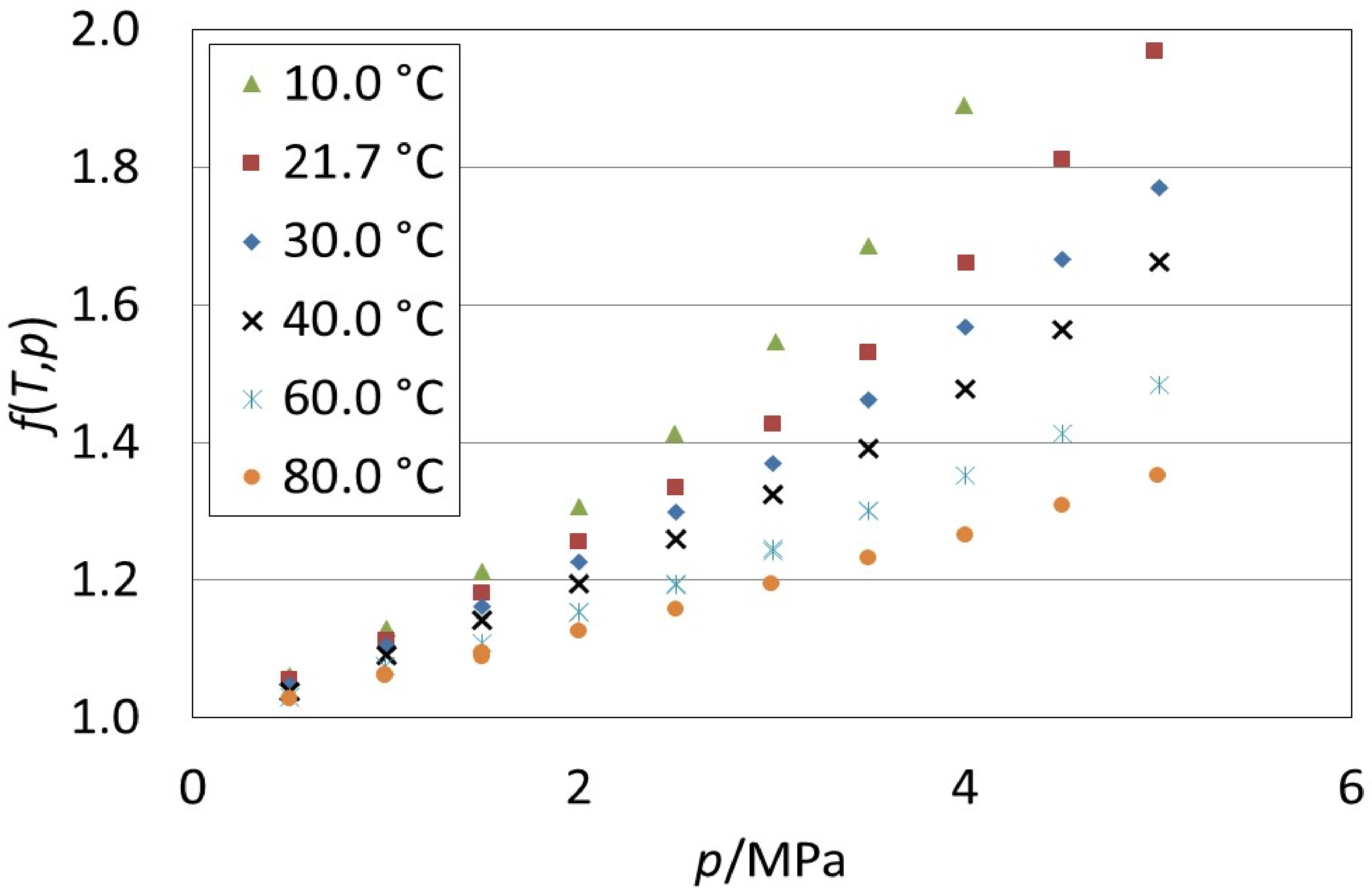
- Pressure and temperature measurements determine gas density (CO_2 equation of state well known)
- Laser interferometer measures piston displacement to determine gas volume, therefore total moles of gas
- Alternating pistons allow continuous gas flow

Experimental Program

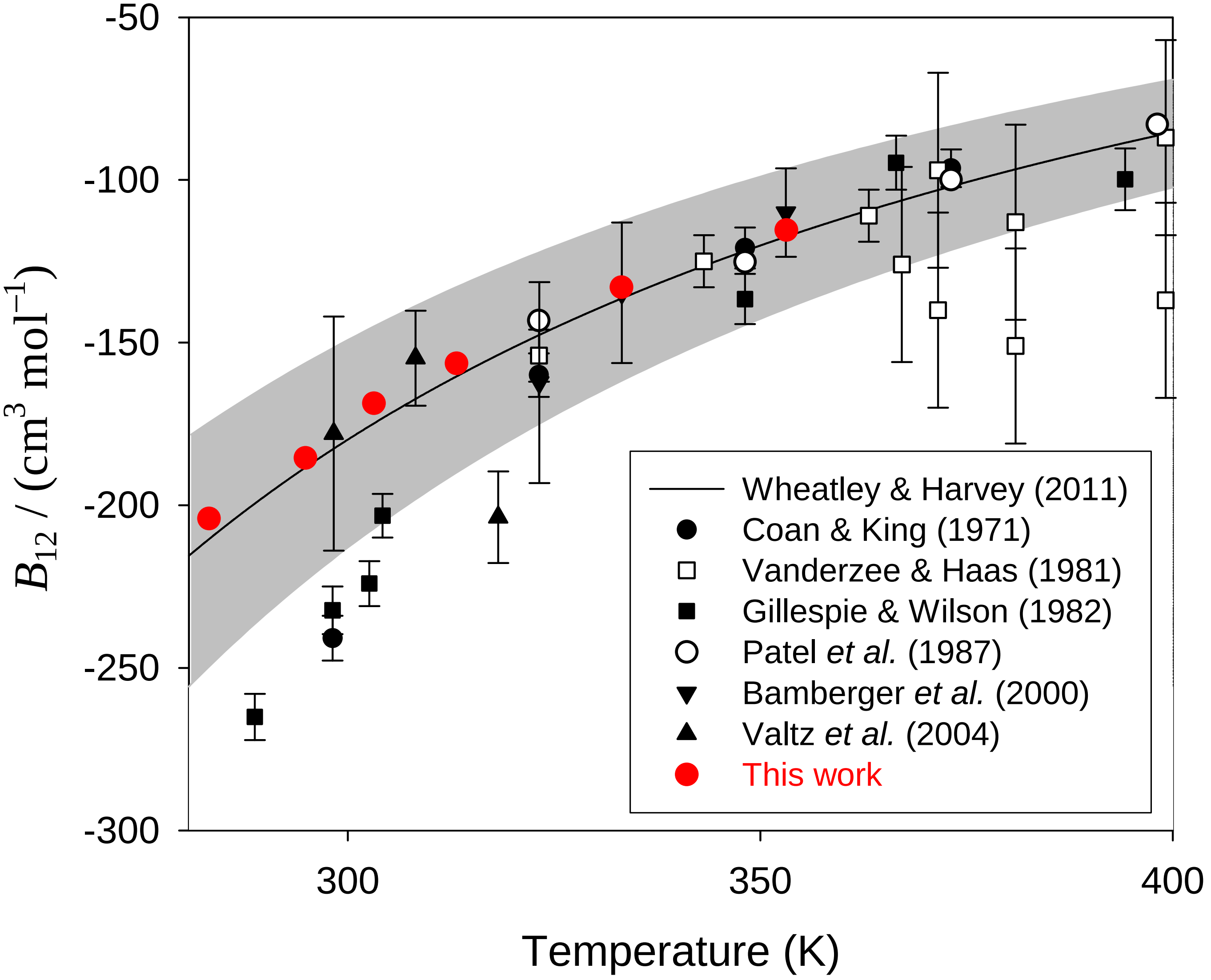
- Report saturated vapor composition (dew point) and enhancement factor (ratio of H_2O partial pressure in vapor phase to pure H_2O vapor pressure)
- 6 Temperatures from 10 °C to 80 °C
- Pressures up to 5 MPa (higher-pressure saturator could be built in the future)
- Avoid conditions where gas hydrates 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 CO_2



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 CO_2 power cycles.
- Extension of dew-point experiments to higher pressures.
- Materials compatibility for CO_2-rich fluids (for pipelines and power cycles).