Property Data for Low-GWP Refrigerants: What Do We Know and What Don't We Know?

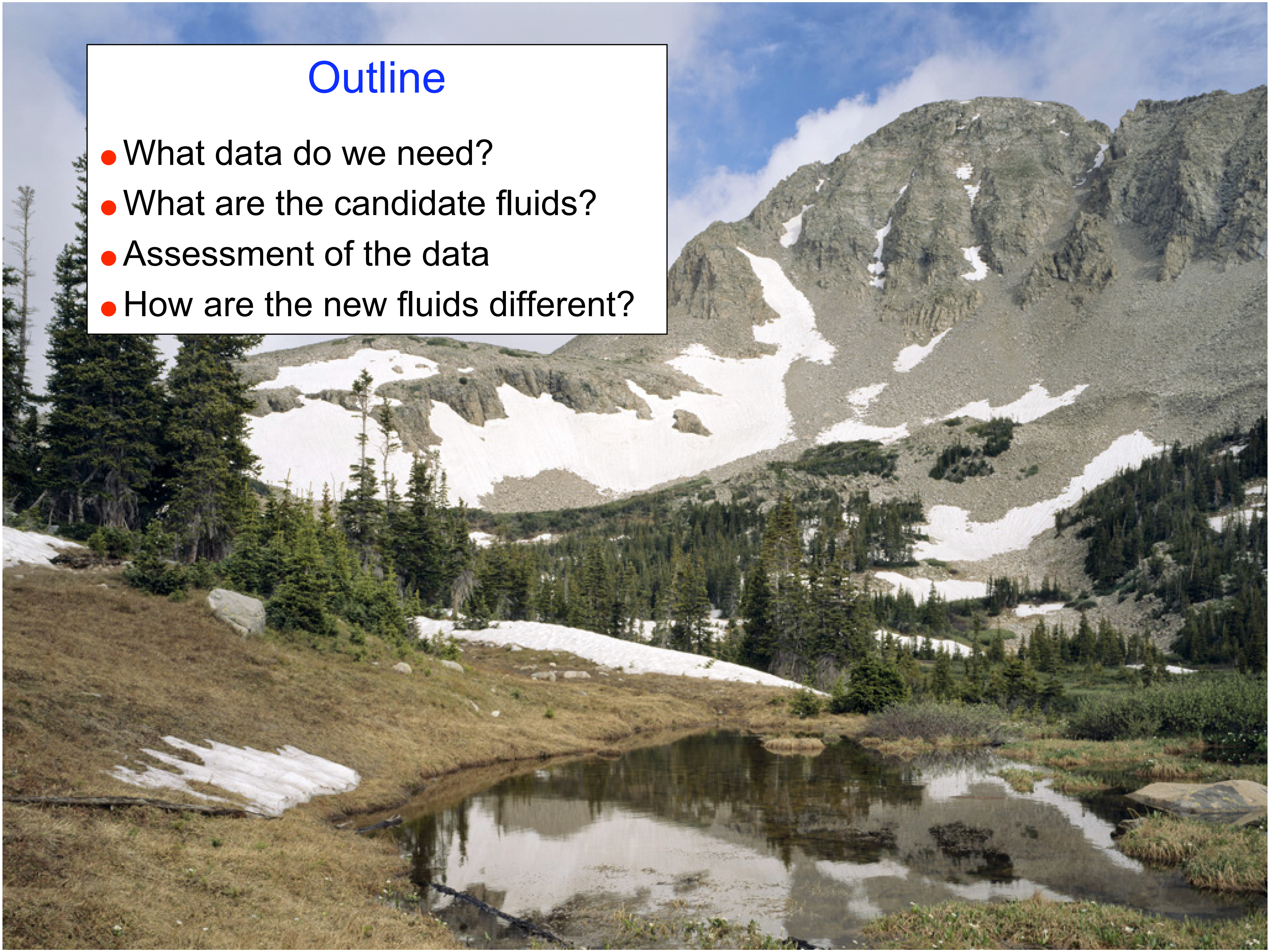
Mark O. McLinden

Thermophysical Properties Division
National Institute of Standards and Technology
Boulder, Colorado USA

Removing Barriers to Low-GWP Refrigerants

Learning Objectives

- ➤ Describe the climate change issue associated with high-GWP refrigerants and the leading low-GWP options available today
- ➤ Explain the refrigerant thermophysical property requirements needed for new low-GWP refrigerants and how property data may be used
- ● Be able to explain the challenges with measuring the flammability properties of refrigerants that are only marginally flammable and options to make these measurements
- ● Explain the development history of hydrofluoroolefin low-GWP refrigerants such as HFO-1234yf and why this new class of compounds has unique properties
- ● Describe the codes and regulations in the U.S., Europe, and Japan that govern the use of low-GWP refrigerants, such as CO_2, ammonia, hydrocarbons, and HFOs, and the barriers in current standards for their potential use
- ● Apply learnings from seminar to begin selecting low-GWP refrigerants for specific applications and begin designing new HVAC&R systems with these refrigerants

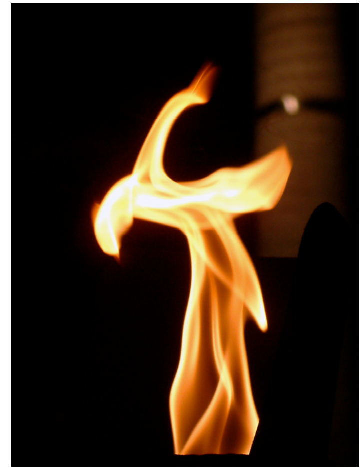


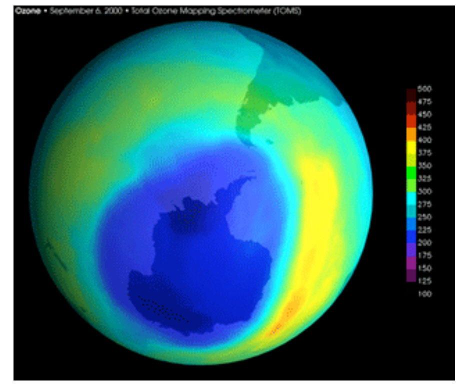
Outline

- What data do we need?
- What are the candidate fluids?
- Assessment of the data
- How are the new fluids different?

What Data Do We Need on a Refrigerant?

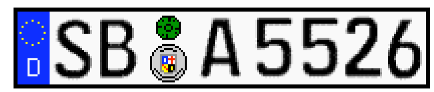
- Safety
  - toxicity (acute and chronic)
  - flammability
- Environmental
  - ozone depletion potential (ODP)
  - green house warming potential (GWP)
  - atmospheric life (impacts ODP & GWP)
- Materials
  - compatibility with metals, seals, etc.
  - lubricant
  - stability (hydrolysis, polymerization, etc.)
- Performance
  - thermodynamic properties
  - transport properties





What Counts as "Low-GWP"?

- R134a: GWP = 1430
  (relative to CO_2 w/ 100-year time horizon)
  ∴ must have GWP << 1430
- EU regulation for automotive A/C:
  GWP < 150
  (takes effect 2011 for new models)
- North American Proposal to Montreal Protocol:
  85 % phase-down by 2033 ($0.15 \times 1430 = 215$)

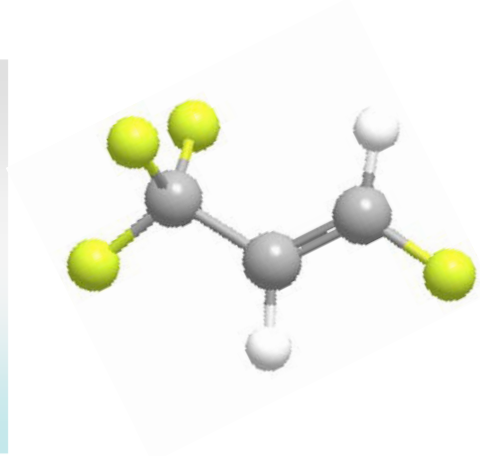


Low-GWP Options (Current Fluids)

Fluid		NBP (˚C)	GWP [CO_2 = 1]	ASHRAE class (tox/flam)
HFC	41	–78.3	92	N/A (flam)
	32	–51.7	675	A2L
	161	–37.6	12	N/A (flam)
	134a	–26.1	1430	A1
	152a	–24.0	124	A2
HCFC	123	27.8	77	B1
HC	290 (propane)	–42.1	20	A3
	600a (isobutane)	–11.7	20	A3
	600 (butane)	–0.5	20	A3
CO_2	744	–56.6	1	A1
NH_3	717 (ammonia)	–33.3	<1	B2L
H_2O	718 (water)	100.0	<1	A1
Ether	E170	–24.8	1	A3

Low-GWP Refrigerants—New Possibilities

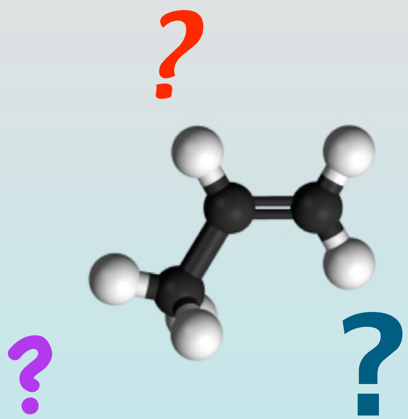
- Hydro-Fluoro-Olefin (HFO)
  - C=C double bond
  - fluorine-containing
  - hydrogen-containing



Fluid		NBP (˚C)	GWP [CO_2 = 1]	ASHRAE class (tox/flam)
HFO	1234yf	–29.5	4	A2L
	1234ze(E)	–19.0	6	2L(pending)

Additional HFOs Under Development

- Announced in talks and conference papers
  - ↳but not identified
- Many (most?) are in patent or chemical literature
  ∴ molecules themselves are not patentable
  (production processes are patentable)
- Blends w/ HFOs also being developed
  - ↳azeotropic blends are patentable
  - ↳zeotropic blends may be patentable

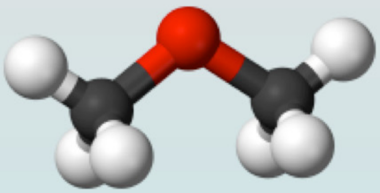


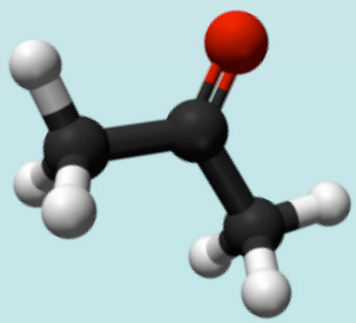
➔This is the major *"What We Don't Know"* ➔

Low-GWP Refrigerants—Additional Possibilities

- Interest in fluorinated ethers in 1990s
- Examples among specialty solvents and heat-transfer fluids:
  - –fluorinated ethers
    especially “segregated” ethers (all H on a single carbon)
  - –fluorinated ketones

  ↳non-flammable
  ↳low(ish) GWP
  ↳commercially available
  (but boiling points higher than typical refrigerants)

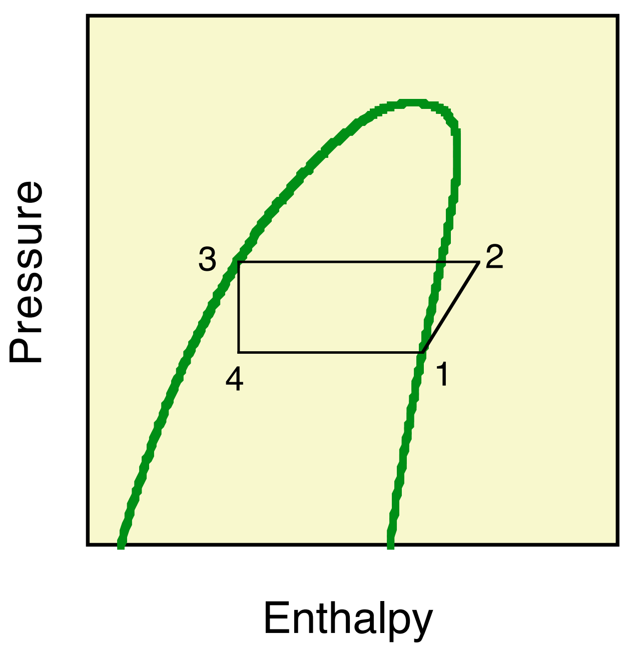


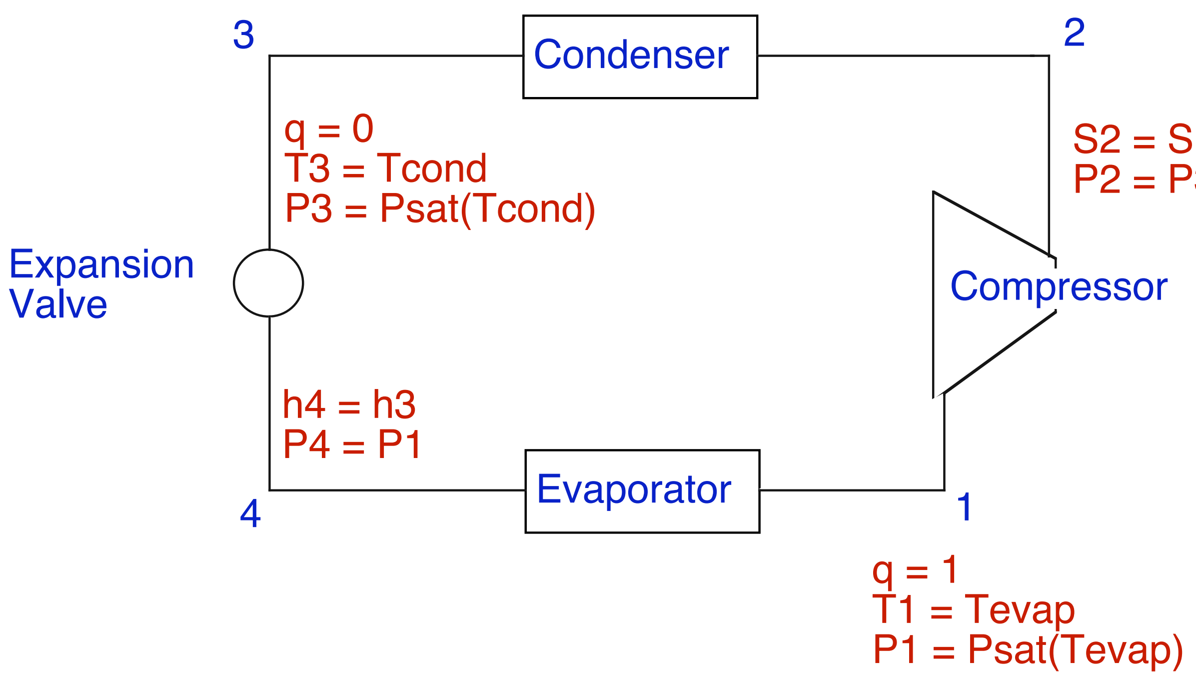


Property Data and Equations of State

Fluid Properties—Why Should ASHRAE Care?

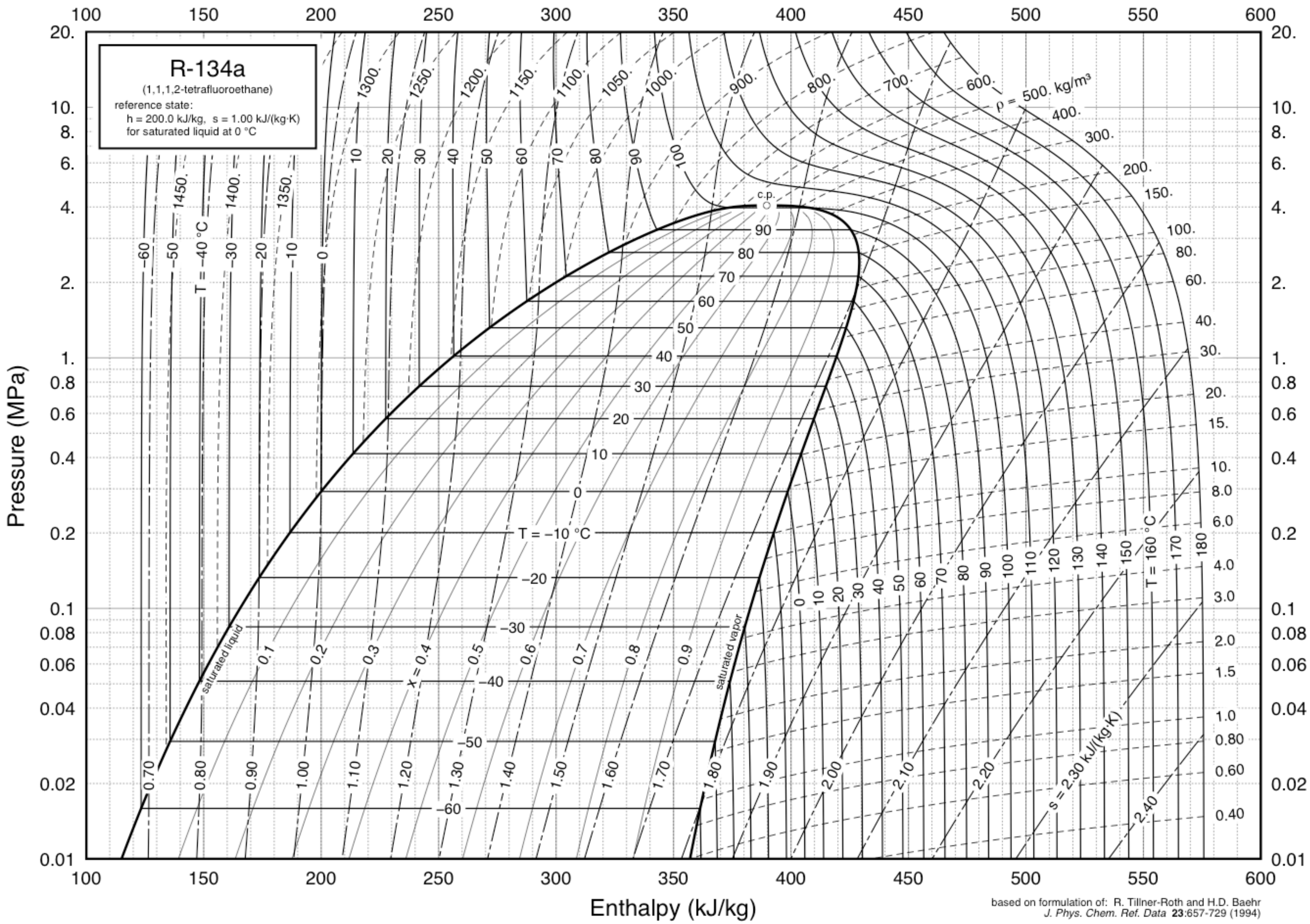
Cycle analysis *IS* properties





$$COP_R = \frac{h_1 - h_4}{h_2 - h_1} = f\left(T_{\text{evap}}, T_{\text{cond}}, properties\right)$$

Equation of State
(Thermodynamic Properties)



Equation of State—Helmholtz Energy Form

A thermodynamically consistent representation of the properties of a fluid

$$\alpha = \frac{A}{RT} = \alpha^{ideal} + \sum_i N_i \tau^{t_i} \delta^{d_k}$$

"traditional terms"

$$+ \sum_j N_j \tau^{t_j} \delta^{d_j} \exp\left(-a_j \delta^{l_j}\right)$$

"Gaussian terms" (critical region)

$$+ \sum_k N_k \tau^{t_k} \delta^{d_k} \exp\left(-a_k (\delta - \varepsilon_k)^{l_k}\right) \exp\left(-\beta_k (\tau - \gamma_k)^{m_k}\right)$$

where: $\delta = \rho/\rho_{crit}$, $\tau = T_{crit}/T$

All other properties by differentiation:

$$p = RT\rho\left[1 + \frac{\partial \alpha^r}{\partial \delta}\right], \qquad C_V = R\left[-\tau^2 \frac{\partial^2 \alpha}{\partial \tau^2}\right]$$

Equation of State—Mixture Form

Sum pure component contributions + "excess" (mixing) term

$$\alpha_{mix} = \sum_i x_i \left[\alpha_i^0(\delta,\rho) + \ln(x_i) \right] + \sum_i x_i \alpha_i^r(\delta,\rho)$$

ideal solution terms (ideal gas & "real gas")

$$+ \sum_i \sum_{j=i+1} x_i x_j F_{ij} \underbrace{\sum_k N_k \delta^{i_k} \tau^{j_k}}_{\text{"mixing function"}}$$

"excess" contribution

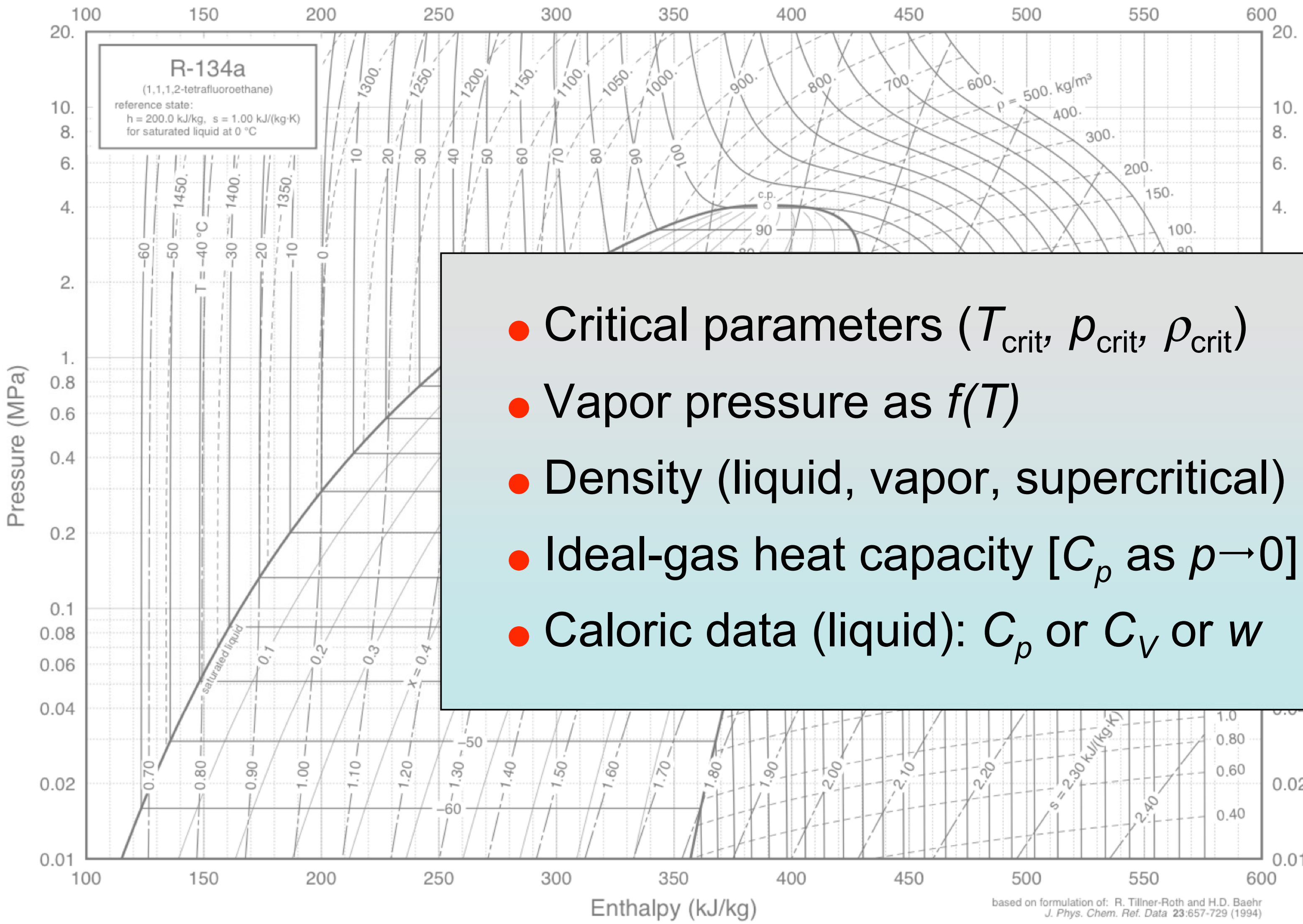
Evaluate at reduced *T*,*ρ* (not mixture *T*, *ρ*) given by "reducing parameters"

$$\tau = T^* / T \qquad \delta = \rho / \rho^*$$

$$T^* = \sum_{i=1}^{n} x_i T_i^{crit} + \sum_i^{n-1} \sum_{j=i+1}^{n} x_i x_j \zeta_{ij} \qquad \frac{1}{\rho^*} = \sum_{i=1}^{n} \frac{x_i}{\rho_i^{crit}} + \sum_i^{n-1} \sum_{j=i+1}^{n} x_i x_i \xi_{ij}$$

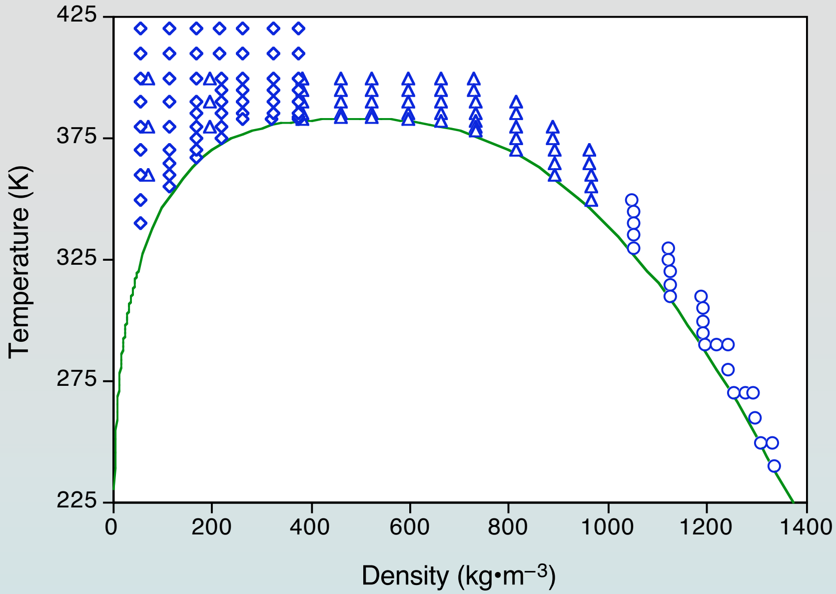
Adjustable parameters ζ, ξ, F_{ij} + mixing function give great flexibility in fitting mixtures with limited or extensive data

Data Needed to Establish Equation of State
(Thermodynamic Properties)

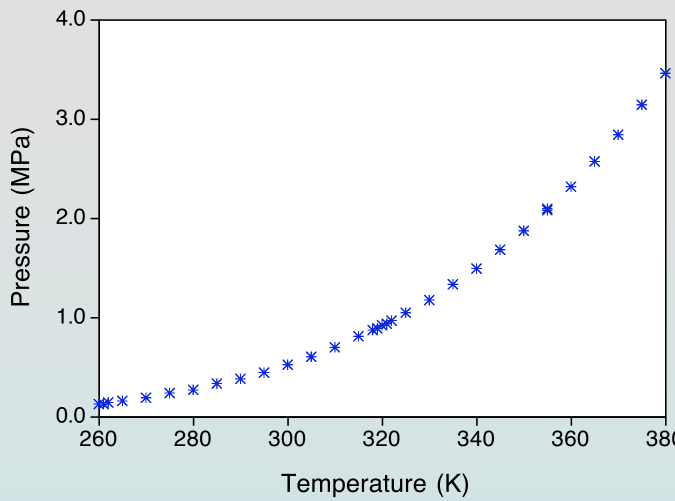


- Critical parameters (T_{crit}, p_{crit}, ρ_{crit})
- Vapor pressure as $f(T)$
- Density (liquid, vapor, supercritical)
- Ideal-gas heat capacity [C_p as $p \rightarrow 0$]
- Caloric data (liquid): C_p or C_V or w

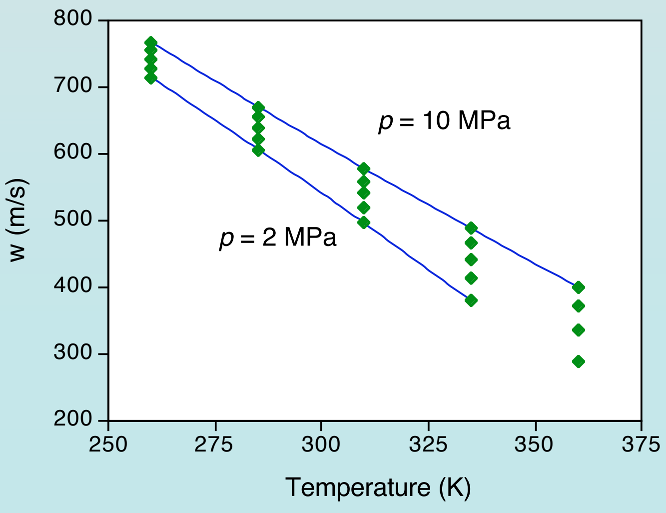
Recent R1234ze(E) Data



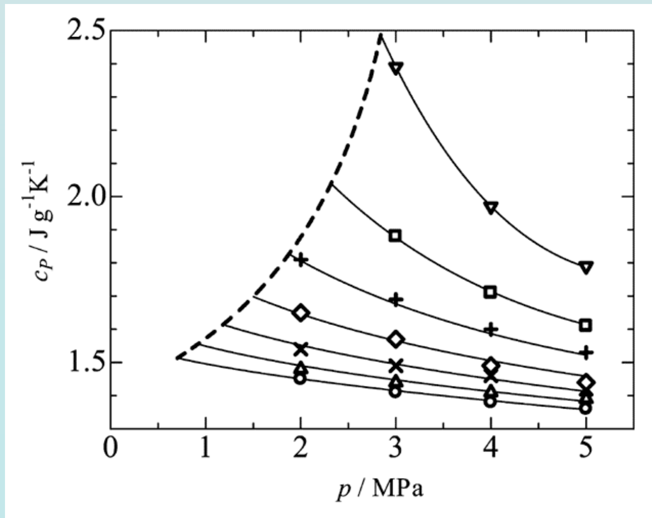
p-ρ-T and vapor pressure data
McLinden, *et al.*, *Int. Ref. Conf. Purdue* (2010)



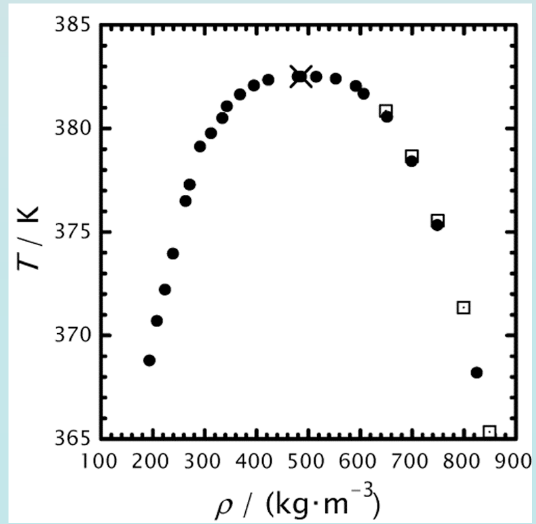
Liquid-phase speed of sound
Lago, *et al.* (2010)



Liquid-phase heat capacity
Tanaka, *et al.*, *J. Chem. Eng. Data* (2010)

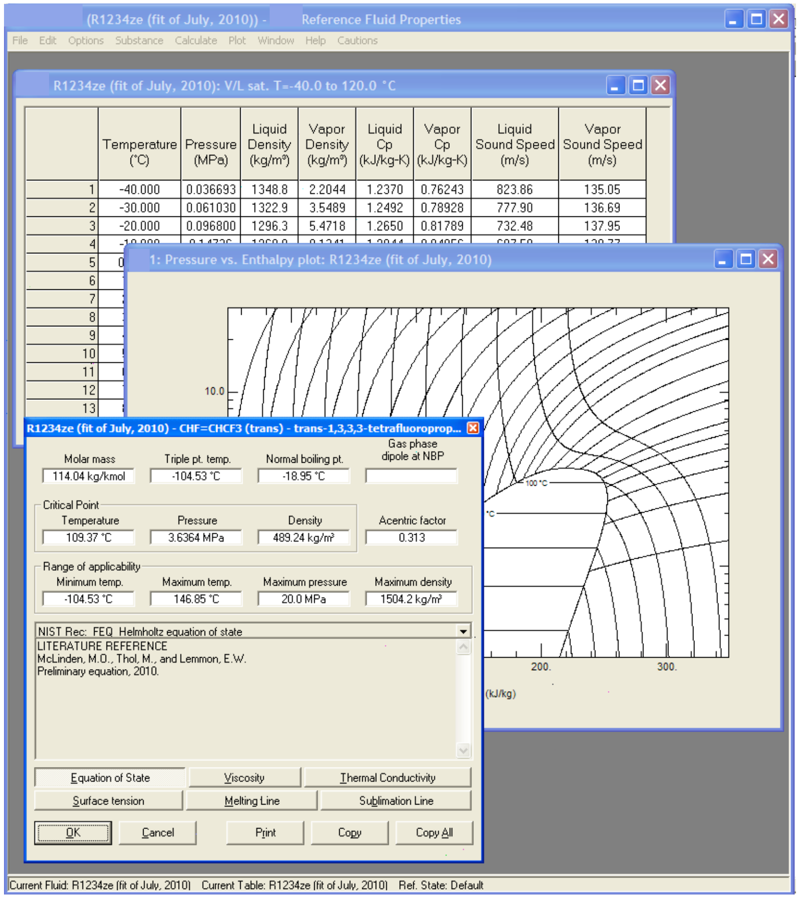


Critical region data, Higashi, *et al.*, *J. Chem. Eng. Data* (2010)



Equation of State—Fitting Process
(R1234ze(E) as Example)

- Non-linear in the parameters
  - ➥must start with initial guess for EOS
  - ➥propane equation with 14 terms
- Objective function:
  - ➥minimize sum of squares
- Fit numerical coefficients
- Fit exponents on temperature terms
  - ➥(0 ~ 5), max for R1234ze is 2.5
- Fixed exponents on density terms
  - ➥integers ≥ 1
- Highly iterative process (1000’s of iterations)



Equation of State—Fitting Process (Constraints)

- Numerous further constraints
  e.g., shape of critical isotherm

for $\rho < \rho_{\text{crit}}$:

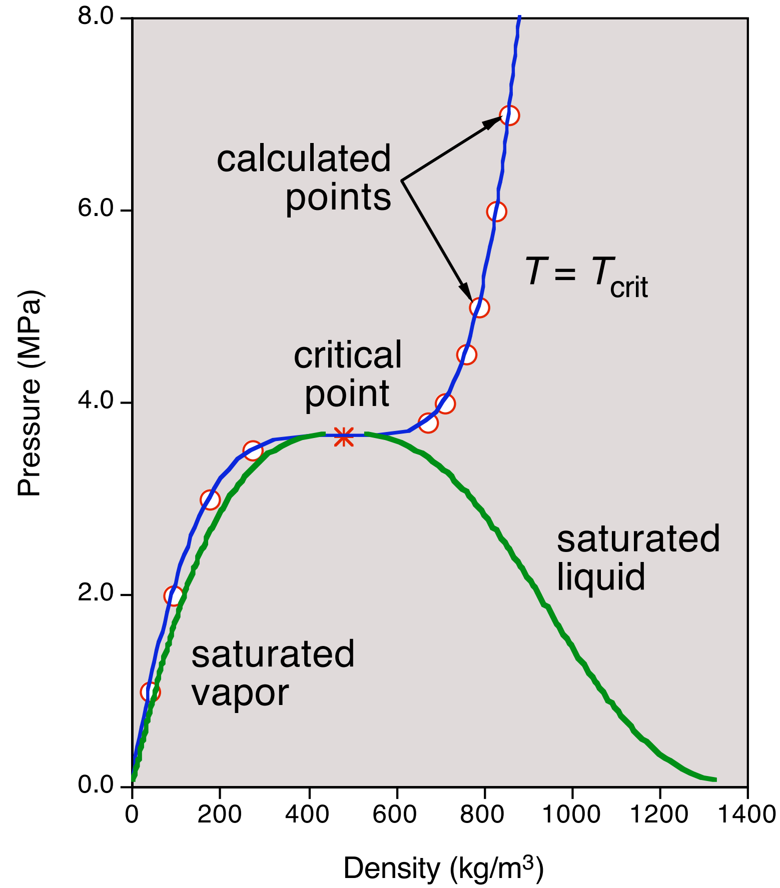
$$\frac{\partial p}{\partial \rho} > 0; \quad \frac{\partial^2 p}{\partial \rho^2} < 0; \quad \frac{\partial^3 p}{\partial \rho^3} > 0; \quad \frac{\partial^4 p}{\partial \rho^4} < 0;$$

for $\rho > \rho_{\text{crit}}$:

$$\frac{\partial p}{\partial \rho} > 0; \quad \frac{\partial^2 p}{\partial \rho^2} > 0; \quad \frac{\partial^3 p}{\partial \rho^3} > 0; \quad \frac{\partial^4 p}{\partial \rho^4} > 0;$$

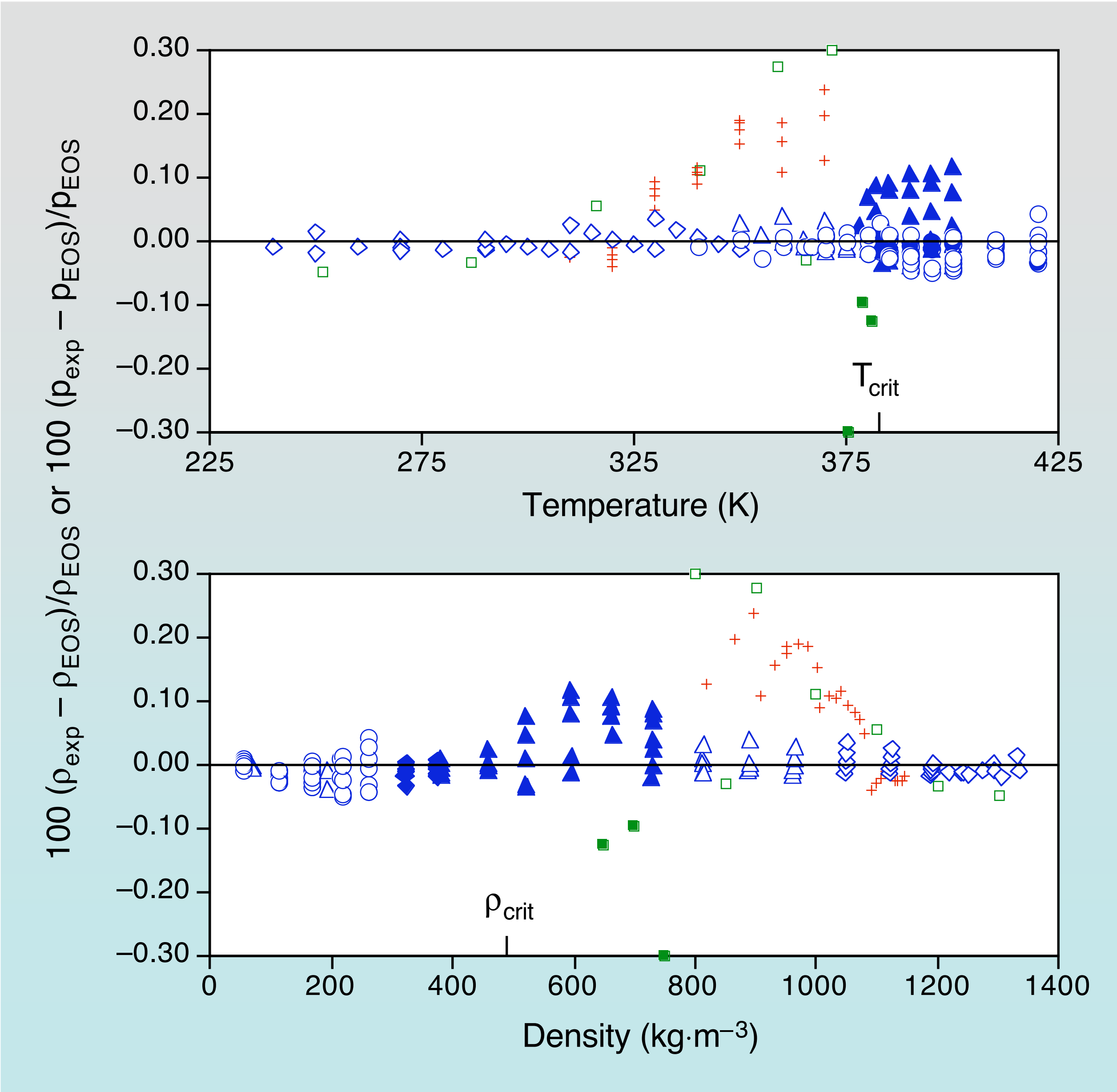
add $exp\left[-\frac{\partial p}{\partial \rho}\right]$ to *sum of squares*

- EOS with correct shape:
  ↳small addition to sum of squares
- EOS with incorrect shape:
  ↳large penalty to sum of squares



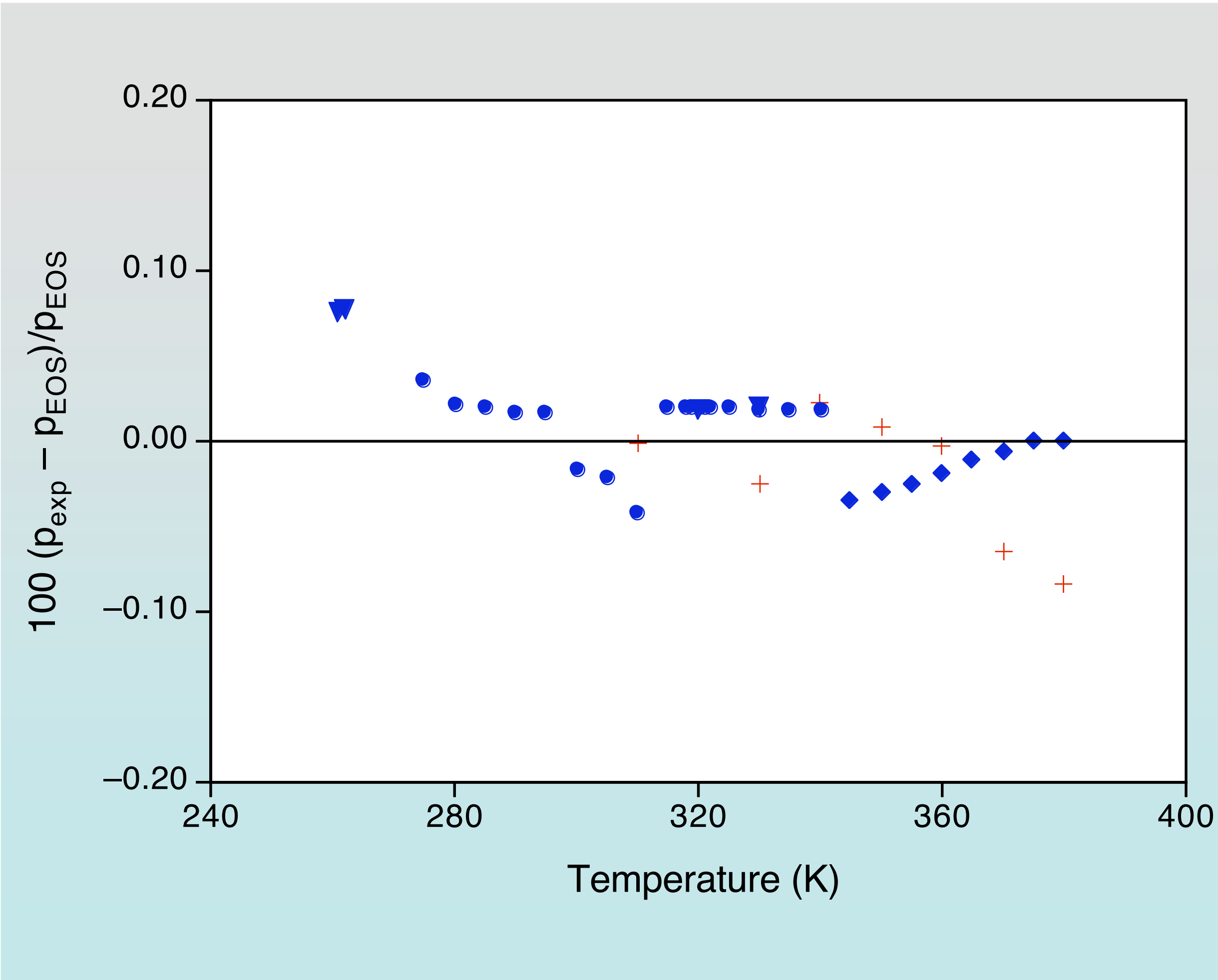
Data Comparisons and Assessments

Data Comparisons—EOS vs. *p*-*ρ*-*T* Data, R1234ze(E)



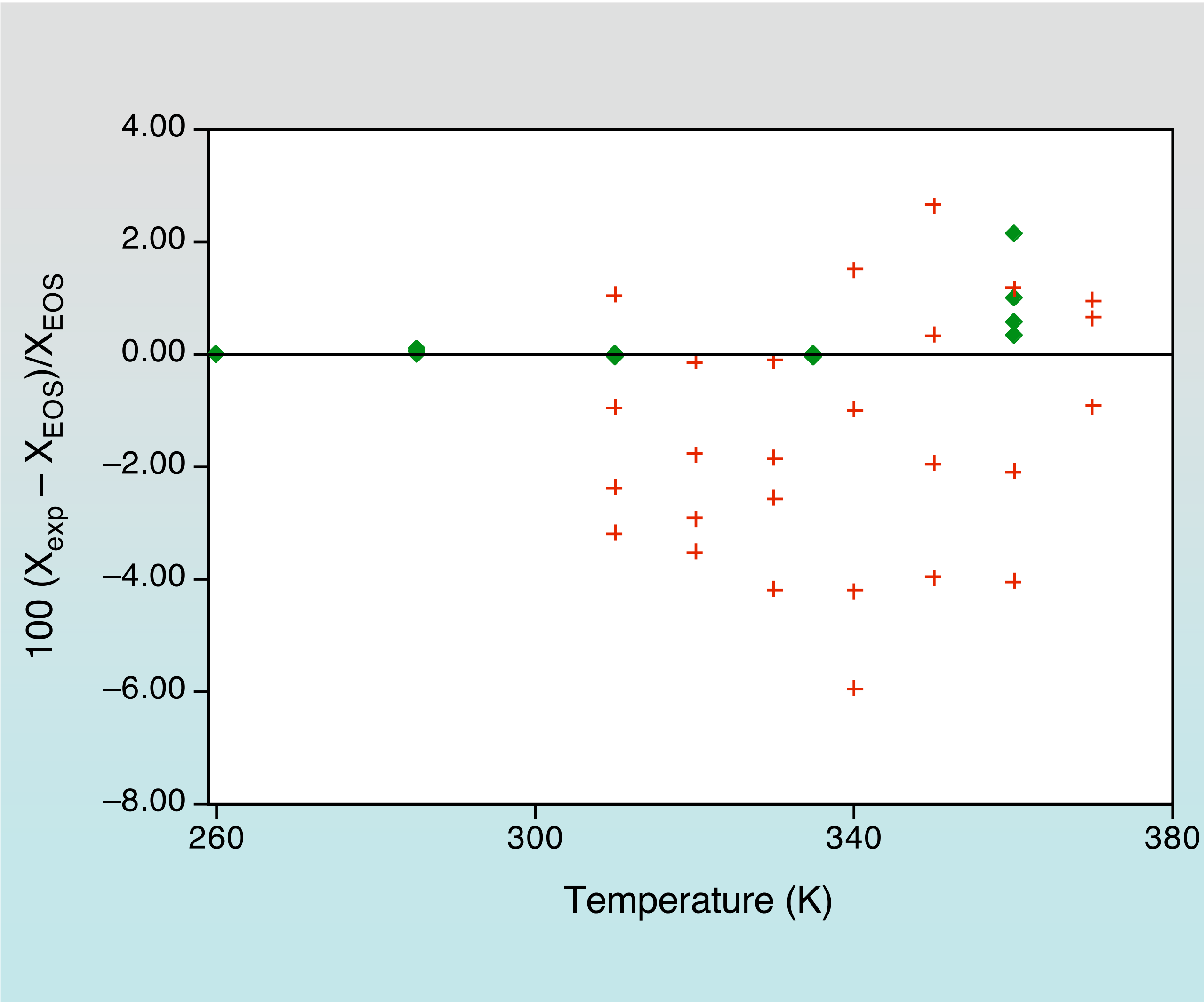
Source	σ (%)
McLinden et al. ○◇△	0.032
Tanaka +	0.087
Grebenkov (sat'n) ■	0.22
Grebenkov (liquid)	0.52
Grebenkov (vapor)	1.31

Data Comparisons—EOS vs. p_{sat} Data, R1234ze(E)



Source	σ (%)
McLinden et al. ◆●▼	0.028
Tanaka +	0.039
Grebenkov	1.78

Data Comparisons—EOS vs. C_p and Sound Speed Data R1234ze(E)



Source	σ (%)
Tanaka (C_p) +	2.16
Lago (w) ◆	0.49

Data Summary

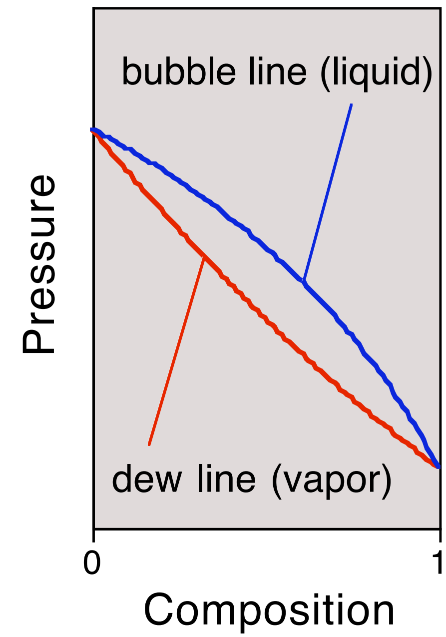
Fluid		Eqn. of State (thermo)	Transport (visc. & t.c.)
HFC	32	good	good
	134a	good	good
	152a	fair (old form)	good
HCFC	123	fair (old form)	fair (visc)–good (t.c.)
HC	290 (propane)	excellent	very good
	600a (isobutane)	very good	very good
	600 (butane)	very good	very good
CO_2	744	excellent	very good
NH_3	717 (ammonia)	fair (!)*	good
H_2O	718 (water)	excellent	excellent
DME	E170	fair (limited data)	fair (limited data)
HFO	1234yf	good (limited data)	limited data
	1234ze(E)	good (limited data)	limited data

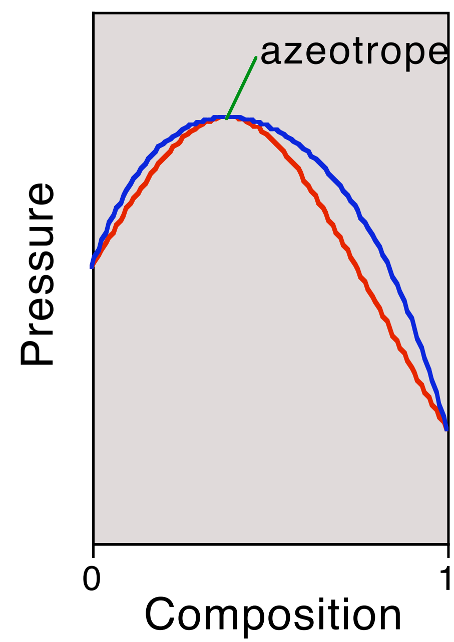
*new EOS under development

Thermo Data Summary—Blends

Blend Class	Data Assessment
HFC 32/125/134a	very good data and model
other HFC blends	numerous mixture pairs, but generally only VLE data (i.e., no $\rho(T,p,x)$)
HFC + HC	limited pairs, generally only VLE data
HFC + ethers	virtually no data
HC blends	very good data and models (natural gas)
HFO + HFC	Arakawa et al. (2010): R32/1234yf*
	proprietary data (azeotropes disclosed)
predictive model for refrigerant blends	available, generally good, but dated (2001)

*additional work in progress in Japan

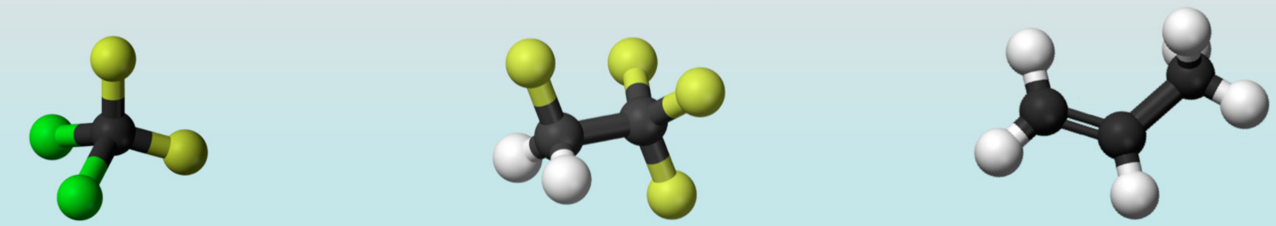


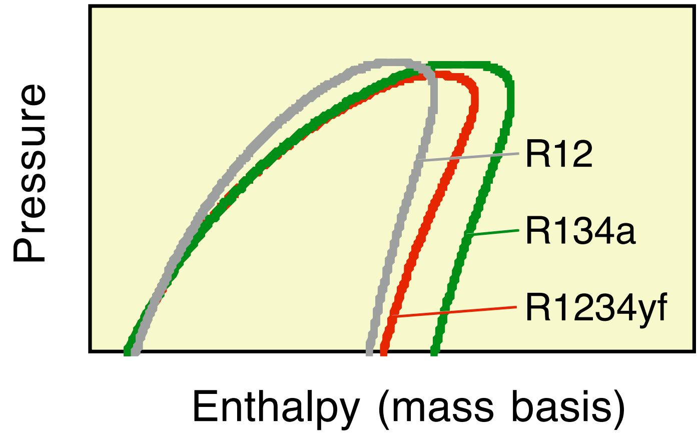


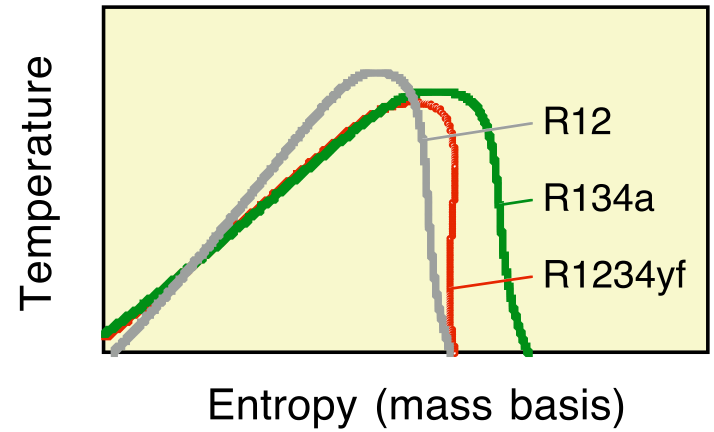
Refrigerant Molecules Are Getting More Complex

CFC-12 ➤ HFC-134a ➤ HFO-1234yf

NBP: (–29.8 ˚C) (–26.1 ˚C) (–29.5 ˚C)



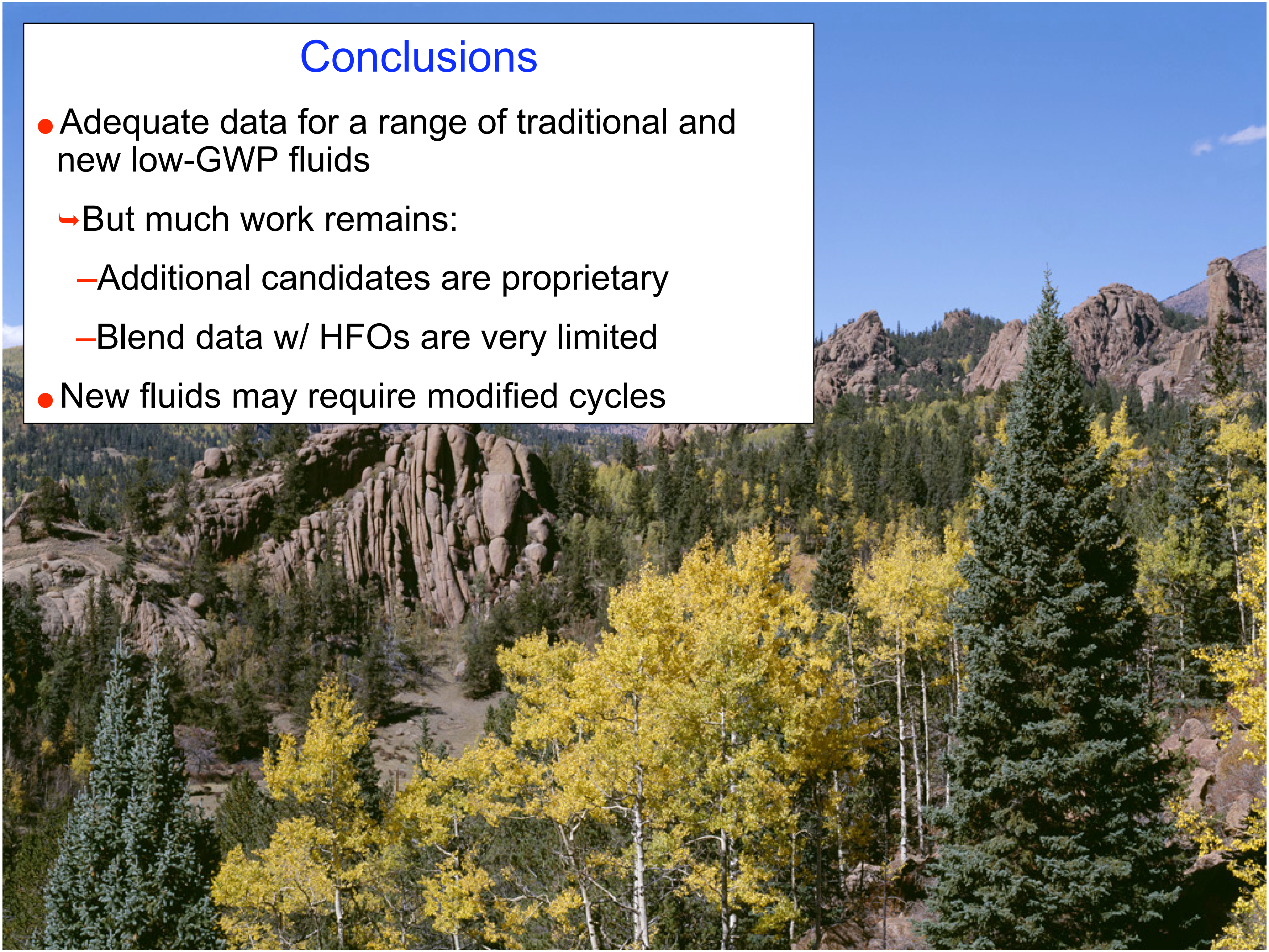




- Increased complexity:
  - ↪changes fundamental shape of thermodynamic surface
  - ↪increased flash losses
- The cycle may need to be modified

Conclusions

- Adequate data for a range of traditional and new low-GWP fluids
  - But much work remains:
    - Additional candidates are proprietary
    - Blend data w/ HFOs are very limited
- New fluids may require modified cycles




Questions?