

Heat Pump Systems

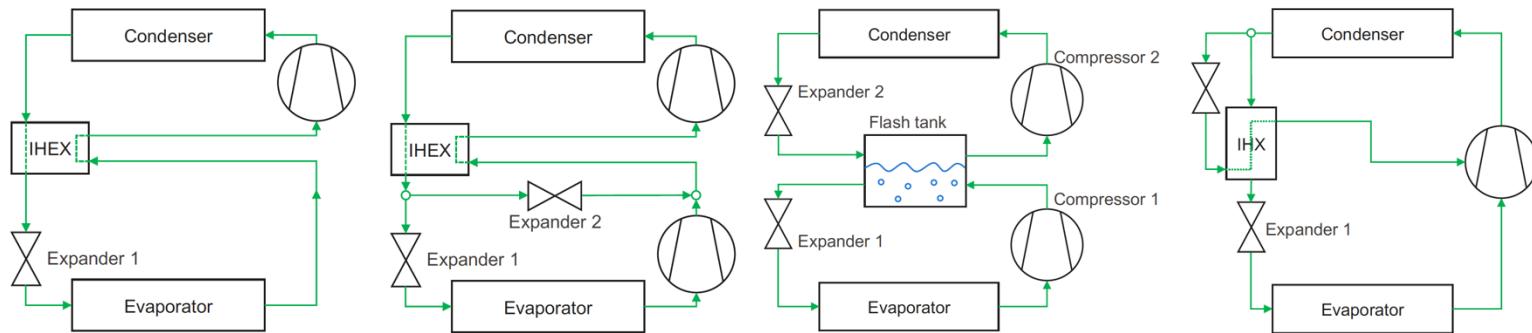
Summary W6

Prof. J. Schiffmann

- High exhaust temperatures damage lubricant / working fluid / compressor
- Compressor must run dry → sufficient superheat at inlet
- Often primary objective is to reduce compressor exhaust temperature to enable high temperature lifts
- Expansion valve requires liquid fluid → vapor bubbles create resistance
- Heat pumps rarely run at nominal condition → wide operating range

Practical Cycle Improvements

- Improvements can be achieved by improving individual component performance or by implementing more advanced thermodynamic cycles
 - Subcooling after condenser
 - Multistage compression with intercooling
 - Splitting expansion process
 - Cascades



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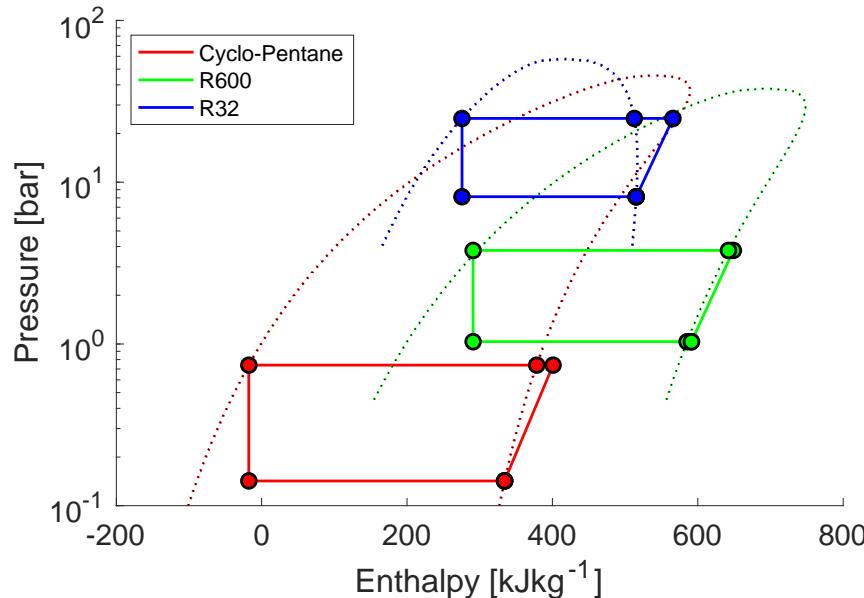
Heat Pump Systems

Working Fluids

Prof. J. Schiffmann

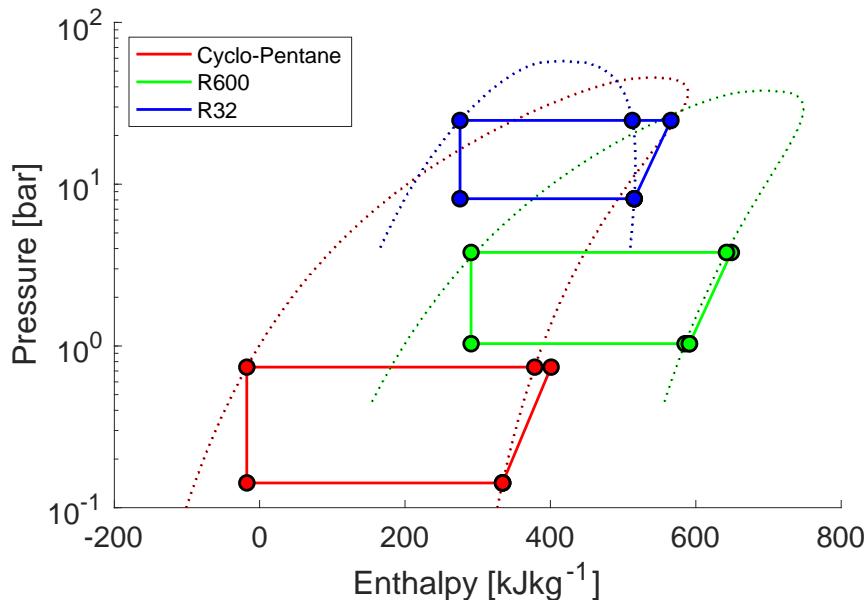
Role of Working Fluid & Selection

- Heat pumps make use of condensation and evaporation of working fluids to approach Carnot cycle
- Fluid selection has major impact on cycle and component design



Working Fluid Selection

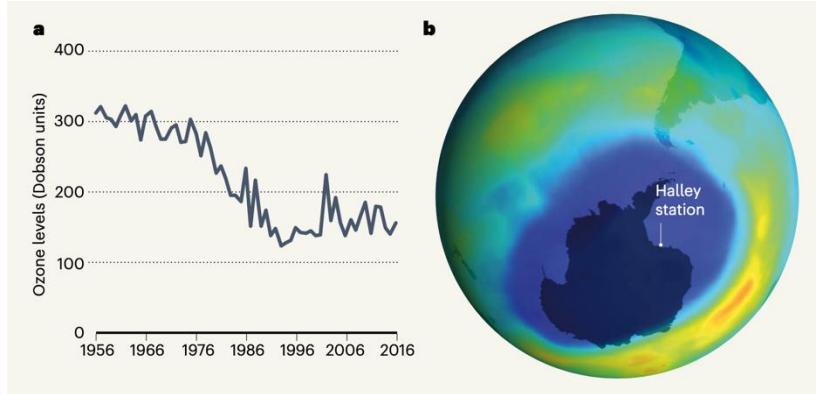
- Working fluid selection has important effect of cycle design
 - Design pressure ratio
 - Latent heat
 - Slope of saturation line
 - Slope of isentropic lines
 - Density
 - Thermophysical properties



Working Fluid Selection (cont.)

▪ Other aspects

- Ozone depletion potential (ODP)
- Global warming potential (GWP)
- Compatibility with oil
- Chemical stability
- Toxicity
- Flammability
- Cost ...



S. Solomon, The discovery of the Antarctic ozon hole, Nature, Vol. 575, 2019, pp. 46-47

	Class	Measured @ 60°C 101.3kPa
High flammability	3	LFL < 0.1kg/m ³ HOC ≥ 19MJ/kg
Flammable	2	LFL > 0.1kg/m ³ & HOC < 19MJ/kg
Low flammability	2L	LFL > 0.1kg/m ³ & HOC < 19MJ/kg, & BV ≤ 10 cm/s
No flammability	1	No flame propagation



■ Generation I (1830-1930)

- Whatever worked, solvents and other volatile fluids (SO₂, HCOOCH₃, NH₃, CH₃Cl, ...)
- Mostly flammable, toxic or highly reactive → accidents
- Leakage prevent domestic refrigerators to replace iceboxes
- Hence, drive for new suitable fluids → shift to fluoroochemicals

History of Working Fluids



■ Generation II (1930-1990)

- Fluids with no toxicity and flammability with suitable boiling points drive shift to fluorochemicals
- Systematic search limits fluids to combinations of C, N, O, S, H, F, Cl, Br
- Chlorofluorocarbons (CFC, R12)
- Hydrochlorofluorocarbons (HCFC, R22) with less chlorine
- Discovery of ozone hole and link to CFC in 1985
→ drive for new fluids with no ODP

History of Working Fluids



■ Generation III (1990-2010)

- Ratification of Montreal protocol (1989)
 - Phase out of CFC by 1996 and transitional shift to HCFC
 - Stepwise phase-out of HCFC: 2004 (65%), 2010 (25%), 2015 (10%), 2020 (0.5%)
- Replacement of HCFC with HFC (hydrofluorocarbons)
- New issue → global warming potential (GWP)
→ drive for low GWP fluids

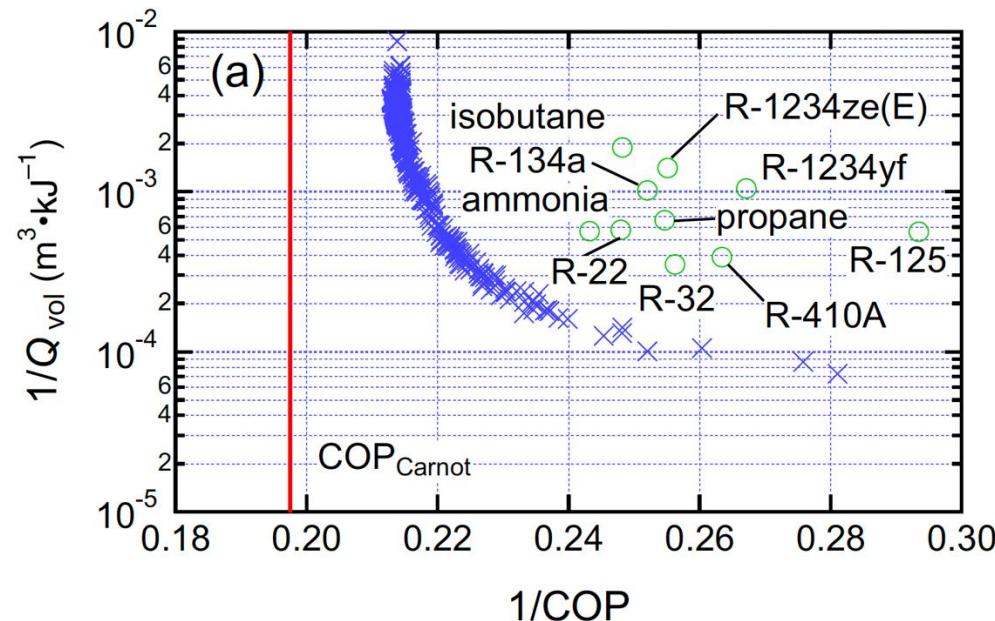
Fluid	GWP
R23	14'800
R404a	3'922
R134a	1'430
R32	675



- Generation IV (2010-?)
 - Kyoto protocol (1997), F-Gas regulation (2014)
 - Reduce greenhouse gas emissions
 - Bans the use of fluids with high GWP
 - Replacement of HFC with HFO (Hydrofluoroolefins)
 - HFO are chemically unstable in atmosphere → low GWP
 - New issue → Per- and poly-fluoroalkyl substances (PFAS), “forever chemicals”
 - Future? → Most likely natural fluids (ammonia, propane, butane, water, CO₂)

Working Fluid Selection (cont.)

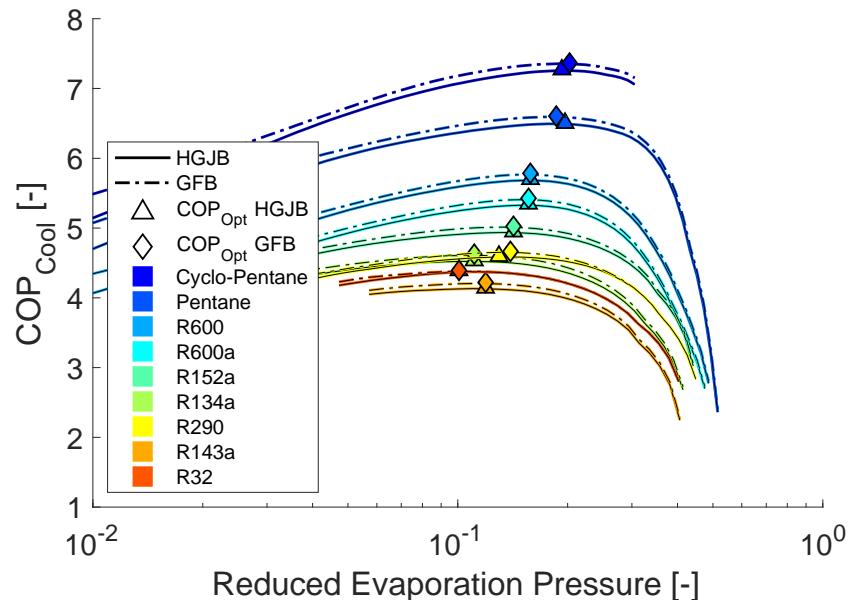
- Analysis of limitations due to working fluids suggests trade-off between system performance and volume
 - Single stage cycle
 - Evaporation at -20°C
 - Condensation at 40°C
 - Compressor efficiency = 1
 - Fluid model via extended corresponding states (ECS)



Working Fluid Selection (cont.)

- Alternative studies suggest ideal fluid is a function of reduced evaporation pressure
 - Performance drops sharply for higher pressures due to saturation dome

	Fluid	NBP [°C]	T_{Crit} [°C]
High P	R32	-51.7	78.1
	R143a	-47.2	72.7
	R290	-42.1	96.7
Medium P	R134a	-26.1	101.1
	R152a	-24	113.3
	R600a	-11.7	134.7
Low P	R600	-0.5	152
	R601	36.1	196.6
	Cyclo-Pentane	49	238.6

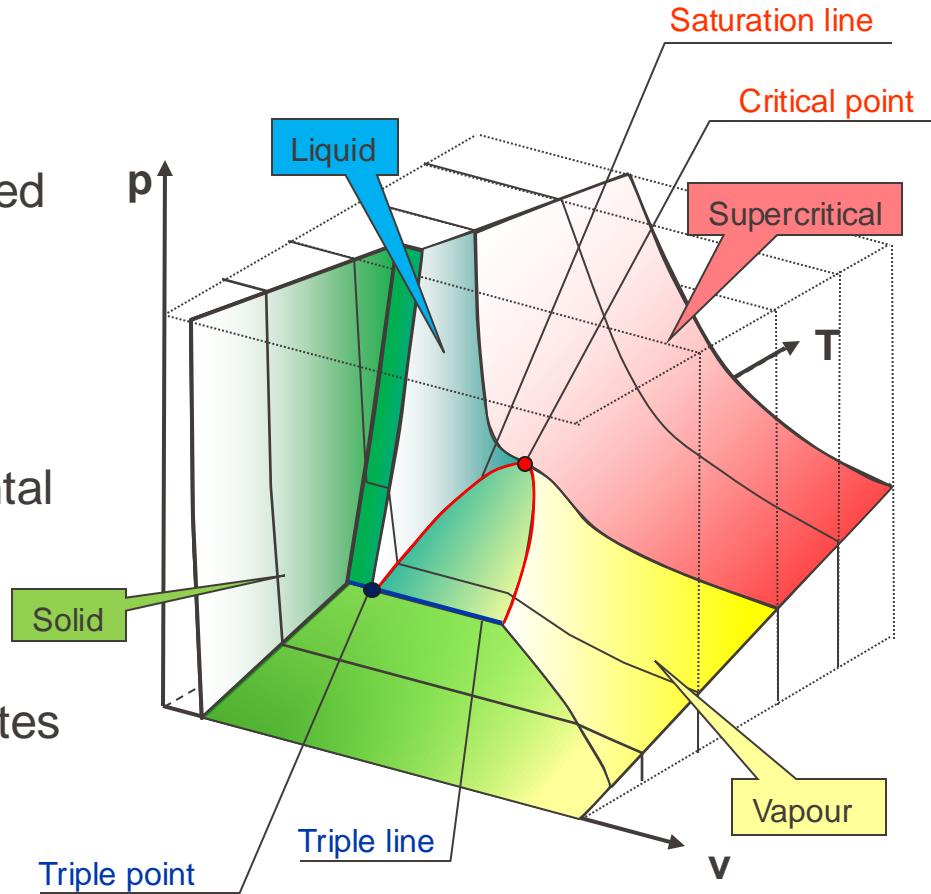


Thermodynamic States of Fluids

- State of fluids can be represented by a surface in P, T, v

$$F(P, T, v) = 0$$

- State function needs experimental identification for each fluid individually
- Surfaces represent different states and two-phase transitions



- Definition of vapor quality

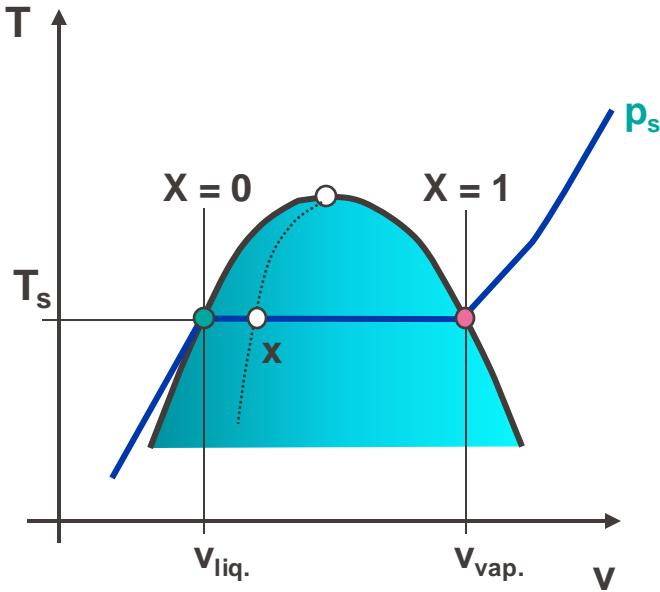
$$x = \frac{m_{vapour}}{m_{liquid} + m_{vapour}}$$

- State under saturation line

$$v(x) = x v_{vap} + (1 - x) v_{liq}$$

$$h(x) = x h_{vap} + (1 - x) h_{liq}$$

$$s(x) = x s_{vap} + (1 - x) s_{liq}$$



- Ideal gas follows simple equation of state

$$Pv = rT$$

- Enthalpy

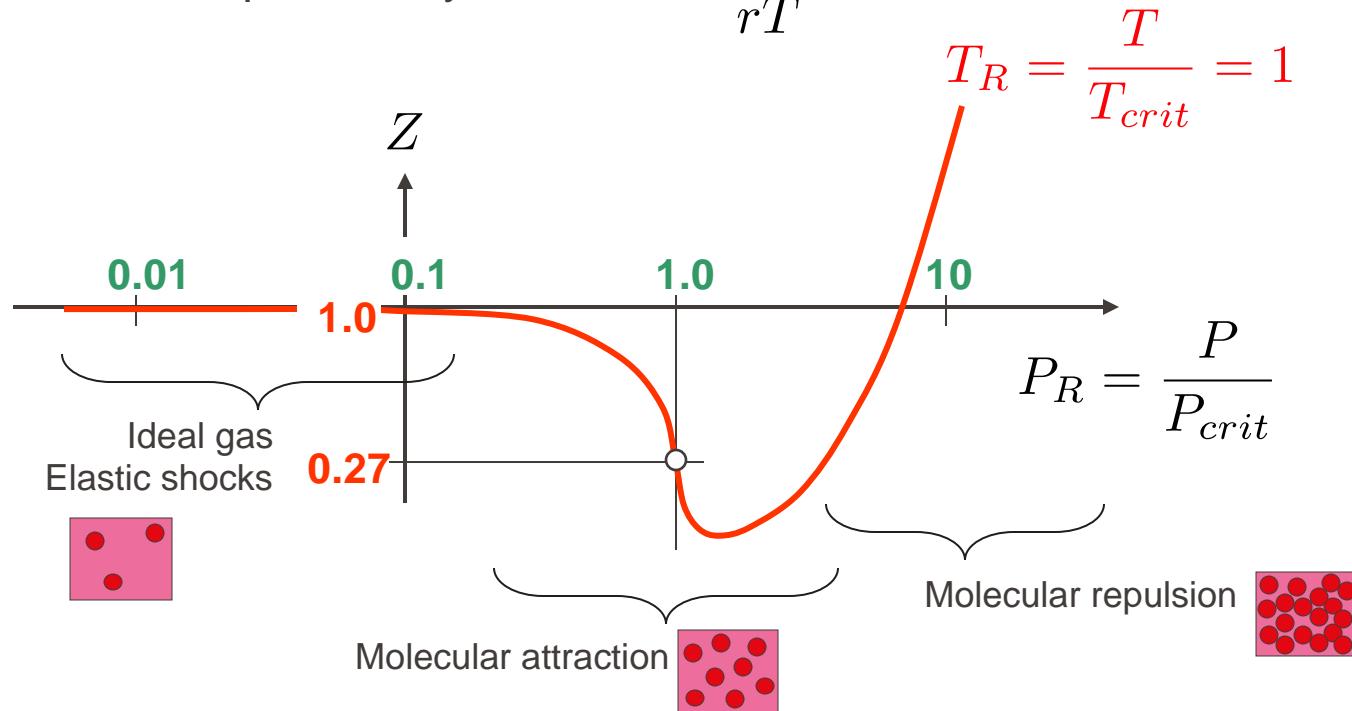
$$h - h_{ref} = c_p (T - T_{ref})$$

- Entropy

$$s - s_{ref} = c_v \ln \left(\frac{T}{T_{ref}} \right) + r \ln \left(\frac{v}{v_{ref}} \right)$$

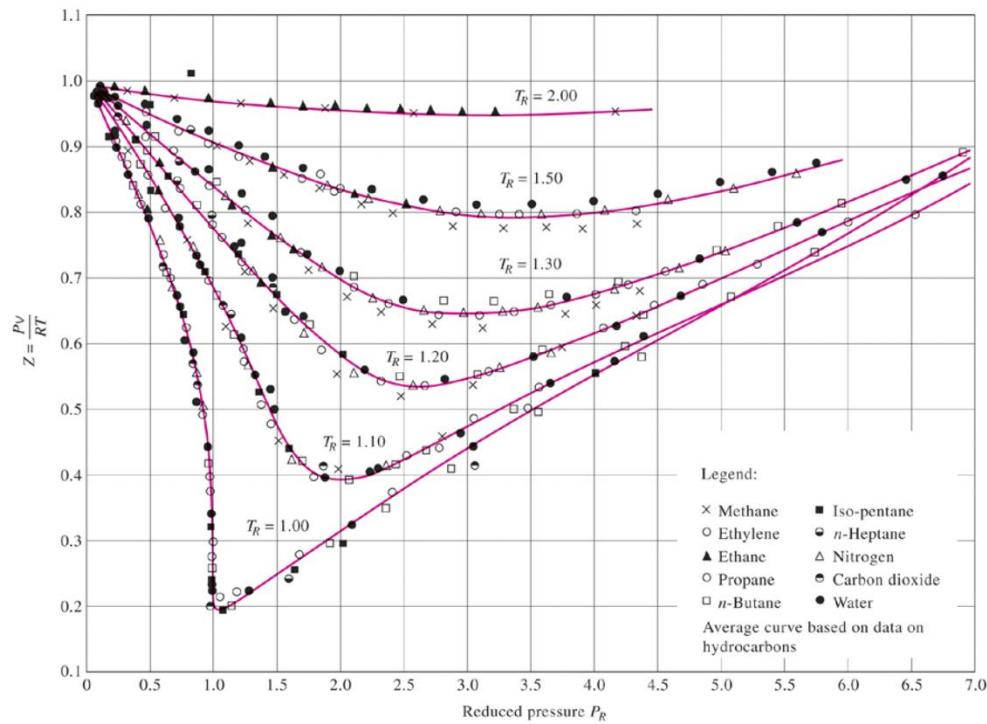
Real Gas Effects

- Measured with compressibility factor $Z = \frac{Pv}{rT}$



Compressibility Factor Z

- Measured compressibility factors for different fluids collapse to same curves
- Compressibility factor can be used for estimation of properties
- Better laws needed for higher accuracy



Equation of State (EOS)

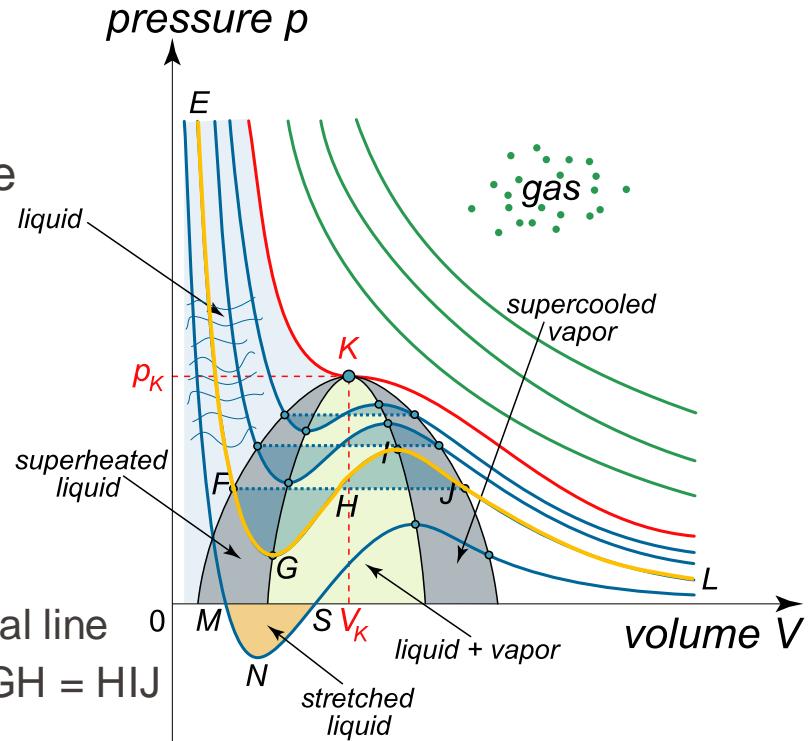
- Van der Waals cubic equation of state

$$P = \frac{rT}{(v - b)} - \frac{a}{v^2}$$

Pressure from interactions
 Finite molecule volume

- Zero slope at critical point
- Unstable states (IG)
- Metastable states (JI & GF) \rightarrow spinodal line
- Plateau JF defined such that areas FGH = HIJ

- Work in reversible cycle with one T source:



<https://math24.net/van-der-waals-equation.html>

- More accurate cubic equation of state

$$P = \frac{rT}{(v - b)} - \frac{a\alpha}{(v^2 + uvb + wb^2)}$$

EOS	u	w
Van der Waals (1873)	0	0
Redlich-Kwong (1949)	1	0
Soave-Redlich-Kwong (1972)	1	0
Peng-Robinson (1976)	2	-1

- Significant increase in accuracy compared to van der Waals
- Good results for gas phase, poor for liquid, satisfactory for enthalpy and entropy departure functions
- Increased accuracy around critical point
- Better for liquid and gas than SRK

- For Peng-Robinson

$$P = \frac{rT}{(v - b)} - \frac{a\alpha}{(v^2 + 2vb - b^2)}$$

with

$$\left. \begin{array}{l} a = f_a(R, T_{crit}, P_{crit}) \\ b = f_b(R, T_{crit}, P_{crit}) \\ \alpha = [1 + \kappa (1 - T_R^{0.5})]^2 \\ \kappa = f_\kappa(\omega) \end{array} \right\} \begin{array}{l} \text{Requires critical} \\ \text{temperature } T_{crit}, \text{ critical} \\ \text{pressure } P_{crit}, \text{ and} \\ \text{acentric factor } \omega \end{array}$$
$$\omega = -1 - \log_{10}(P_\sigma/P_{crit})$$
$$P_\sigma = P_{sat} @ T_R = 0.7$$

- Departure (from ideal gas) functions to calculate other states

$$h - h_{ideal} = \int_0^P \left[v - T \frac{\partial v}{\partial T} \right] dP$$

$$s - s_{ideal} = \int_0^P \left[-\frac{\partial v}{\partial T} + \frac{R}{P} \right] dP$$

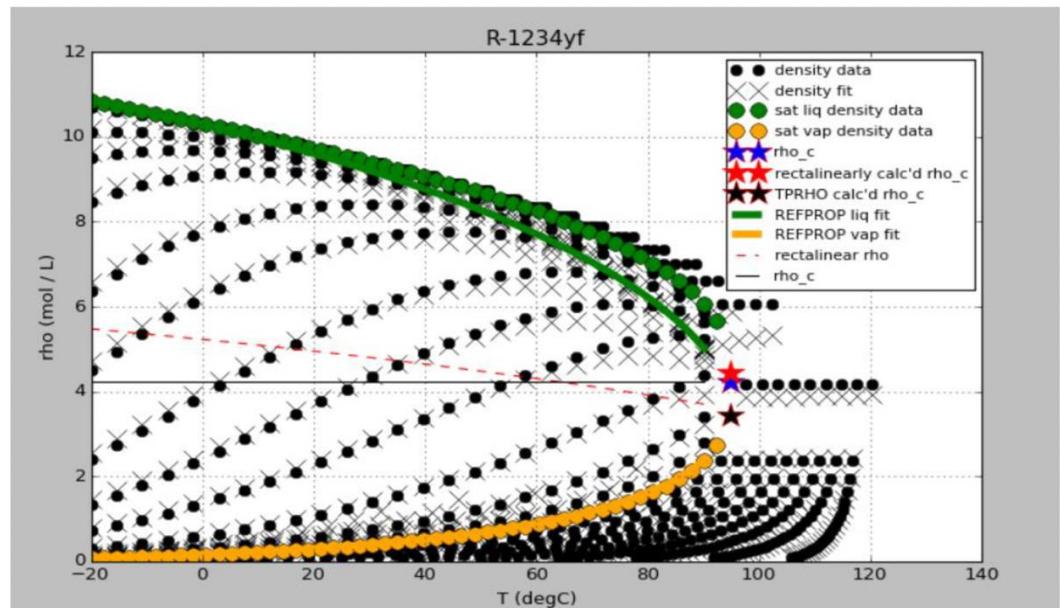
- Peng-Robinson EOS requires minimal measurements of sample fluid
 - Critical pressure & temperature, vapor pressure, heat capacity, liquid density
 - Ideal for use in R&D for new working fluids

Performance of Peng-Robinson EOS

- Comparison between Peng-Robinson & experimental data for HFO R1234yf

- Deviations

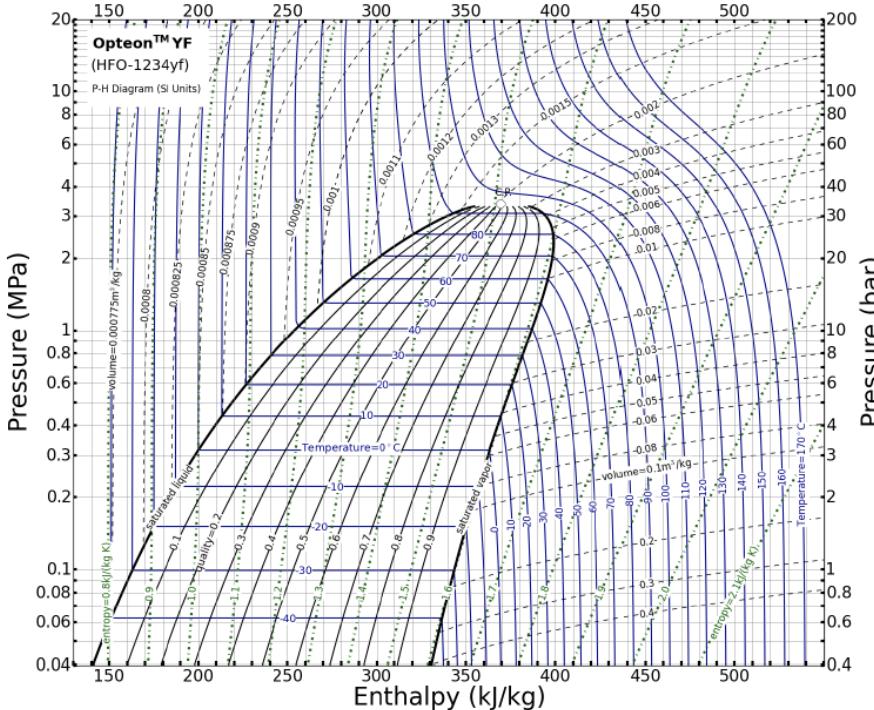
- Density: 14%
- Enthalpy: 0.7%
- Entropy: 0.5%
- c_v : 5%
- c_p : 5%



Source: Chemours lecture for PCHP

More Sophisticated Models for Fluid Properties

- State-of-the-art is Refprop from NIST and Coolprop with more sophisticated equations of state corrected with measurements
- Helmholtz-explicit EOS
- PC-SAFT



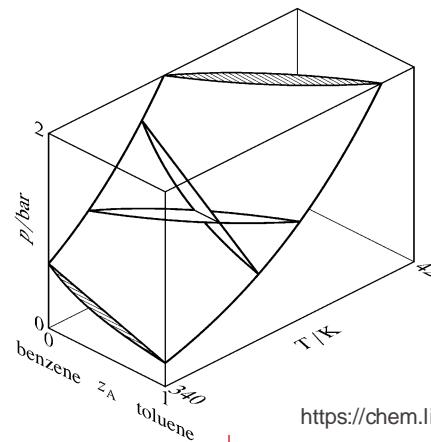
- Classification of single component fluids: $R (M)XYZ(q)$

- Number of C $\rightarrow X+1$
- Number of H $\rightarrow Y-1$
- Number of F $\rightarrow Z$
- M \rightarrow unsaturated fluid
- q \rightarrow defines molecular arrangement

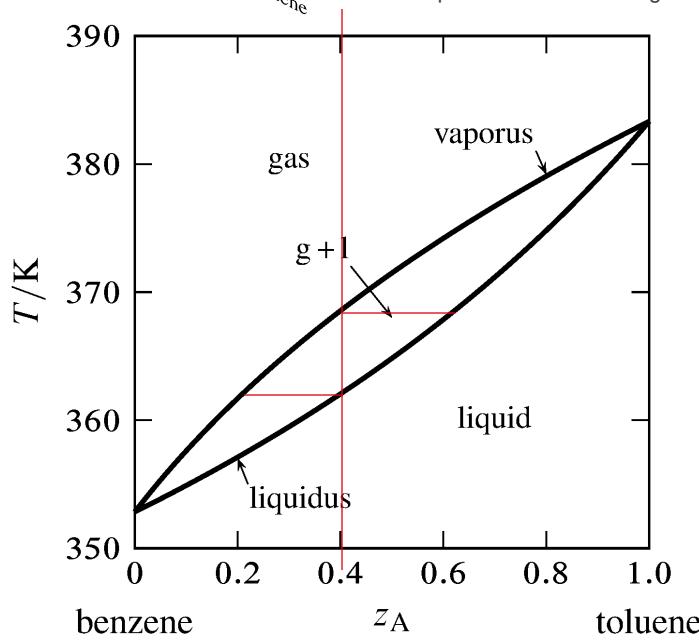
- Examples
 - R134a: CH₂F-CF₃
 - R114: CF₂Cl-CF₂Cl
 - R22: CHClF₂
 - R290: CH₃-CH₂-CH₃

Multi-component blends

- Behavior represented in p-x & T-x diagrams
 - Surfaces for saturated liquid and vapor delimiting volume of two-phase region
- Non-azeotropic (zeotropic) blends
 - Mixture yields temperature glide during phase change → can be beneficial
 - Risk of distillation, issues when leakage, challenging when maintenance and end of life, poorer heat transfer coefficients
- Azeotropic blends
 - Mixture yields no temperature glide

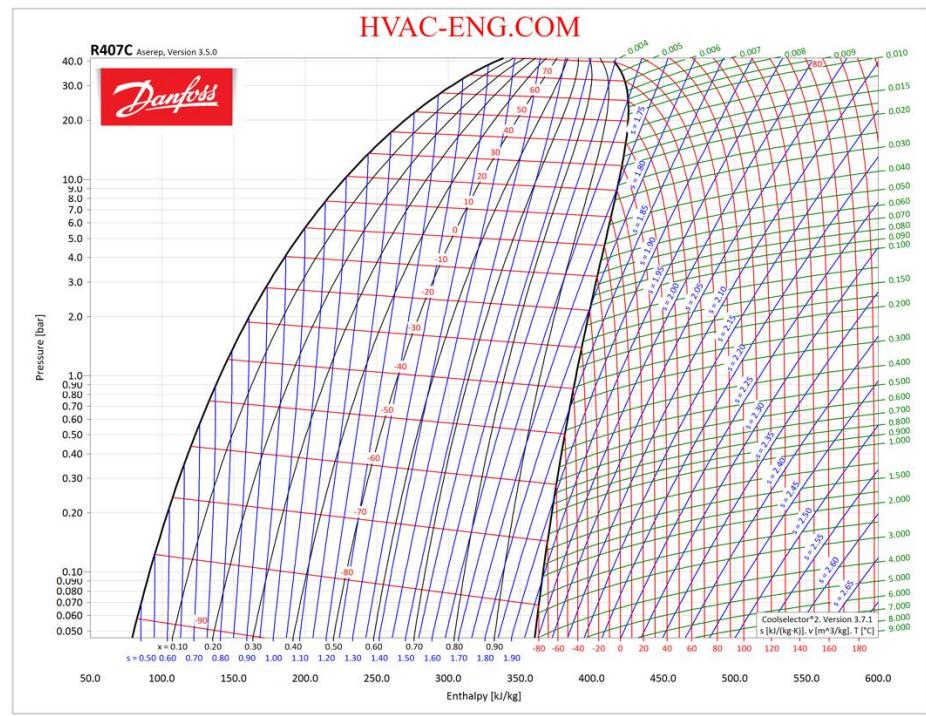


<https://chem.libretexts.org>



Nomenclature (cont.)

- Non-azeotropic blends → R400
 - R32, R125, R134a → R407
 - Different compositions noted with upper case letter (R407C)
- Azeotropic blends → R500
 - R134a, R1234yf → R513
- Inorganic working fluids
 - R700 + molecular weight



- R717: NH₃
- R718: H₂O
- R744: CO₂