

# Heat Pump Systems

Summary W6

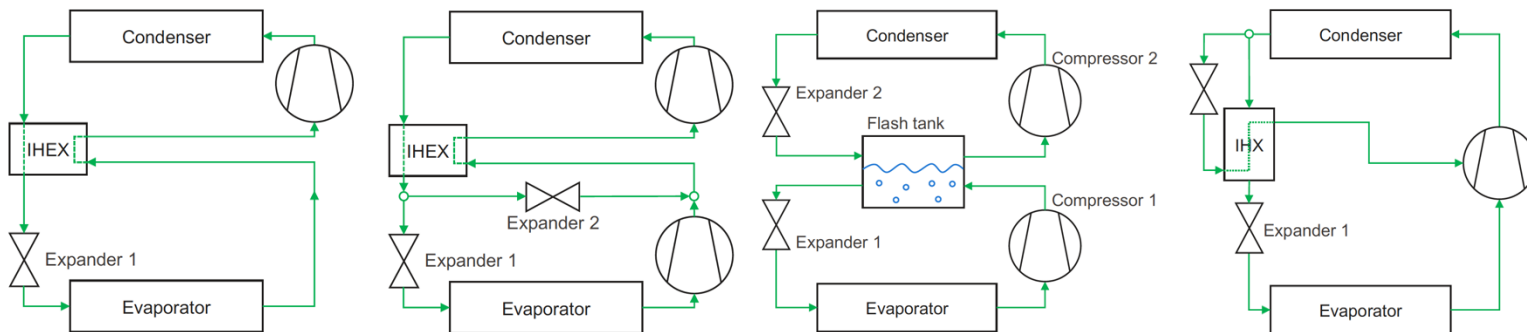
Prof. J. Schiffmann

# Practical Aspects for Cycle Implementation

- 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



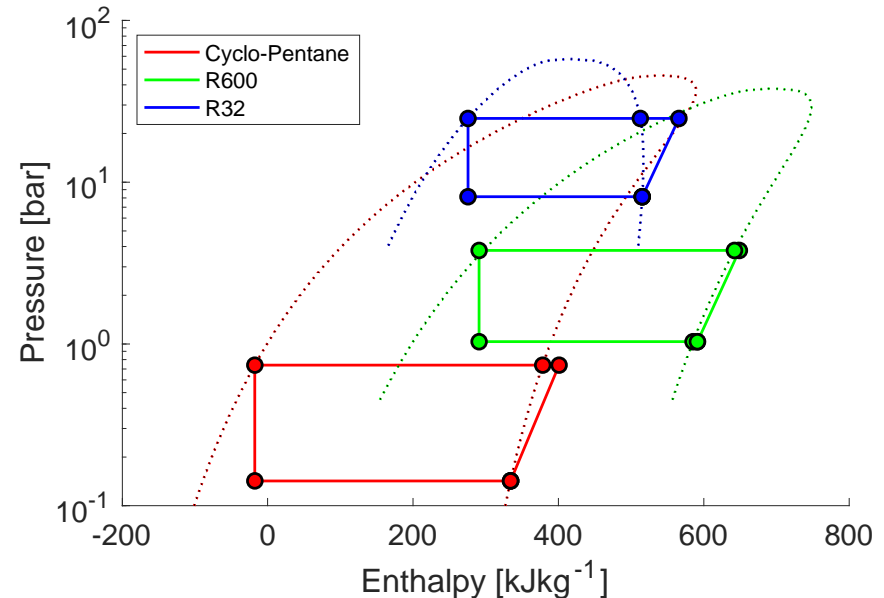


# Heat Pump Systems

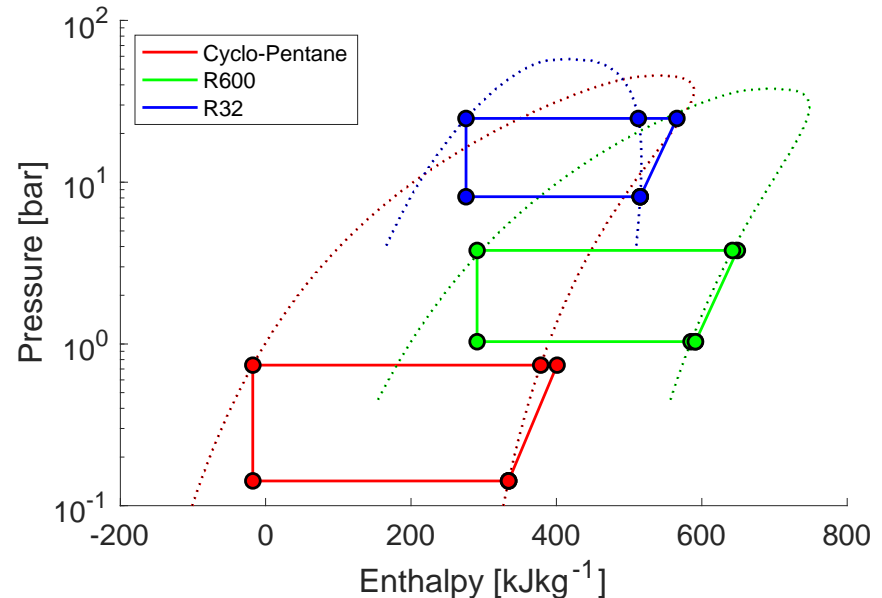
Working Fluids

Prof. J. Schiffmann

- 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

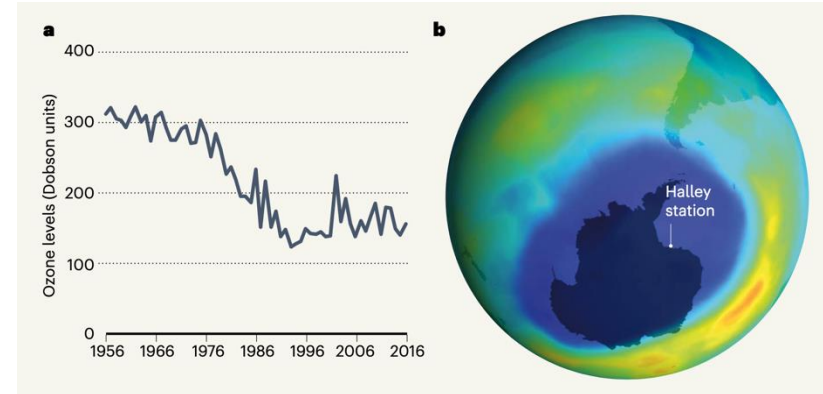


- Working fluid selection has important effect of cycle design
  - Design pressure ratio
  - Latent heat
  - Slope of saturation line
  - Slope of isentropic lines
  - Density
  - Thermophysical properties



## Other aspects

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



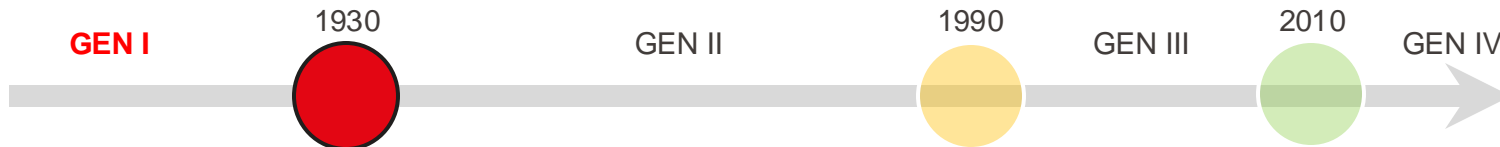
S. Solomon, The discovery of the Antarctic ozone hole, Nature, Vol. 575, 2019, pp. 46-47

	Class	Measured @ 60°C 101.3kPa
High flammability	3	$LFL < 0.1\text{kg/m}^3$   $HOC \geq 19\text{MJ/kg}$
Flammable	2	$LFL > 0.1\text{kg/m}^3$ & $HOC < 19\text{MJ/kg}$
Low flammability	2L	$LFL > 0.1\text{kg/m}^3$ & $HOC < 19\text{MJ/kg}$ , & $BV \leq 10\text{ cm/s}$
No flammability	1	No flame propagation

LFL: Lower flammability limit  
HOC: Heat of combustion  
BV: burning velocity



# History of Working Fluids



## ■ Generation I (1830-1930)

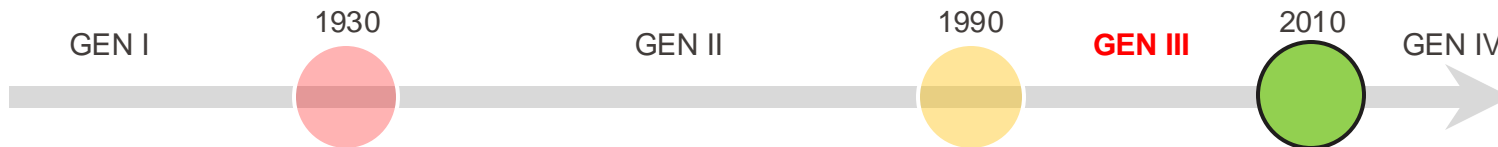
- Whatever worked, solvents and other volatile fluids ( $\text{SO}_2$ ,  $\text{HCOOCH}_3$ ,  $\text{NH}_3$ ,  $\text{CH}_3\text{Cl}$ ,...)
- Mostly flammable, toxic or highly reactive → accidents
- Leakage prevent domestic refrigerators to replace iceboxes
- Hence, drive for new suitable fluids → shift to fluorochemicals

# 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



## ■ 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

# History of Working Fluids



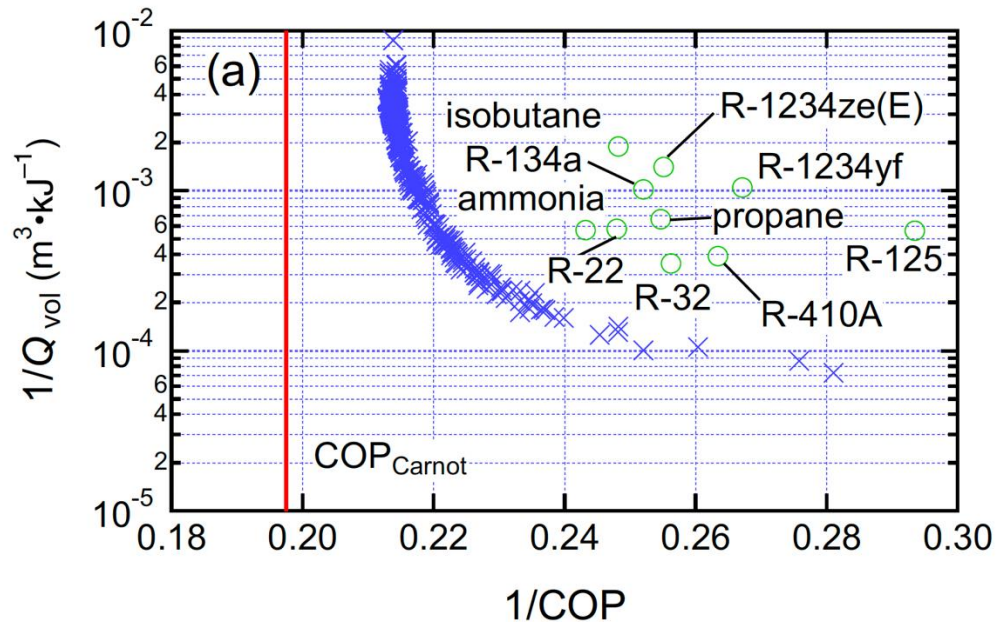
## ■ Generation IV (2010-?)

- 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, CO<sub>2</sub>)

# Working Fluid Selection (cont.)

- Analysis of limitations due to working fluids suggests trade-off between system performance and volume

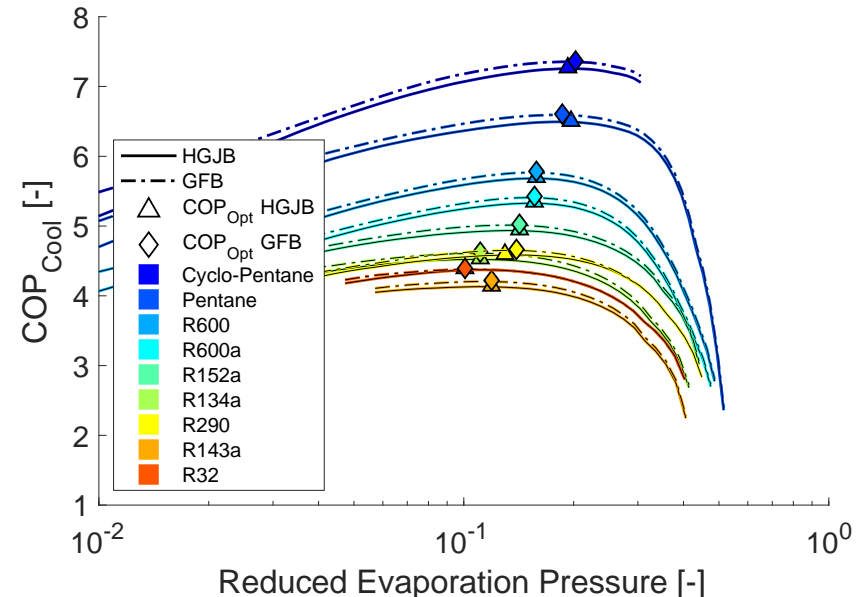
- Single stage cycle
- Evaporation at  $-20^{\circ}\text{C}$
- Condensation at  $40^{\circ}\text{C}$
- Compressor efficiency = 1
- Fluid model via extended corresponding states (ECS)



P. A. Domanski et al., *A thermodynamic analysis of refrigerants: Performance limits of the vapor compression cycle*, International Journal of Refrigeration, Vol. 38, 2014, pp 71-79

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



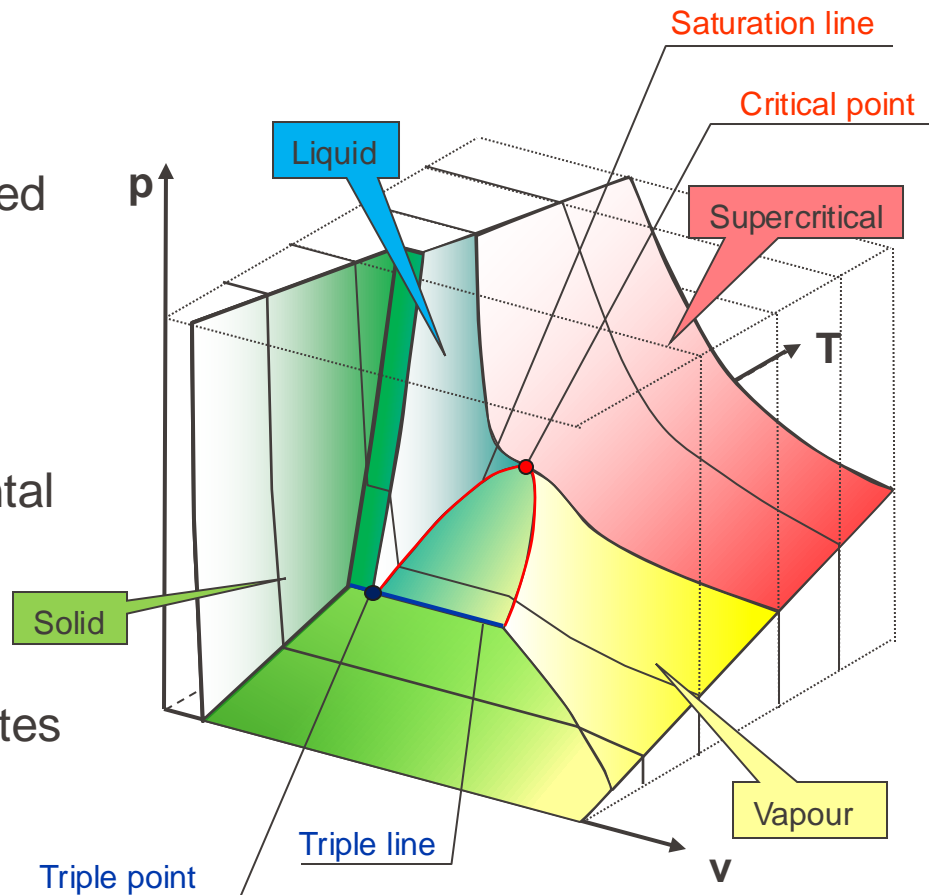
J. Schiffmann et al., *Scale limitations of gas bearing supported turbocompressors for vapor compression cycles*, International Journal of Refrigeration, Vol. 109, 2020 pp 92-104

# 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



# States under Saturation Line

- Definition of vapor quality

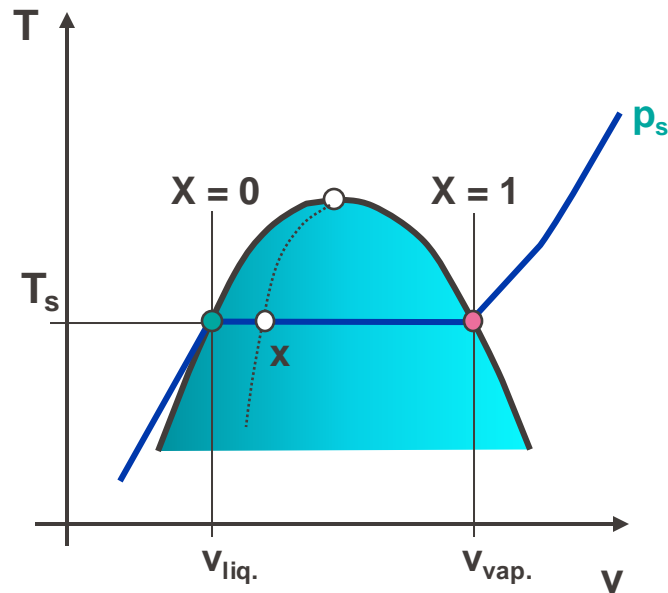
$$x = \frac{m_{vapour}}{m_{liquid} + m_{vapour}}$$

- State under saturation line

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

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

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





- Ideal gas follows simple equation of state

$$Pv = rT$$

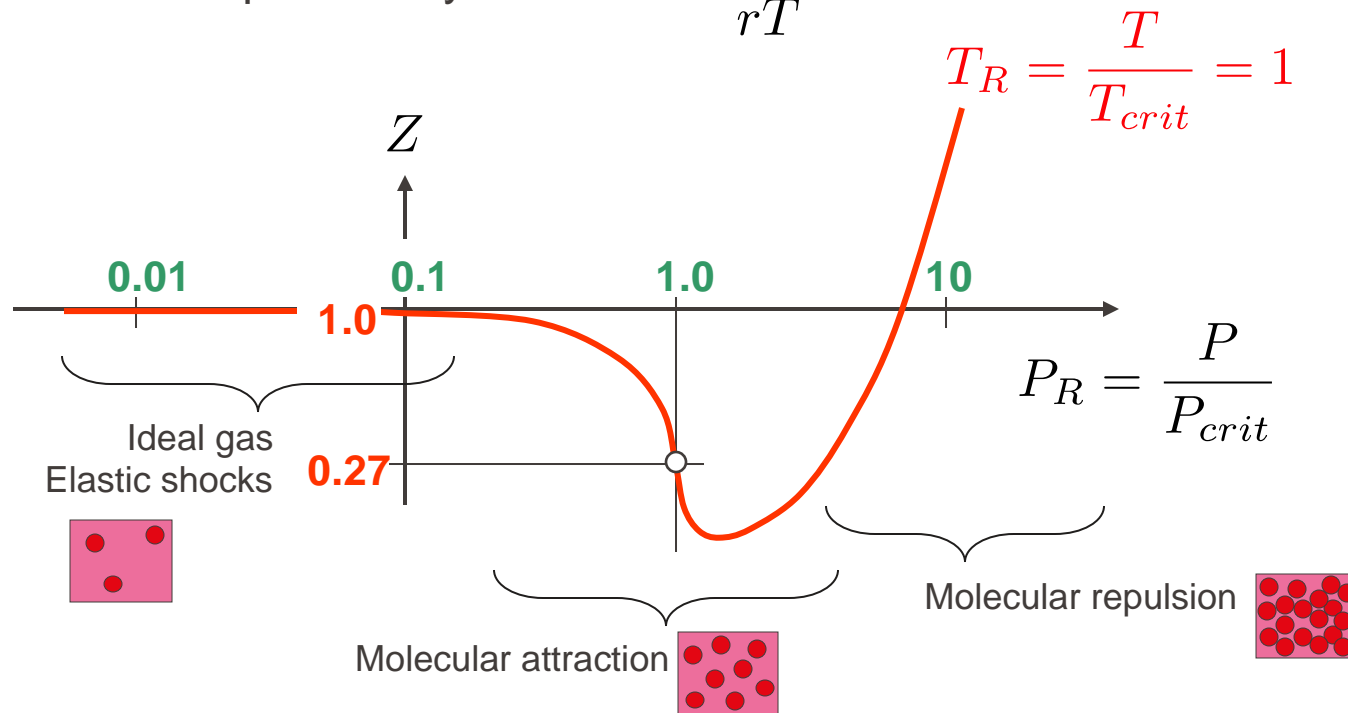
- Enthalpy

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

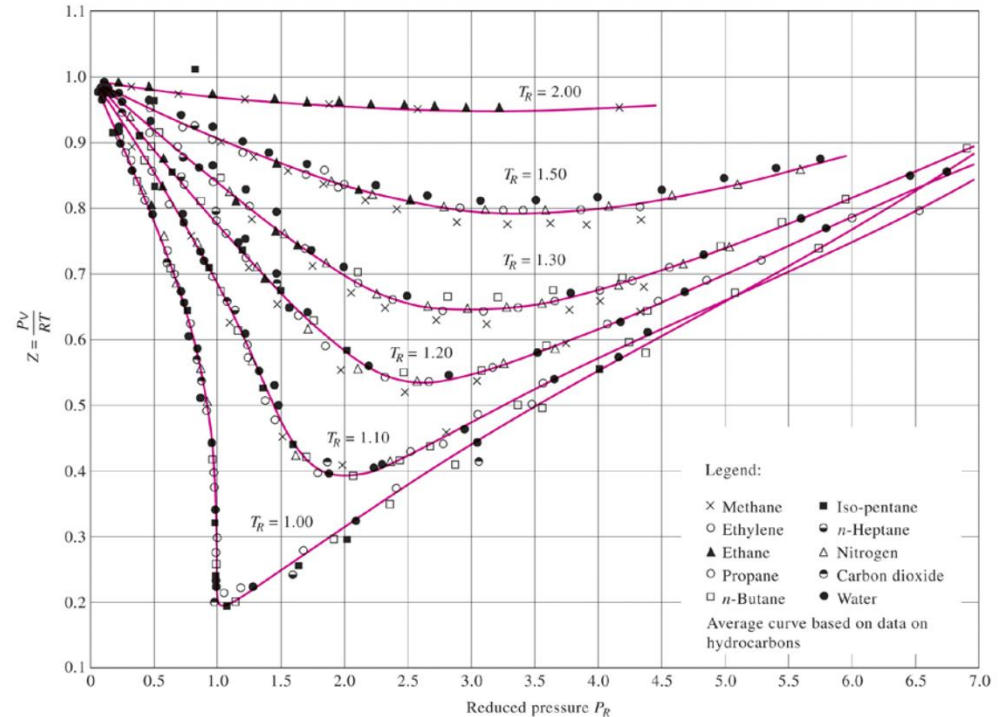
- Entropy

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

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



- 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



- $$P = \underbrace{\frac{rT}{(v - b)}}_{\text{Finite molecule volume}} - \frac{a}{v^2} \left. \vphantom{\frac{rT}{(v - b)}} \right\} \begin{array}{l} \text{Pressure from} \\ \text{interactions} \end{array}$$

- Work in reversible cycle with one T source:



$$\oint P dv = 0$$

# Evolution of Equation of State (EOS)

- 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

$$a = f_a(R, T_{crit}, P_{crit})$$

$$b = f_b(R, T_{crit}, P_{crit})$$

$$\alpha = [1 + \kappa(1 - T_R^{0.5})]^2$$

$$\kappa = f_\kappa(\omega)$$

Requires critical temperature  $T_{crit}$ , critical pressure  $P_{crit}$ , and acentric factor  $\omega$

$$\omega = -1 - \log_{10}(P_\sigma / P_{crit})$$

$$P_\sigma = P_{sat}@T_R = 0.7$$

# How to Calculate Other States?

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

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

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

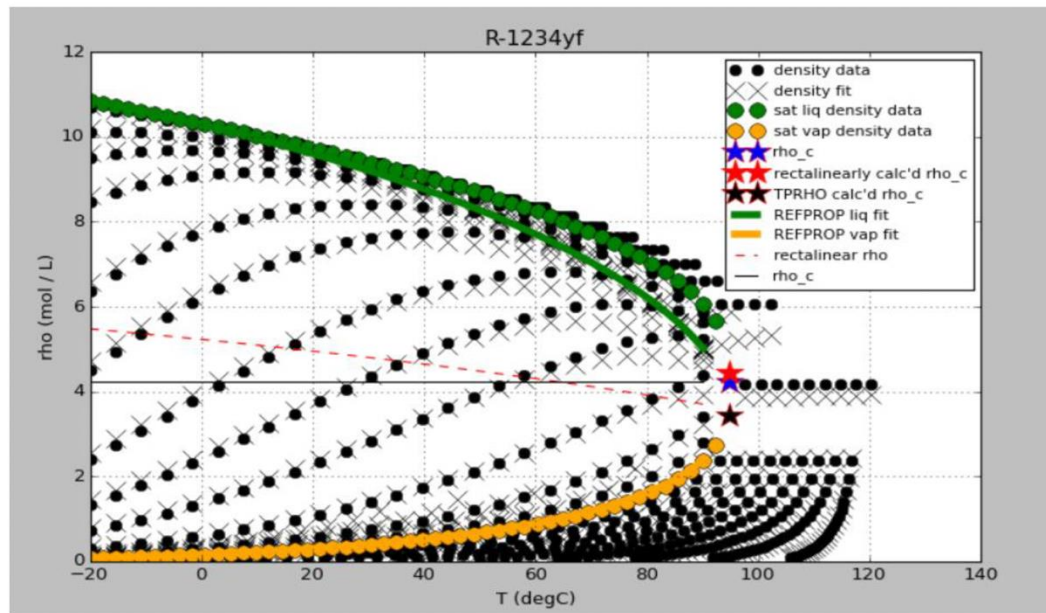
- Peng-Robinson EOS requires minimal measurements of sample fluid
  - Critical pressure & temperature, vapor pressure, heat capacity, liquid density
  - Ideal for use in R&D for new working fluids

# Performance of Peng-Robinson EOS

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

- Deviations

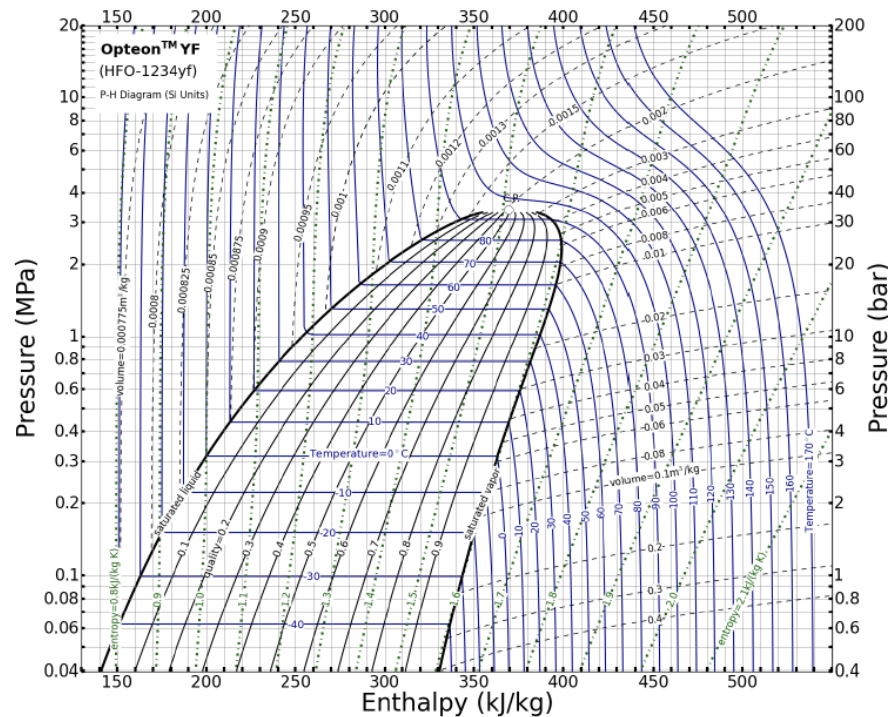
- Density: 14%
- Enthalpy: 0.7%
- Entropy: 0.5%
- $c_v$ : 5%
- $c_p$ : 5%



Source: Chemours lecture for PCHP

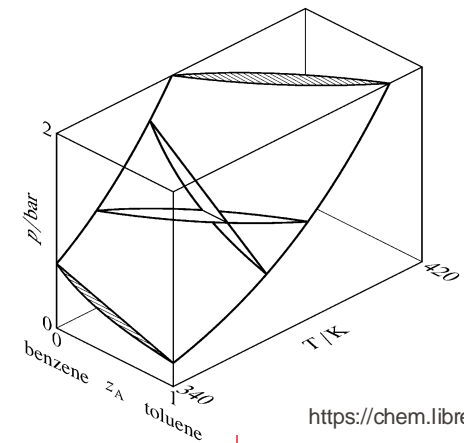


- State-of-the-art is Refprop from NIST and Coolprop with more sophisticated equations of state corrected with measurements
- Helmholtz-explicit EOS
- PC-SAFT

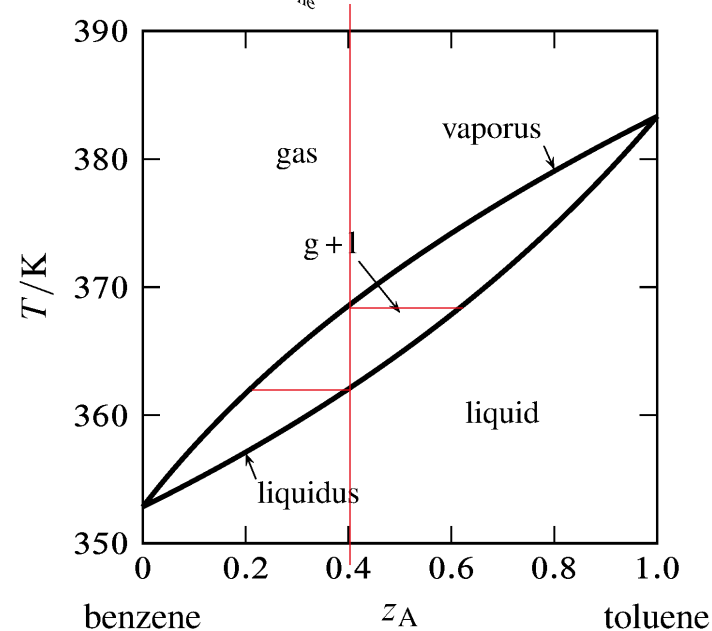


- Classification of single component fluids: R (M)XYZ(q)
  - Number of C  $\rightarrow$  X+1
  - Number of H  $\rightarrow$  Y-1
  - Number of F  $\rightarrow$  Z
  - M  $\rightarrow$  unsaturated fluid
  - q  $\rightarrow$  defines molecular arrangement
- Examples
  - R134a: CH<sub>2</sub>F-CF<sub>3</sub>
  - R114: CF<sub>2</sub>Cl-CF<sub>2</sub>Cl
  - R22: CHClF<sub>2</sub>
  - R290: CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>3</sub>

- 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

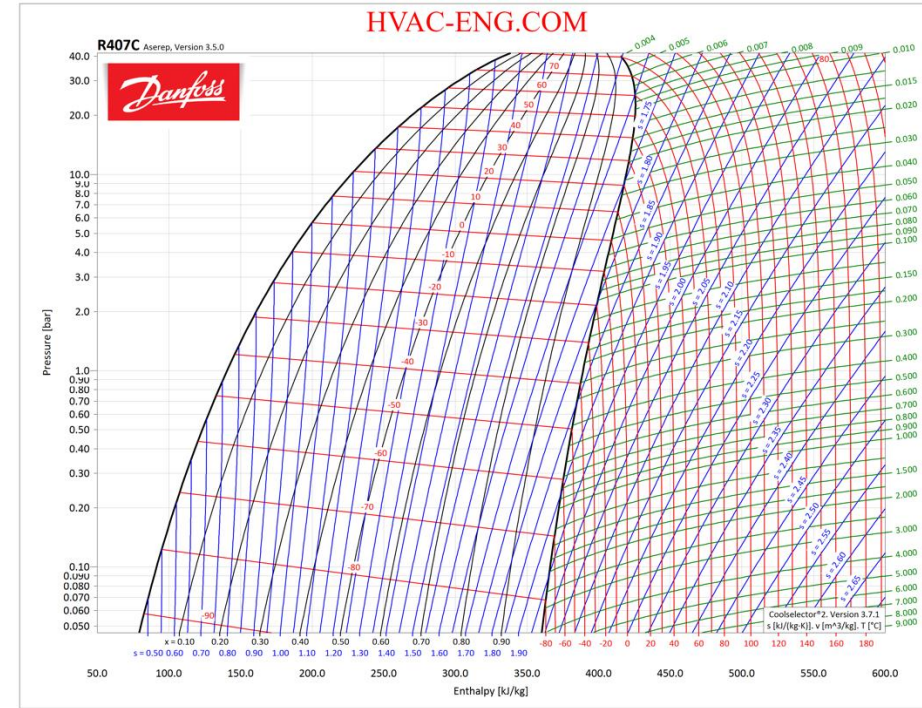


<https://chem.libretexts.org>



# 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