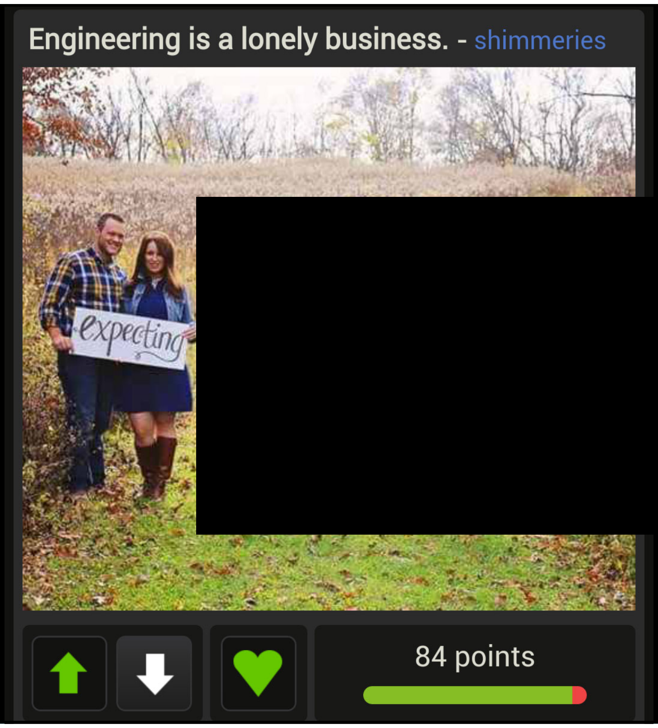


Engineering is a lonely business. - shimmeries

[redacted]

Courtesy
Corbin Critchfield

Business

- This is class 17 of 36 before the case study!
- Next exam given out on Monday, Oct. 17
  - Due Friday, Oct 21

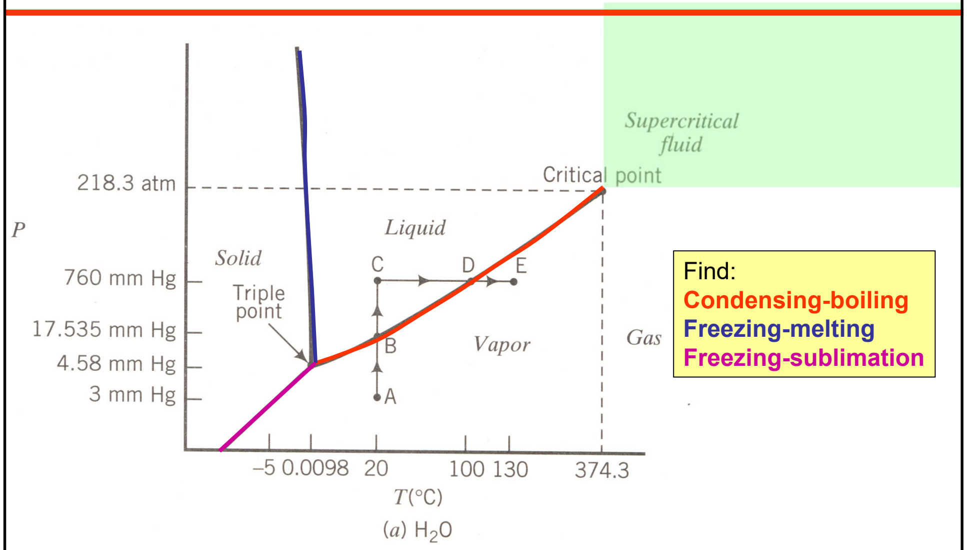
Review – Non-ideal Gases

- **Equations of State**
  - ✓ Van der Waals
  - ✓ SRK
  - ✓ Use P_c, T_c, and ω which are species-specific
- **Corresponding States (Compressibility Factor)**
  - ✓ Use P_r and T_r to get z
  - ✓ $PV = znRT$ or $P\dot{V} = z\dot{n}RT$
  - ✓ Kay's rule for mixtures
    - $P_c' = \sum y_i P_{c,i}$ and $T_c' = \sum y_i T_{c,i}$

Multiphase Systems
Ch. 6

P vs T Diagram: Water

(pure component)



(a) H_2O

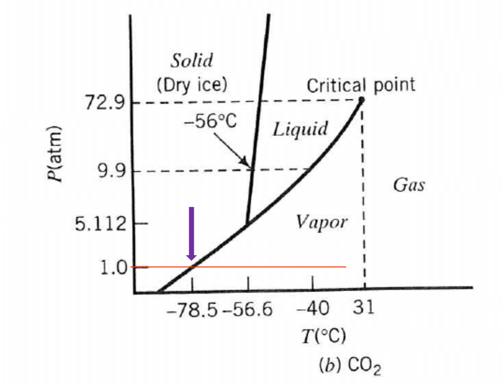
Find:

Condensing-boiling

Freezing-melting

Freezing-sublimation

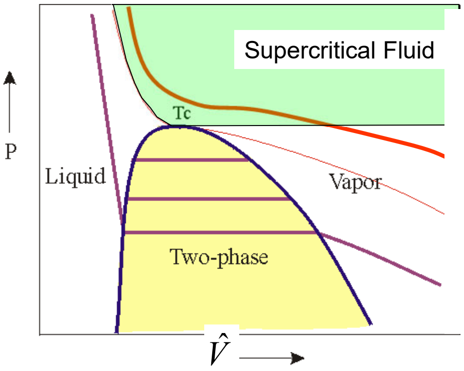
P vs T Diagram: CO_2

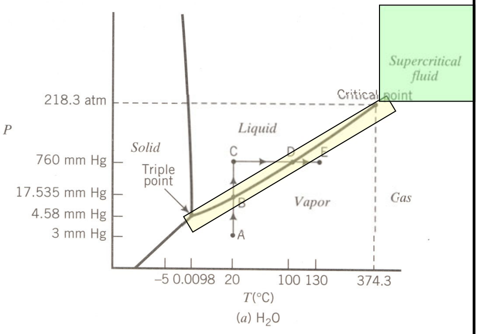


(b) CO_2

At atmospheric pressure, CO_2 sublimes at -78°C (Table B.1)
At 9.9 atm, melting at -56°C, vaporization at about -40°C

P vs V and P vs T
Phase Diagrams for H_2O





Note big changes in density ($1/\hat{V}$) in 2-phase region

Two Phases: Vapor & Liquid

- All charts above were for a PURE component
  - Pure H_2O or pure CO_2
- Wanted:
  - If at phase boundary, how much vapor and how much liquid at equilibrium?
  - If not at phase boundary (pure component), we only have vapor or liquid, not both!
- Also, what if we have more than one component?
  - What is the equilibrium composition of the liquid and the vapor?

Definitions

- Boiling point
  - Temperature at which pure liquid changes to vapor
  - Is a function of P
- Normal boiling point
  - Boiling point at 1 atm
- Freezing point
  - Temperature at which liquid changes to solid
  - Is a function of P
- Sublimation point (you get the idea!)

Vapor Pressure

note that these examples have more than one species (air + liquid)

- Why does a wet sidewalk become dry on a cold day if water boils at 212°F?
- Why does a 2-liter bottle of Sprite stay fizzy until you open it for the first time?
- Why is humid air so uncomfortable in the summer?
- Why do swamp coolers work in the desert but not in the swamp?
- Why does a wet finger dry faster when I blow on it?
- What happens to the steam plume from a power plant?
- How do raindrops evaporate before hitting the ground sometimes?

So What Is Vapor Pressure?

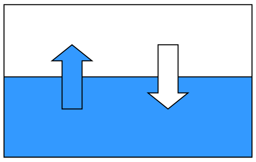
- P_i^*
- Measure of the volatility of a species
- For <u>pure</u> component:
  - The pressure of the vapor above a pure liquid at equilibrium (2-phase line)
- Redefine boiling point
  - T when $P_i^* = P_{tot}$
    (pure substance)

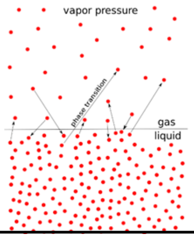
Class Answers

• Name some compounds with high vapor pressures (i.e., evaporate quickly)	• Name some compounds with low vapor pressures (i.e., evaporate slowly)

Molecular Level

- As T ↑, molecules are more excited
- Some molecules exit the liquid phase
- Some molecules condense
- Equilibrium is steady-state condition when the same # of molecules condense and vaporize
- So…. P_i^* is related to the number of moles that evaporate at a given temperature





Properties of Vapor Pressure

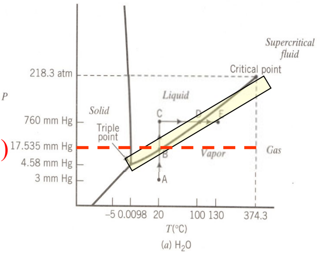
- P_i^* is a function of T
  - If you raise the T, more of the substance wants to be vapor
  - Related to volatility, or tendency to evaporate at a given T
- P_i^* is different for each species
  - Related to MW_i
  - Related to chemical structure (aromatic, paraffinic, etc.)

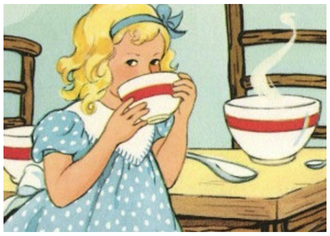
For A Pure Component

- If $P_{tot} < P^*$ (point A)
  - All vapor (i.e., gas)
- If $P_{tot} > P^*$ (point C)
  - All liquid
- If $P_{tot} = P^*$ (point B)
  - 2-phase (vapor and liquid)

(more complicated with multiple species)

P*(20°C)





Example: Non-ideal gas n-butane at 12 atm and 300 K

- Valerie and I got P_r =.32and T_r=.71, then a z = .76
  - This was from the dotted region on the compressibility chart
- The SRK equation would not converge using the $\hat{V}$ from the ideal gas equation!
- $P^*_{\text{n-butane}}$ = 2.5463 atm
- Since P > P*, this was a liquid!!!

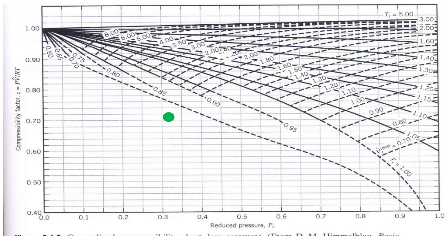
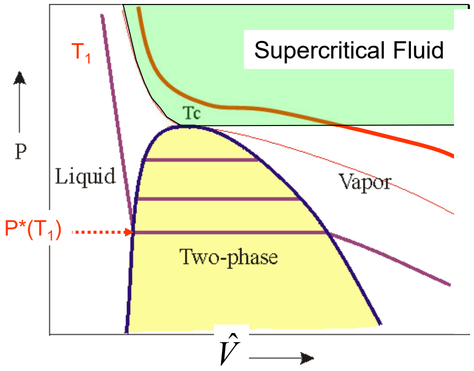
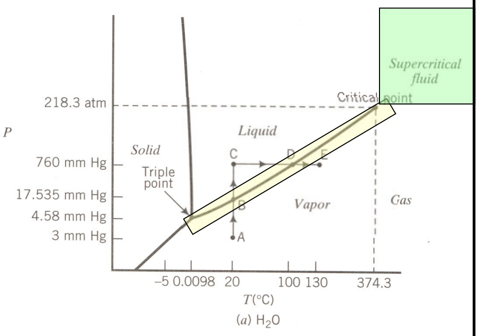


Figure 5.4-2 Generalized compressibility chart, low pressures. (From D. M. Himmelblau, *Basic Principles and Calculations in Chemical Engineering*, 3rd Edition, copyright © 1974, p. 175. Reprinted by permission of Prentice Hall, Inc., Englewood Cliffs, NJ.)

P vs V and P vs T Phase Diagrams for H_2O





Note big changes in density ($1/\hat{V}$) in 2-phase region

P* is a function of T

Consider a pure water system (i.e., no air present)

- What is P^*_{H2O} at 100°C and P_{tot} = 1 atm?

  P^*_{H2O} = 1 atm, and since $P_{tot} = P^*_{H2O}$, 2-phase

- What is P^*_{H2O} at 100°C and P_{tot} = 10 atm?

  P^*_{H2O} = 1 atm, and since $P_{tot} > P^*_{H2O}$, 1-phase, liquid

- What is P^*_{H2O} at 100°C and P_{tot} = 0.01 atm?

  P^*_{H2O} = 1 atm, and since $P_{tot} < P^*_{H2O}$, 1-phase, gas

Vapor pressure depends on T, not P_{tot}!

Relationship to ΔH_{vap}

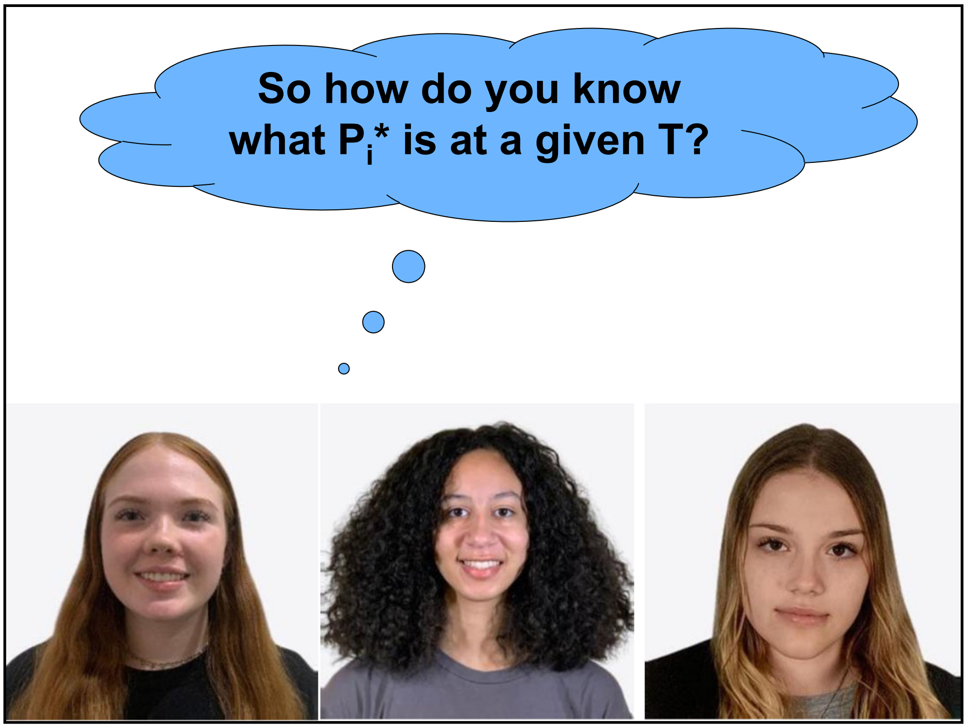
- From thermodynamics:

$$\frac{dP^*}{dT} = \frac{\Delta H_{vap}}{T\left(\hat{V}_{gas} - \hat{V}_{liq}\right)}$$

- Assuming $\hat{V}_{liq}$ is negligible and that ΔH_{vap} is constant with T, and ideal gas,

$$\ln P^* = \frac{-\Delta H_{vap}}{RT} + B$$

- This is the Clausius-Clapeyron equation



So how do you know what P_i^* is at a given T?

Vapor Pressure Chart

(which compounds have highest vapor pressure?)

- Figure 6.1-4

Vapor Pressures of Water

- Table B.3 in Textbook
  - – P^*_{ice} from T = -14.0 to 0.0°C
  - – P^*_{water} from T = 0.0°C to 101.9°C

Antoine Equation

- Table B.4

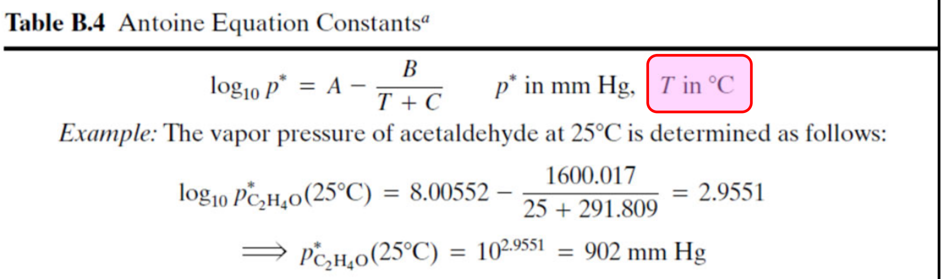


Table B.4 Antoine Equation Constants[a]

$$\log_{10} p^* = A - \frac{B}{T + C} \qquad p^* \text{ in mm Hg}, \quad T \text{ in } ^\circ\text{C}$$

Example: The vapor pressure of acetaldehyde at 25°C is determined as follows:

$$\log_{10} p^*_{C_2H_4O}(25^\circ\text{C}) = 8.00552 - \frac{1600.017}{25 + 291.809} = 2.9551$$

$$\Longrightarrow p^*_{C_2H_4O}(25^\circ\text{C}) = 10^{2.9551} = 902 \text{ mm Hg}$$

DIPPR Database

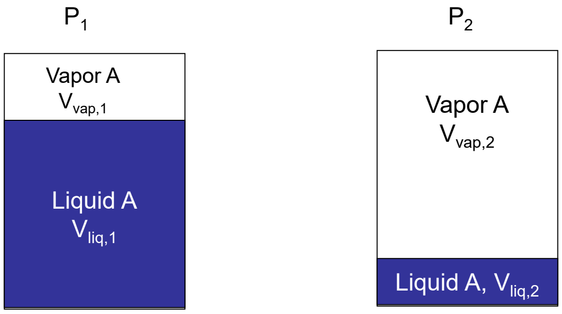
$$\ln P^* = A + \frac{B}{T} + C \ln T + DT^E$$

Access the DIPPR database by:

1. Being on a campus server or college/university VPN
2. Navigating to https://dippr.aiche.org/ or dippr.byu.edu
3. Clicking the button “Log in to DIPPR® Website”

P_i^* is NOT dependent on volume!

Example: pure component A, both at same T



$$P_1 = P_2 = P_A^*$$

What about moles in liquid vs vapor?
$n_{vap,1} = P_1 V_{vap,1}/(RT)$
$n_{liq,1} = \rho_{liq} V_{liq,1}/MW_A$

For pure single species!

Therefore the gas-phase mole fraction in each vessel is the same, but the number of moles is proportional to volume

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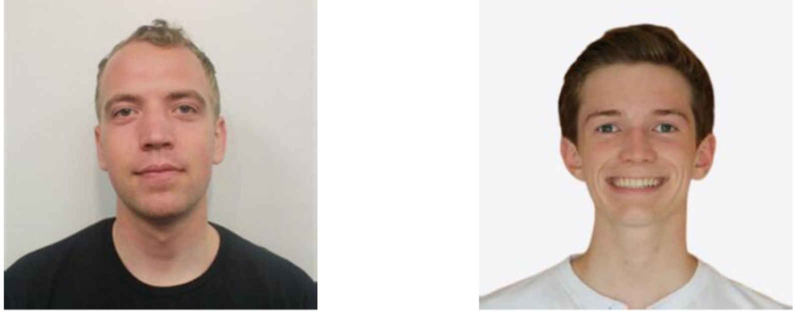
What about mixtures?



Liquid Mixtures: Raoult's Law

(simplified)

- Multiple species in liquid and gas phases

Memorize! $P_i = y_iP_{tot} = x_i\, P_i^*$

  - x_i is mole fraction in liquid phase
  - P_i is the partial pressure ($= y_iP_{tot}$)
  - y_i is mole fraction in gas phase

Yikes! Another definition for x_i

Special cases:

- 1 species with both liquid and vapor present

$$P_{tot} = P_i^*$$

  - Because $x_i = 1$ and $y_i = 1$ (i = 1 in both phases)
- 1 species in liquid, 2 or more species in gas phase

$$y_i\, P_{tot} = P_i = P_i^*$$

  - Because $x_i = 1$ but not y_i (i = 1 in liq and 2+ in gas)
- 2 or more species in liquid… coming up later

Gibb's Phase Rule

$$DF = 2 + c - \Pi$$

- DF - Degrees of freedom for phase rule
- c – # of components (i.e., species)
- Π - # of phases ("Pi" starts with a "p")

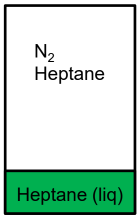
- Single species, 2 phases
  - DF = 2 + 1 – 2 = 1 (need to specify T or P)
- 2 species, 2 phases
  - DF = 2 + 2 – 2 = 2 (need to specify both T and P)

This is different than the degrees of freedom in material balances

Example

1 liquid species, 2 gas species

Goal: Find the equilibrium mole fraction of *n*-heptane in the gas phase



Gibbs Phase Rule
DF = 2 + 2 species – 2 phases = 2
(must specify T & P)

P_{tot} = 1 atm
T = 25°C
Find: $y_{heptane}$ in gas phase

Procedure:
Find $P^*_{heptane}$ at 25°C
$y_{heptane} P_{tot} = x_{heptane} P^*_{heptane}$
but $x_{heptane} = 1.0$, so
$y_{heptane} = P^*_{heptane}/P_{tot}$

Look up Antoine eq constants
$P^* = 10^{\left(A-\frac{B}{T+C}\right)} = 10^{\left(6.87689-\frac{1238.122}{25+216.823}\right)}$
P^* = 45.68 mm Hg

$y_{heptane} = P^*_{heptane}/P_{tot}$ = 45.68 mm Hg/760 mm Hg = 0.0601

Homework

- **16.1** – T, P*, and V given
  - P_{tot} (easy!)
  - Wanted m_{tot}
    - calculate m_{liq} from density and volume
    - calculate m_{vapor} from ideal gas law & MW
- **16.2** – from manometer, get P* vs T
  - Check with Clausius Clapeyron eqn.
- **16.3** – (a) Gibbs phase rule; (b) find P*
  - Please use both Antoine and DIPPR to find P*
  - $y_i = P_i^*/P_{tot}$
- **16.4 –** Explain vapor pressure to a non-engineer