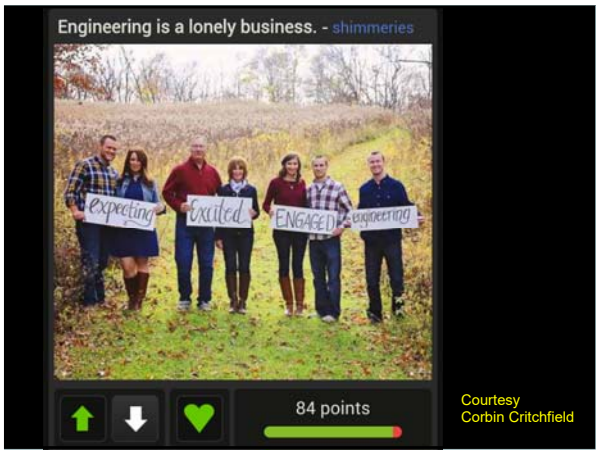



## Business

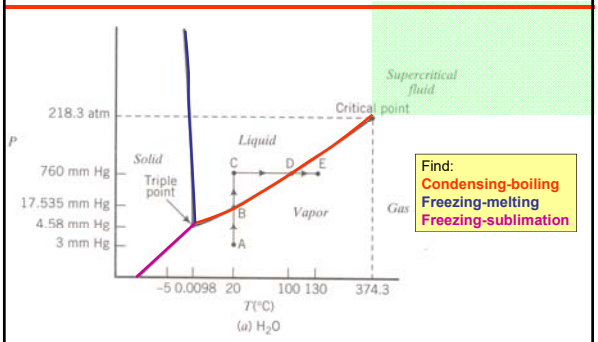
- **LYNN ORR**
  - Izatt-Christensen Lecturer
  - Former Assistant Secretary of Energy
  - Public lecture Thursday 11 am, JSB Auditorium
  - Technical lecture, Friday, 11 am, Varsity Theater

## Business

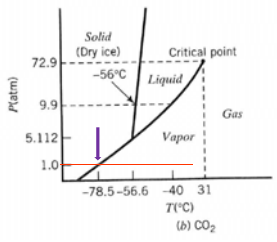
- **This is class 18 of 36 before the case study!**

## Multiphase Systems
## Ch. 6

## P vs T Diagram: Water
(pure component)

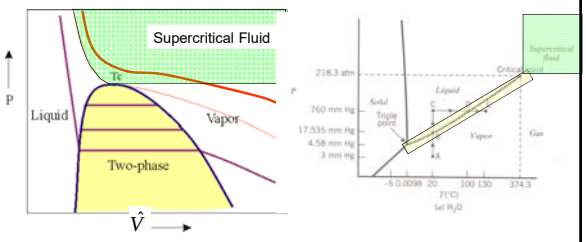



## P vs T Diagram: $CO_2$




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

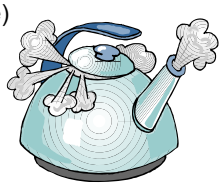
- Boiling point
  - Temperature at which liquid changes to vapor
  - Is a function of P
- Normal boiling point
  - Boiling point at 1 atm
- Freezing point
  - Temperature at which liquid changes to solid
  - Is a function of P
- Sublimation point (you get the idea!)

## Vapor Pressure

- 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 pure 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)



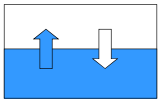
## Class Answers

- 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



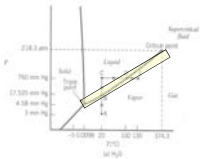
## Properties of Vapor Pressure

- $P_i^*$ 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.)

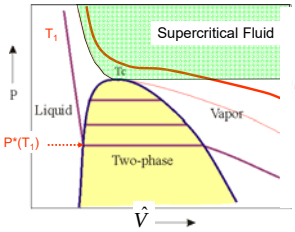
## For A Pure Component

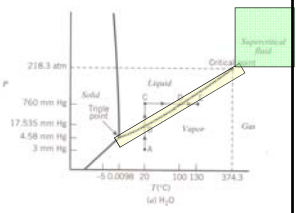
- If $P_{tot} < P^*$
  - All vapor (i.e., gas)
- If $P_{tot} > P^*$
  - All liquid
- If $P_{tot} = P^*$
  - 2-phase (vapor and liquid)

(more complicated with multiple species)



## 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

- 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

## Relationship to $\Delta H_{vap}$

- From thermodynamics:

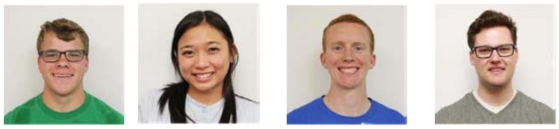
$$\frac{dP^*}{dT} = \frac{\Delta H_{vap}}{T\left(\hat{V}_{gas} - \hat{V}_{liq}\right)}$$

- Assuming $\hat{V}_{liq}$ is negligible and that $\Delta H_{vap}$ 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]

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

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

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

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

## DIPPR Database

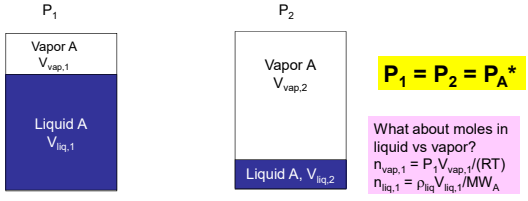
$$\ln P^* = A + \frac{B}{T} + C \ln T + DT^E$$

- Search DIPPR BYU
  http://dippr.byu.edu
- Use the "public" access
- This only works on Caedm computers
  - Log into citrix or set up a VPN into the BYU secure system if you are at home

Login details

## $P_i^*$ is NOT dependent on volume!

- Example: pure component A



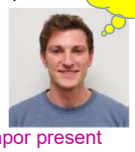

$P_1 = P_2 = P_A^*$

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!**


# Liquid Mixtures: Raoult's Law
## (simplified)

Yikes! Another definition for $x_i$



- Multiple species in liquid and gas phases

Memorize! $P_i = y_i P_{tot} = x_i P_i^*$

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

**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)

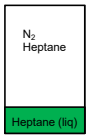
# Gibb's Phase Rule

**DF = 2 + c - Π**

- 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




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
$y_{heptane} P_{tot} = x_{heptane} P^*_{heptane}$
$y_{heptane} = P^*_{heptane}/P_{tot}$

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

- **6.2** – 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
- **6.5 (6.6 3rd Ed.)** – from manometer, get P* vs T
  - Check with Clausius Clapeyron eqn.
- **6.8 (6.9 3rd Ed.)** – (a) Gibbs phase rule; (b) find P*
  - Please use both Antoine and DIPPR to find P*
  - $y_i = P_i^*/P_{tot}$
- **Special Problem 6** (see handout)