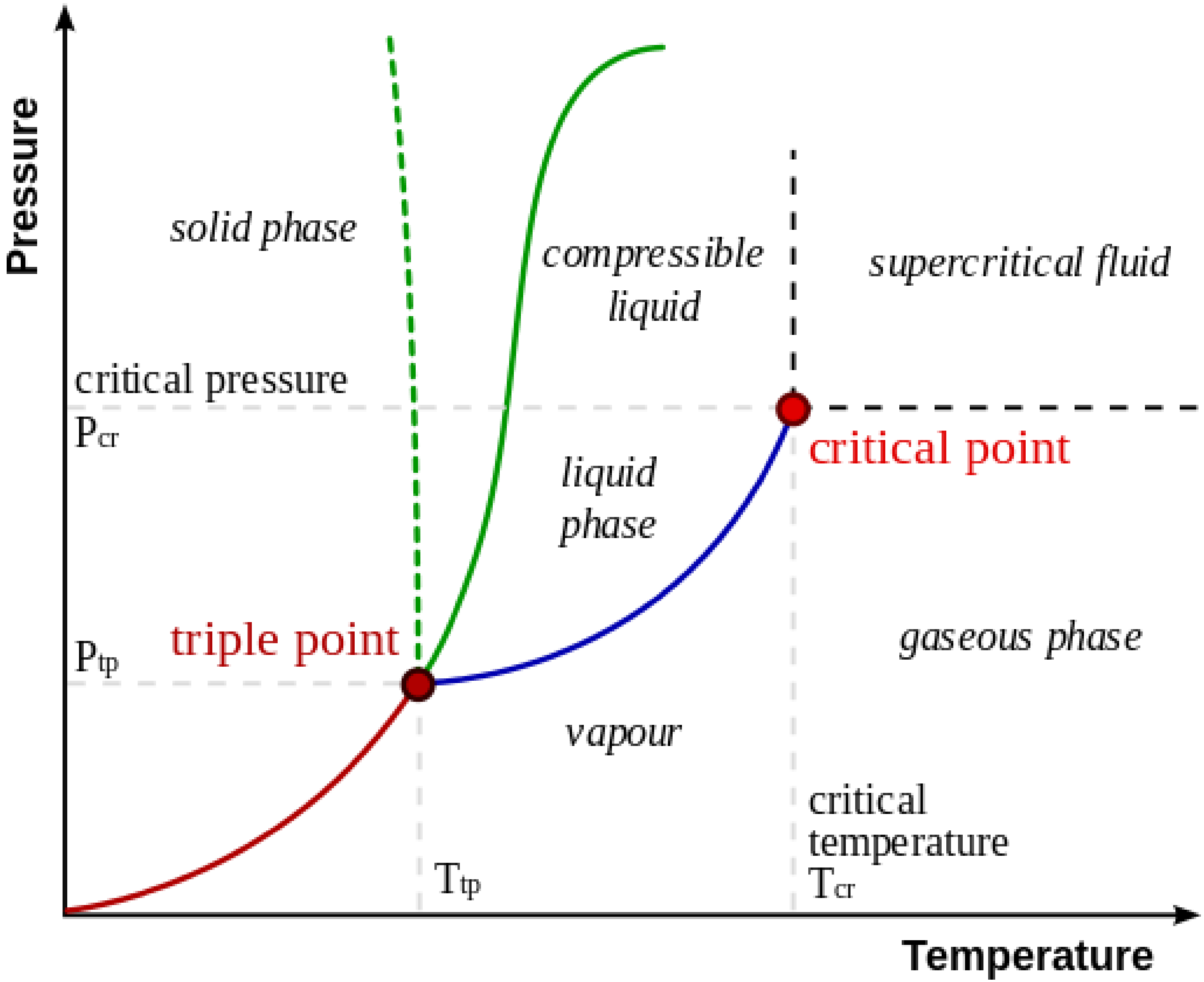
ABE 201
Biological Thermodynamics 1

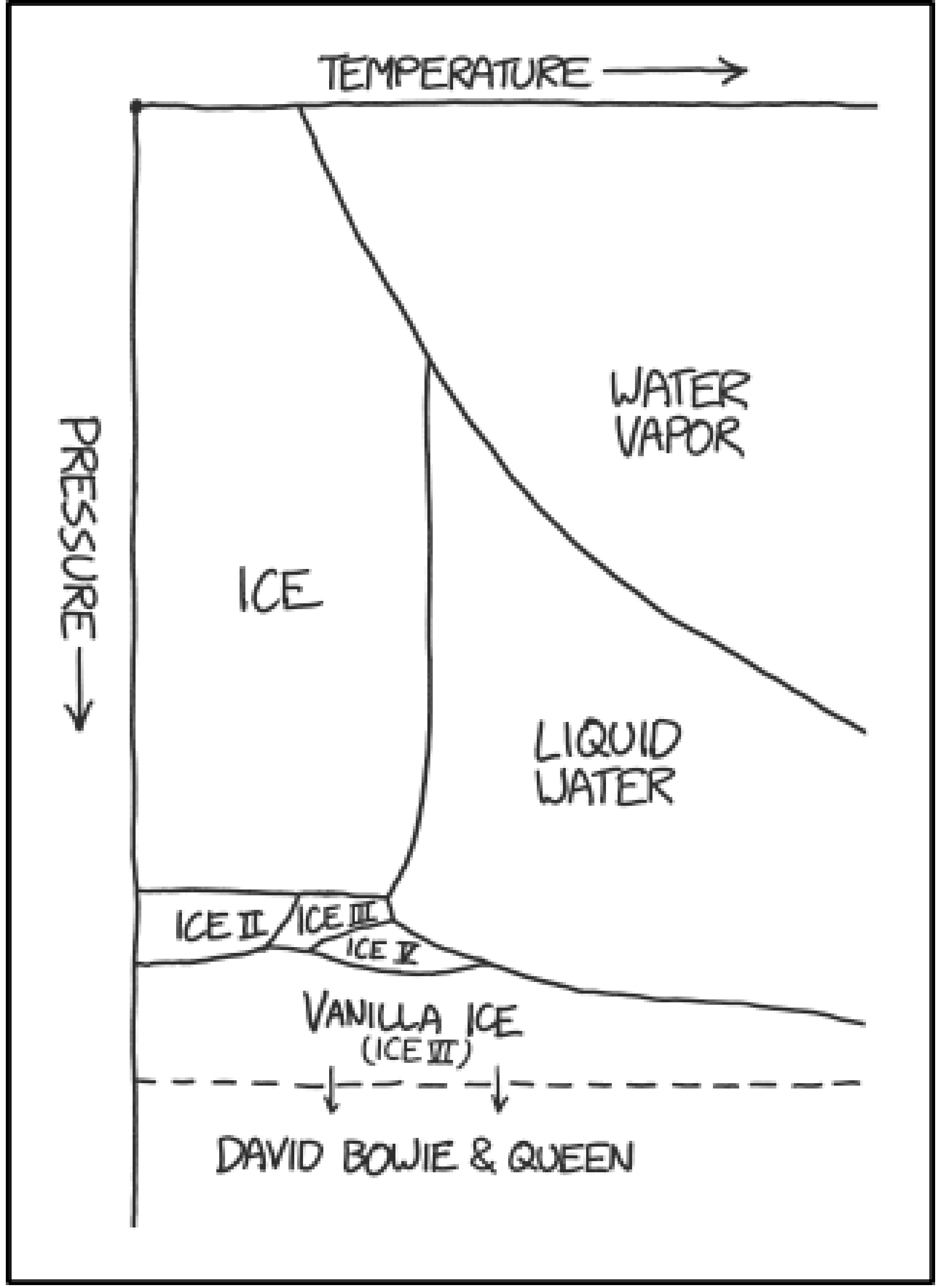
Module 8:

Phase Equilibria

Summary

- A state property describes the equilibrium state of a system.
- State properties do not depend on the path by which the system arrived at its present state.
- Phase (ϕ) is a state property that can be related to other state properties (m, T, P, V, n, etc.).
- Phase property relationships are usually based on thermodynamic equilibrium.
- Vapor/liquid systems in real application are often <u>not</u> at equilibrium, but equilibrium relationships are useful for predicting behavior.


Pressure
solid phase
compressible liquid
supercritical fluid
critical pressure
P_{cr}
critical point
liquid phase
triple point
P_{tp}
gaseous phase
vapour
critical temperature
T_{cr}
T_{tp}
Temperature



https://xkcd.com/1561/

Methods for Finding Phase Information

- Tables
  - Tabulated forms of <u>experimental</u> data for a given substance or mixture.
  - Based on <u>measurement</u> of <u>real</u> materials

- Models (state equations)
  - Statistical/Curve fits (e.g. Antoine equation)
  - Theoretical /based on first principles (e.g. Redlich-Kwong equation)
  - Hybrid (e.g. Clausius-Clapeyron equation)

Example

What is the vapor pressure of water at 50.5 C?

- Interpolate from Table B.3

- Use Clausius-Clapeyron equation

- Use Antoine equation

Table B.3 – 50.5 C = 92.51 mm Hg, 51 C = 97.20 mm Hg

Interpolate $\frac{(51 - 50.5)}{(97.20 - p)} = \frac{(50.5 - 50)}{(p - 92.51)}$

p = 94.86 mm Hg

Clausius-Clapeyron equation

ln(p*) = - ΔHv / R * (1/T) + B

Slope = m = - ΔHv / R = ln (p2/p1)/[(1/T2) – (1-T1)] = ln (97.20/92.51)/[(1/(273+51)) – (1/(273+50))] = -5175.46

B = ln p1 + [ΔHv / R]/T1 = ln(92.51) + 5175.46/(273+50) = 20.55

ln p = ΔHv / RT + B = (-5175.46)/(273+50.5) + 20.55 = 4.55

p = 94.79 mm Hg

Antoine equation

A=8.10765 B=1750.286 C=235.000

log p = A – B/(T+C) = 8.10765 – 1750.286/(50.5) = 1.977

p = 94.85 mm Hg

Raoult's Law

- Vapor is in equilibrium with liquid
- Partial pressures can be calculated using Raoult's Law

$$p_i = x_i p_i^*(T) = y_i = p_i /P$$

- Need Antoine Equation or other way to find relationships for $p_i^*(T)$

Example:

- Air is saturated with pure water at 45^{o}C and 1.5 atm. Estimate the gas-phase composition (mole fraction) of the water using Raoult's law.

$p^*(25C) = 71.9mm\ Hg * (1\ atm / 760\ mm\ Hg) = 0.0946\ atm$
$Xa = 1.000$

$Pa = ya * P = xa * p^*$

$ya = xa * p^* / P = 1 * 0.0946\ atm / 1.5\ atm = 6.3$ mol% H_2O

Relative Humidity

- Defined as partial pressure of water divided by <u>saturation</u> vapor pressure of water at the same temperature * 100%

$$RH\% = \frac{p_{H2O}}{p^{*}_{H2O}} * 100\%$$

RH Example

$$\log_{10}\left(p^*\right) = A - B/(C+T)$$

$$p^* = \text{mm Hg}$$

$$T = {}^0C$$

COMPOUND	RANGE (ºC)	A	B	C
Water	0 to 60	8.10765	1750.286	235.000
Water	60 to 150	7.96681	1668.210	228.000

It is 73F and 56% relative humidity outside

a) What is the partial pressure of water in the air?

b) If the outside air is heated to 120F (pressure is kept constant), what would the relative humidity be?

c) What is the lowest temperature that you could cool the air to without condensing any water vapor?

a)

$$RH\% = \frac{p_{H2O}}{p^{*}_{H2O}} * 100\%$$

$$56\% = \frac{p_{H2O}}{p^{*}_{H2O(73F)}} * 100\%$$

$$p^{*}_{H2O(73F)} = p^{*}_{H2O(23\mathrm{C})} = 21.068 \text{ mm Hg}$$

$$p_{H2O} = 0.56 * p^{*}_{H2O(23\mathrm{C})} = 0.56 * 21.068 \text{ mm Hg}$$

$$= 11.798 \text{ mm Hg}$$

b)

$$RH\% = \frac{p_{H2O}}{p^{*}_{H2O}} * 100\%$$

$$RH\% = \frac{p_{H2O}}{p^{*}_{H2O(120F)}} * 100\%$$

$$p^{*}_{H2O(120F)} = p^{*}_{H2O(48.9C)} = 87.58 \text{ mm Hg}$$

$$RH\% = \frac{p_{H2O}}{p^{*}_{H2O(120F)}} * 100\% = \frac{11.798}{87.58} * 100\%$$

$$= 13.5\%$$

c) $$RH\% = \frac{p_{H2O}}{p^*_{H2O}} * 100\%$$

$$100\% = \frac{p_{H2O}}{p^*_{H2O(XF)}} * 100\%$$

$$p^*_{H2O(XF)} = p_{H2O} = 11.798 \text{ mm Hg}$$

Antoine Equation $$\log(p^*) = A - \frac{B}{T+C}$$

$$\log(11.798) = 8.10765 - \frac{1750.286}{T + 235.000}$$

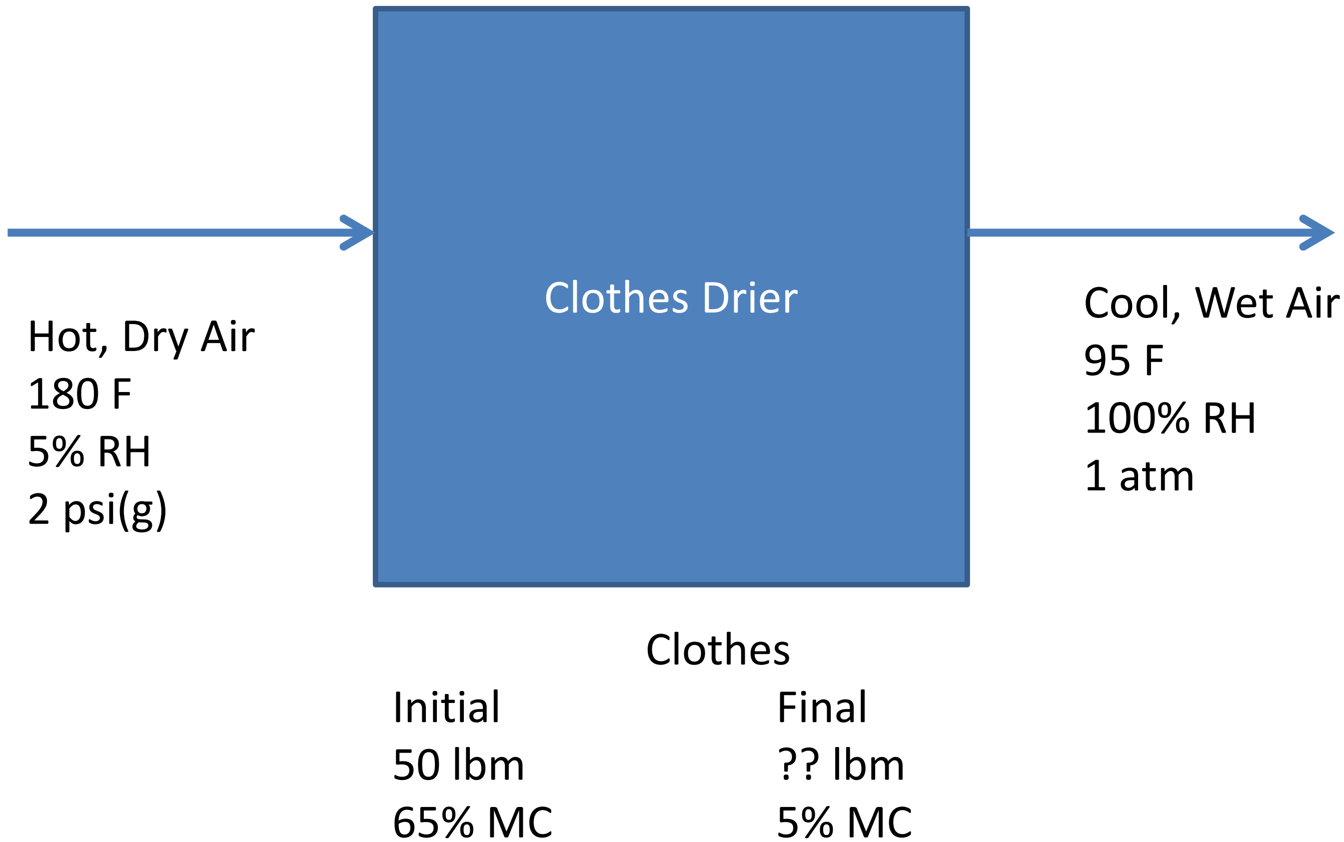
$$T = 13.8C = 56.8F$$

check: Table B.3 $p^*_{H2O(13.8C)} = 11.833$

Clothes Dryer

Hot air (180 F, 5% RH) blows into the dryer at a rate of 200 cubic feet per minute at 2 psig. The air leaves the dryer saturated with water vapor at 95 F and atmospheric pressure.

Assuming that the air inlet and outlet conditions are constant during a drying cycle, how long would it take to dry 50 lbm of wet clothes (65% MC) to 5% MC?



How much water is to be removed?

At what rate is air passing through the system?

At what rate is water leaving the clothes?

How long does it take to dry the clothes?

How much water is to be removed?

50 lbm of wet clothes (65% MC) to 5% MC

Solids: 50 lbm * 0.35 = 17.5 lbm solids (constant!)

Water Initial: 50 lbm * 0.65 = 32.5 lbm water

Water Final: 0.05 = x / (17.5 + x), x = 0.9 lbm water

Water removed = 32.5-0.9 = 31.6 lbm = 14.3 kg

Air in = 200 cu ft/min = 5.66 m^3/min, 180 F = 82.2 C = 355 K

P = 2 psig = 16.7 psia = 115,000 Pa = 863 mm Hg

PV=nRT, n = (115,000Pa)(5.66)/(8.314)/(355K) = 221 mol/min

p*(82.2C) = 388 mm Hg, p_{H2O} = 0.05*388 = 19.4 mm Hg

$y_{H2O,in}$ = 19.4/863 = 0.022, $n_{H2O,in}$ = 221 * 0.022 = 4.9 mol/min

n_{air} = 221 * (1 – 0.022) = 216 mol/min

p*(95F)= p*(35C) = 42.175 mm Hg

$y_{H2O,out}$ = 42.175/760 = 0.055 = $n_{H2O,out}$ /($n_{H2O,out}$ + n_{air})

$n_{H2O,out}$ = 12.6 mol/min

$n_{H2O,removed}$ = ($n_{H2O,out}$ - $n_{H2O,in}$) = 7.7 mol/min , $m_{H2O,removed}$ = 138 g/min

Time to dry = 14,300 g / 138g/min = 104 min = 1 hr 44 min.

Phase Equilibria and Mass Balances

- Don’t forget the fundamentals!
  - Mass is conserved
  - Energy is conserved
  - Momentum is conserved

  Acc = In – Out + Gen - Con

- Relative humidity, gas laws, Antoine Eq., vapor pressure tables, etc. are <u>physical properties</u> that allow you to calculate <u>mass</u> or <u>moles</u> in the system