

Properties of Solutions

Z Ch 17.1-17.4

Almost all the chemical processes which occur in nature, whether in animal or vegetable organisms, or in the nonliving surface of the earth, ... take place between substances in solution." **Friedrich Wilhelm Ostwald, 1890**

(Nobel Prize for Chemistry in 1909 "in recognition of his work on catalysis and for his investigations into the fundamental principles governing chemical equilibria and rates of reaction".)

**Exam II – everything from last exam – Ch 5,
13, 16 (selected sections), 17**

Q6 ave = 6.1

**H_Exp 8 – in-person
lab has lab partners;**

17.1 Solution Composition

17.2 Thermodynamics of Solution Formation (not responsible for)

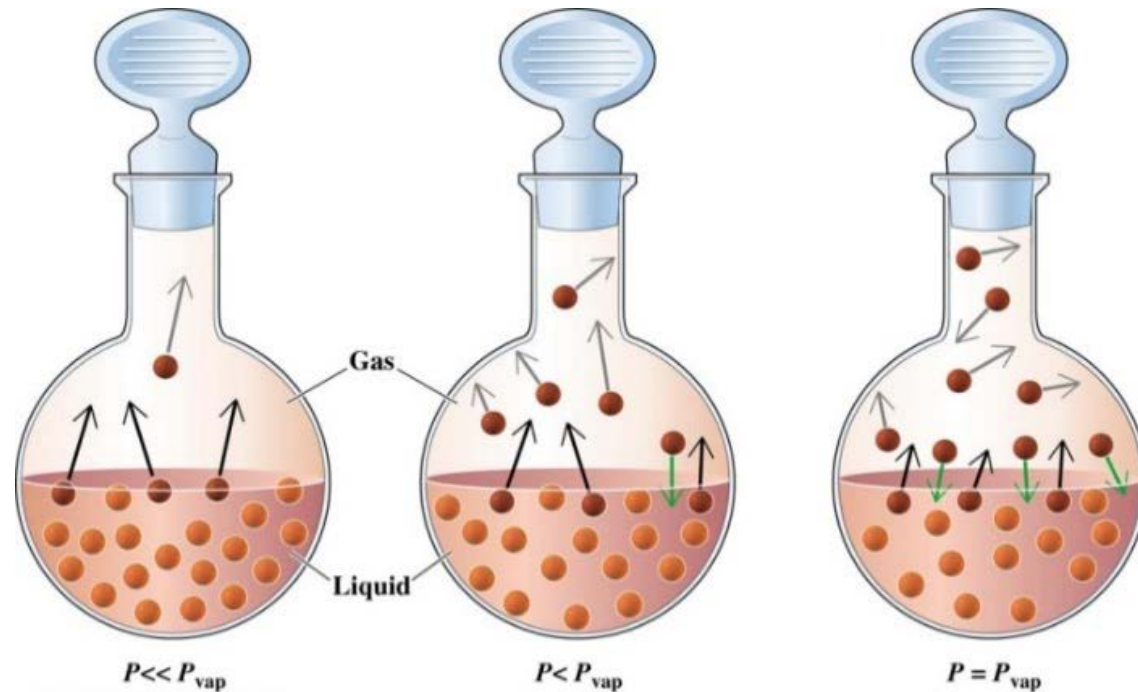
17.3 Factors Affecting Solubility

17.4 Vapor Pressures of Solutions

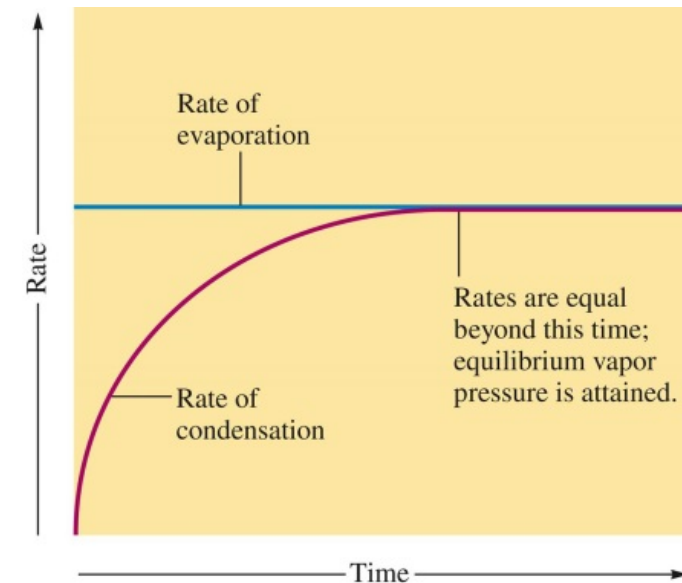
Changes of State and Phase Equilibria

vapor pressure

liquid in equilibrium with its vapor
determined by IMF's
vapor not an ideal gas!
 $P(T)$



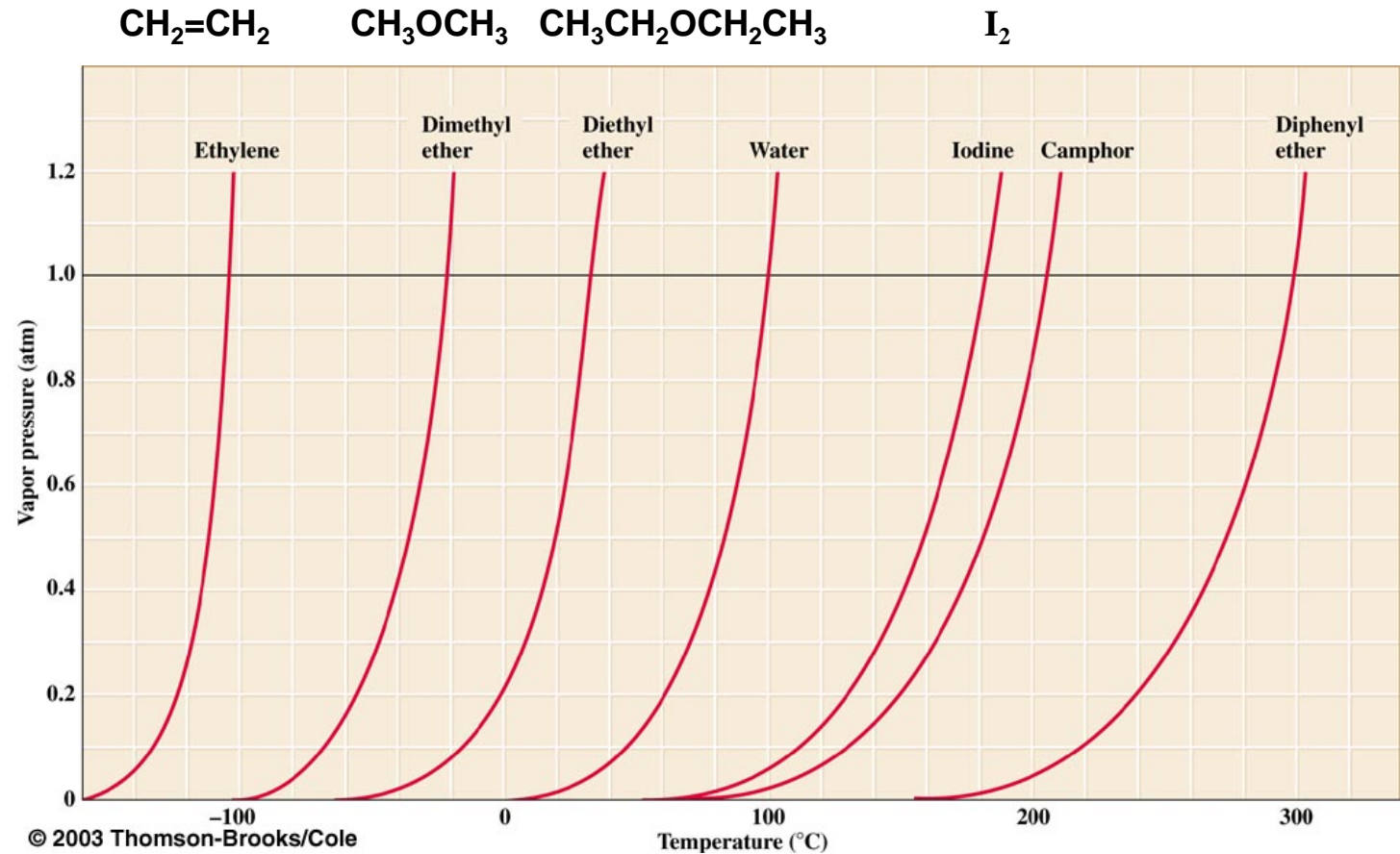
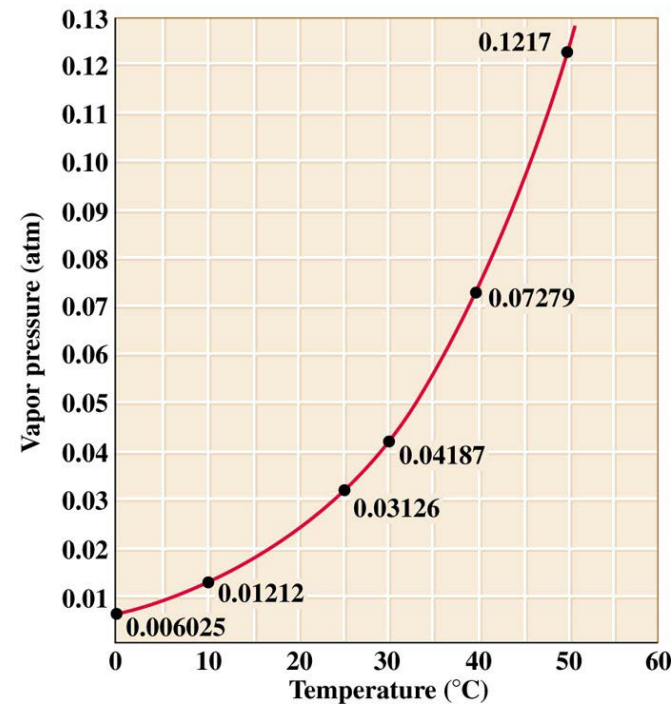
Rates of condensation and evaporation for a liquid sealed in a closed container. Evaporation rate remains constant, condensation rate increases as number of molecules in the vapor phase increases, until the two rates are equal; equilibrium vapor pressure attained.



Vapor Pressure

Vapor pressure is only a function of temperature.

FIG VII – Vapor pressure of water as a function of temperature



Vapor Pressure

A Maxwell Boltzmann distribution also exists for liquids. If the velocities follow a Maxwell Boltzmann distribution then since kinetic energy = $\frac{1}{2} mu^2$, the kinetic energy also does.

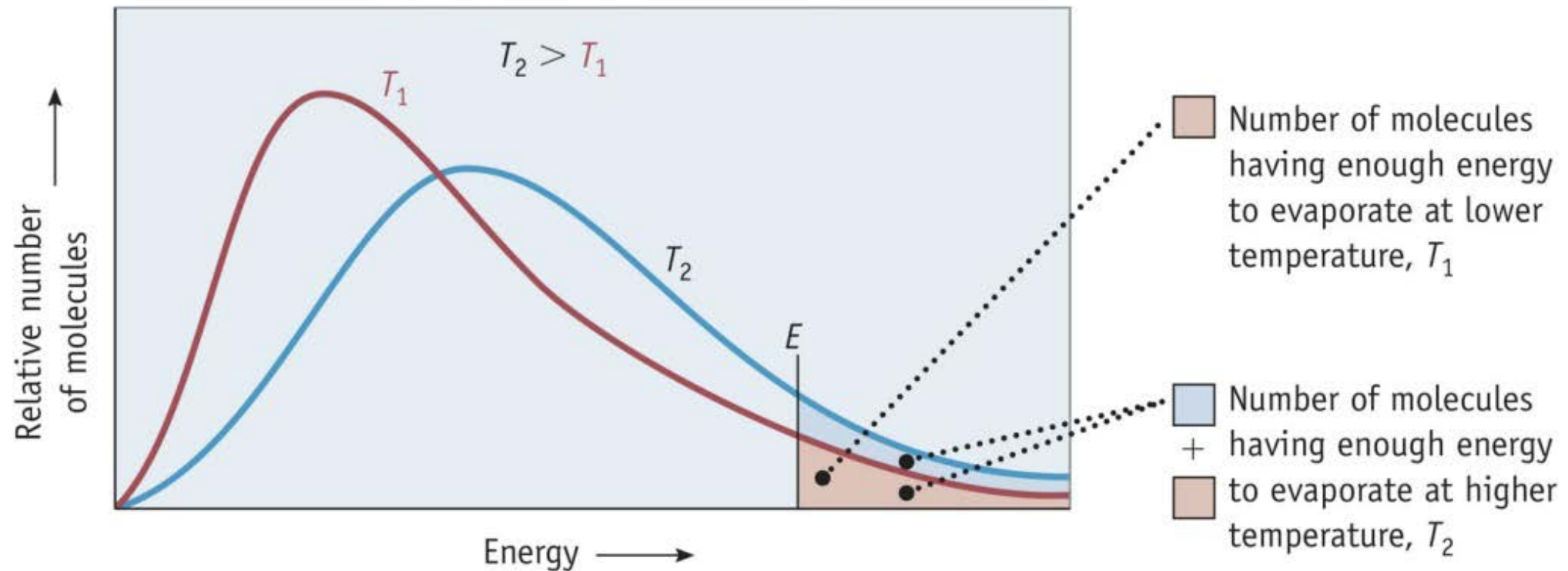


FIG VIII – Distribution of kinetic energies in a liquid

Simple Phase Diagram

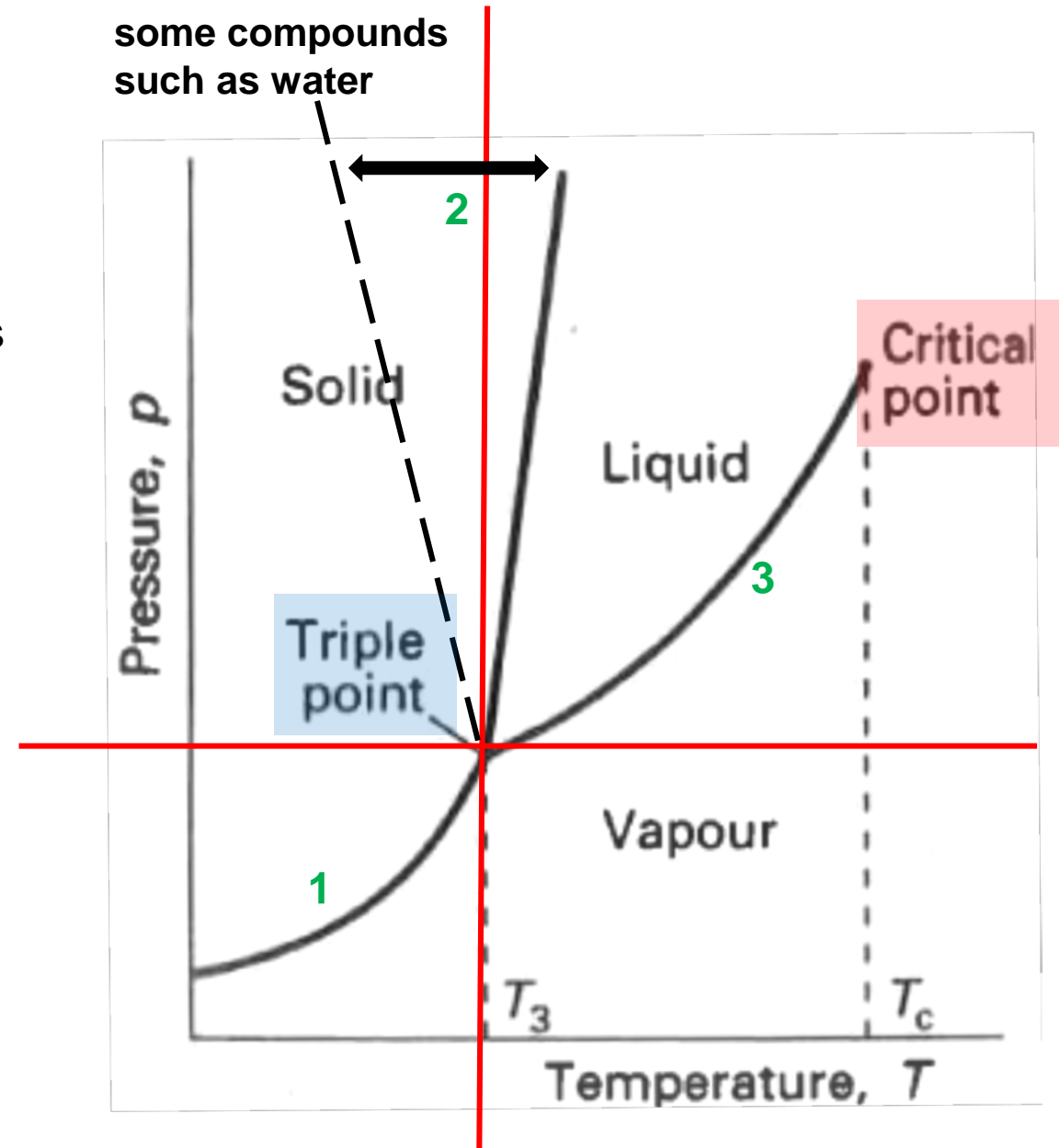
phase diagrams $P(T)$

shows P, T behavior of all solid, liquid, gas phases

- 1) solid \rightleftharpoons gas
- 2) solid \rightleftharpoons liquid
- 3) liquid \rightleftharpoons gas

triple point – single value of P, T where three phases coexist in equilibrium

critical point – value of P, T beyond which a gas cannot be condensed into a liquid



Comparing Phase Diagrams

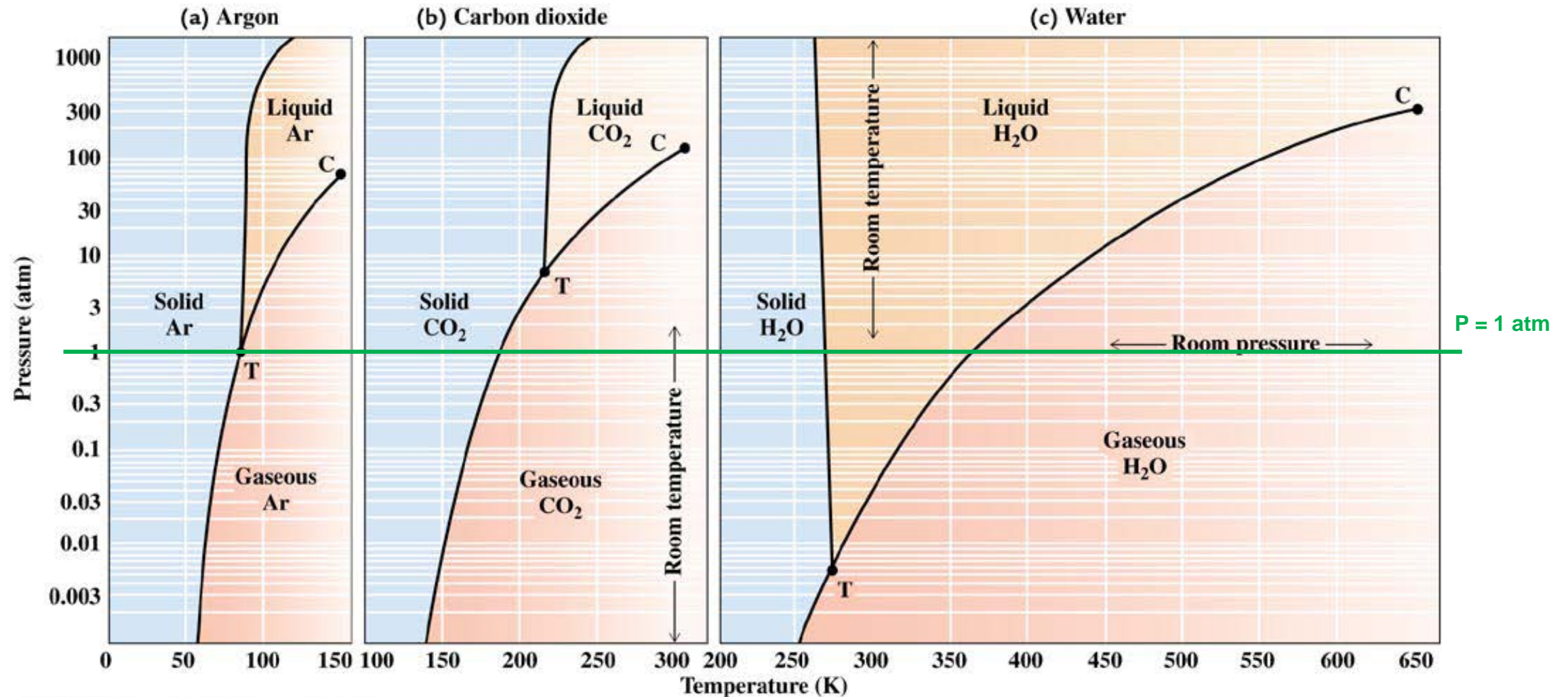
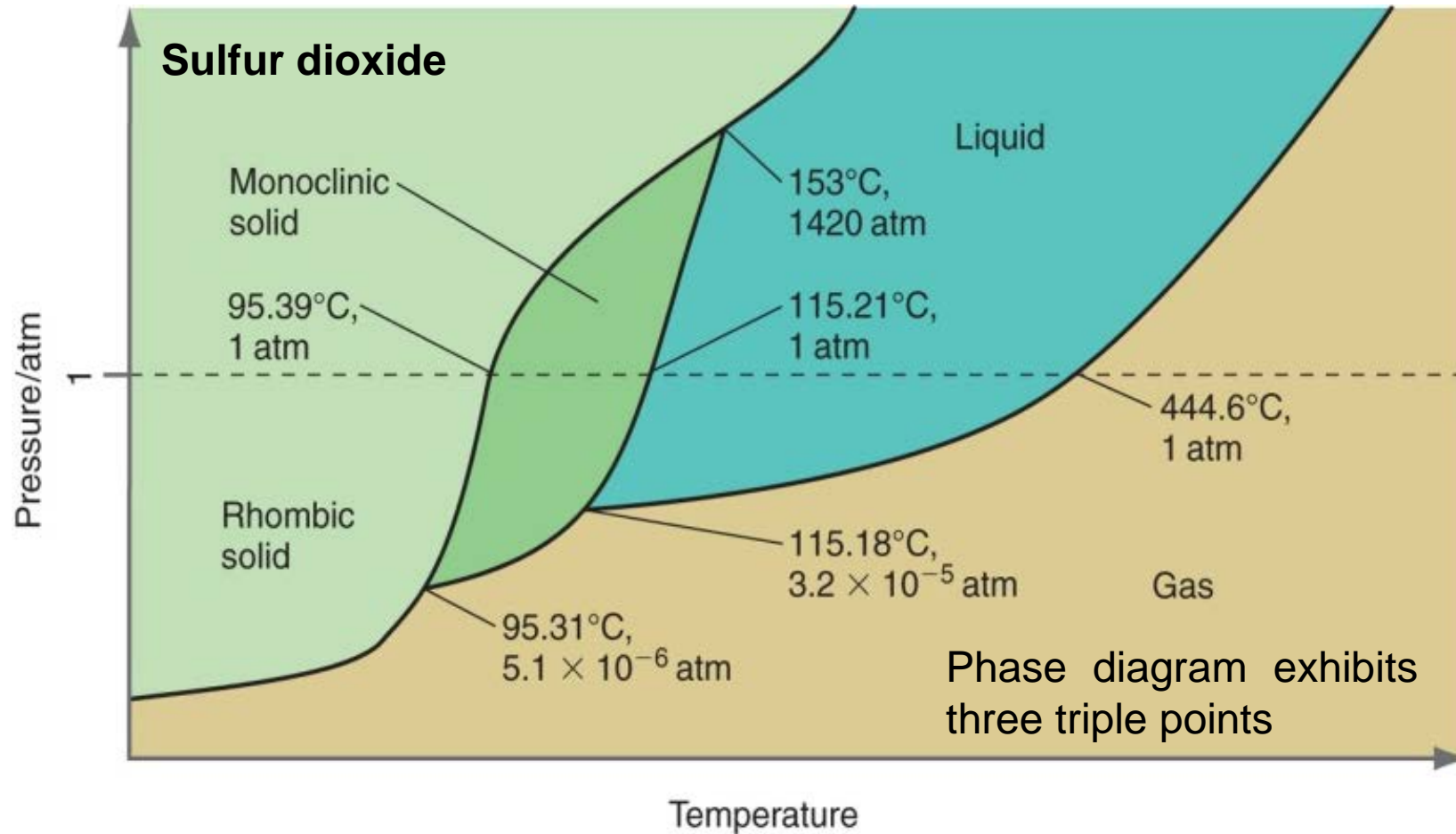
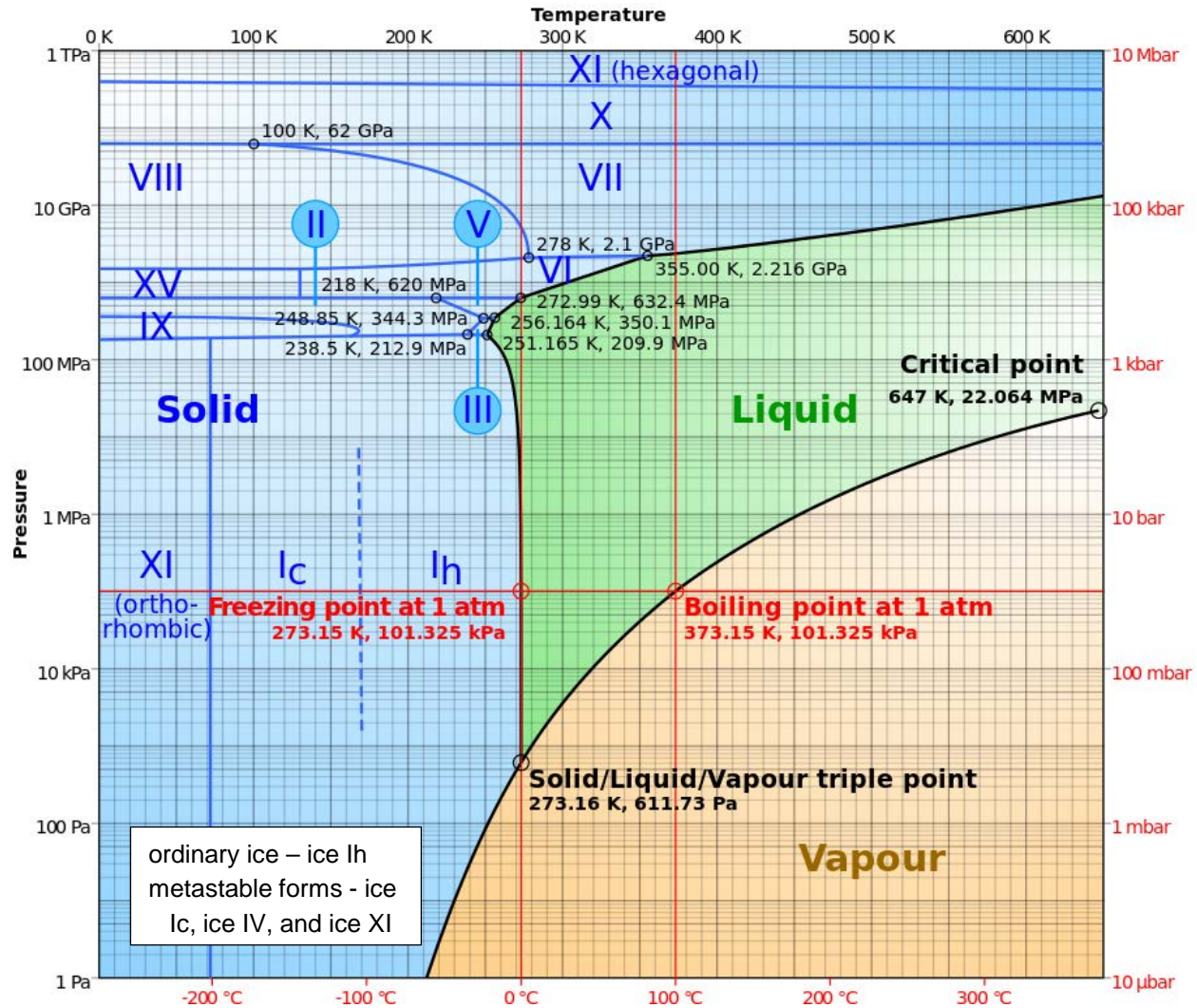


FIG X. Phase diagrams of Ar, CO₂, and water Note: y-axis (pressure) is logarithmic

Comparing Phase Diagrams



Comparing Phase Diagrams



Kurt Vonnegut's novel *Cat's Cradle*, written when only ices I to VIII were known, involves the discovery of ice IX, a form supposed to exist at 1 atm with a mp of 114°F, relative to which liquid water is unstable. Ice IX causes the destruction of life on earth. (Vonnegut's brother Bernard helped develop the method of seeding supercooled clouds with AgI crystals to induce ice formation and increase the probability of snow or rain.)

Critical Points

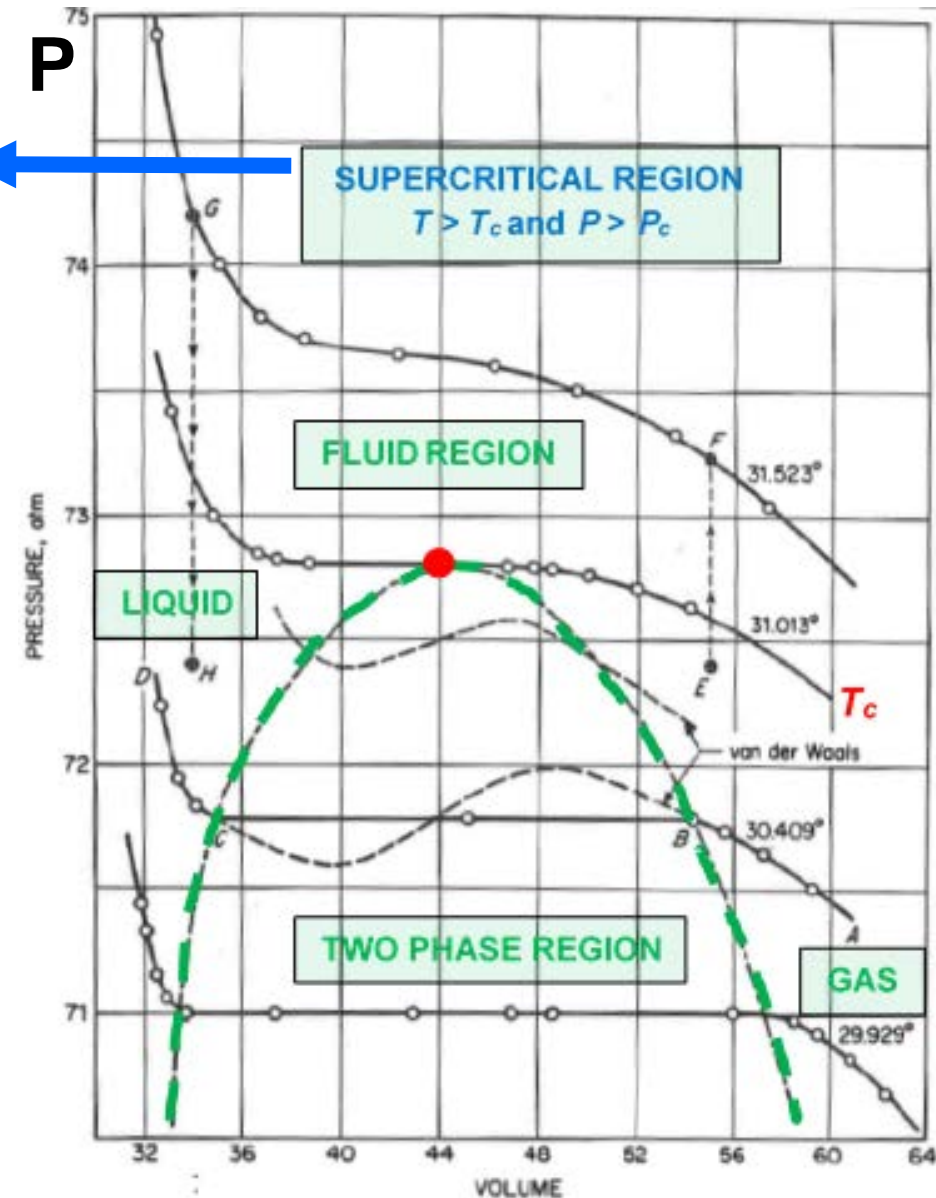
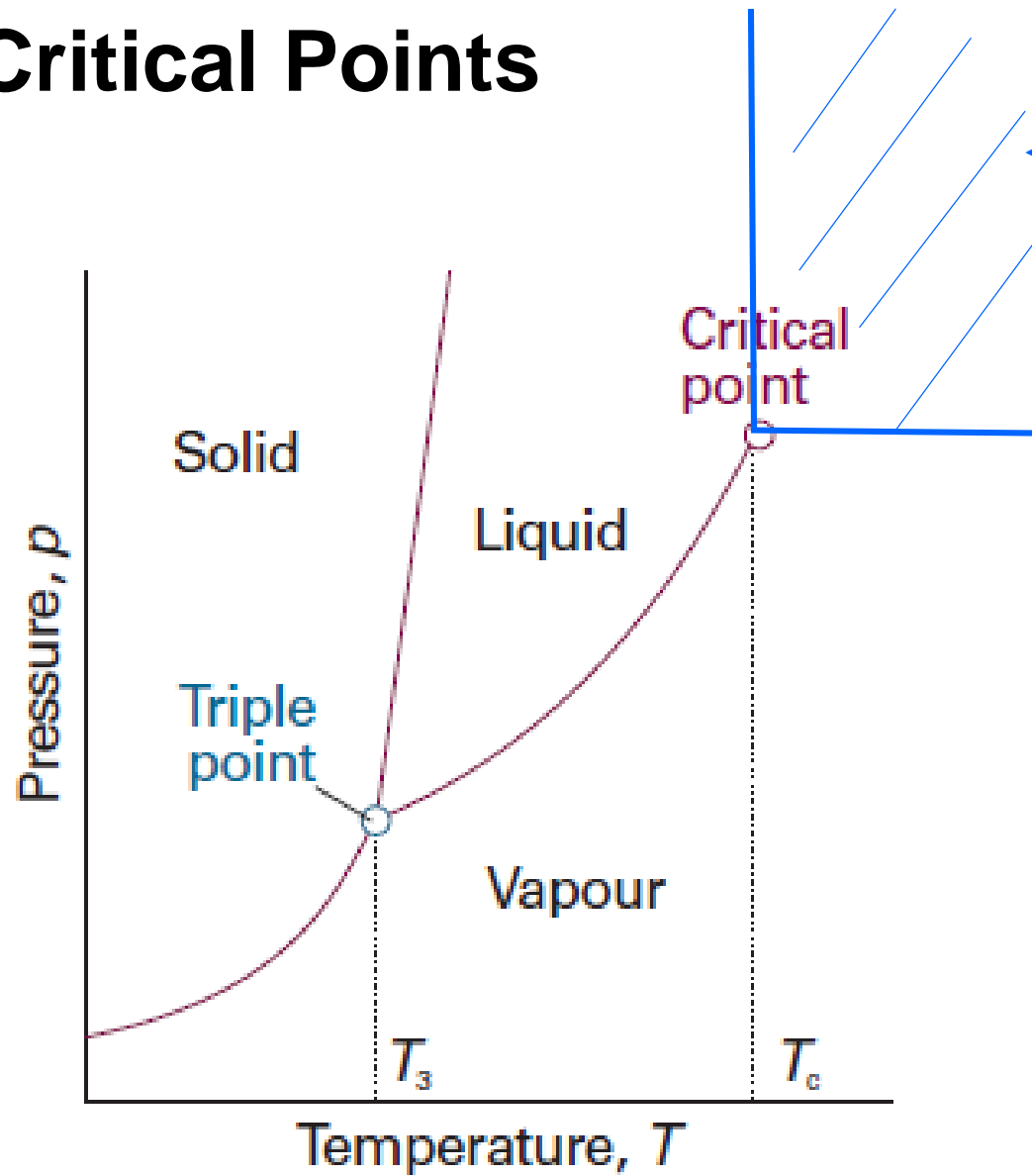


FIG. 1.10 Isotherms of carbon dioxide near the critical point. [Michels, Blaisse, and Michels, *Proc. Roy. Soc. A*, 160, 367 (1937).]

V

Solution Composition

homogeneous mixture of two or more components in a single phase

composition

solute - substance being dissolved, usually minor component

solvent - dissolving medium, generally major component

expressing composition

mass percent – (mass of solute) / (mass of solvent) × 100

molarity, M – (moles of solute) / (1 L of solution)

mole fraction, χ_A – **for two component solution A, B** $\chi_A = n_A / (n_A + n_B)$

molality, m – (moles of solute) / (1 kg of solvent) – independent of temperature, unlike molarity

Solution Composition

EX 1. A solution is prepared from 18.0 g of water ($M = 18.0148$) and 23.0 g of ethanol ($M = 46.0684$).

a) What is the mole fraction of ethanol?

$$\chi_E = n_E / (n_W + n_E) = (23.0 / 46.0684) / (18.0/18.0148 + 23.0/46.0684) = \mathbf{0.333}$$

b) What is the molality of the solution assuming water to be the solvent?

$$m = n_E / (1 \text{ kg water}) = (23.0 / 46.0684) / 18.0 \times 1000 \text{ g} / 1 \text{ L} = \mathbf{27.7 \text{ m}}$$

c) What is the molality of the solution assuming ethanol to be the solvent?

$$m = n_W / (1 \text{ kg ethanol}) = (18.0 / 18.0148) / 23.0 \times 1000 \text{ g} / 1 \text{ L} = \mathbf{43.4 \text{ m}}$$

Molarity and Molality

EX 2. A 5.50 weight percent sulfuric acid ($M = 98.0778$) solution has a density of 1.0352 g cm^{-3} .

a) What is the molarity of the solution?

$$M = n / L = (5.50 \text{ g} / 100 \text{ g sol'n}) (1 \text{ mol} / 98.0778 \text{ g}) (1.0352 \text{ g sol'n} / \text{mL}) \\ \times (1000 \text{ mL} / \text{L}) = \mathbf{0.581 \text{ M}}$$

b) What is the molality of the solution?

$$m = n / \text{kg} = [5.50 \text{ g} / (100 - 5.50 \text{ g water})] (1 \text{ mol} / 98.0778 \text{ g}) (1000 \text{ g} / \text{kg})$$

Colligative Properties

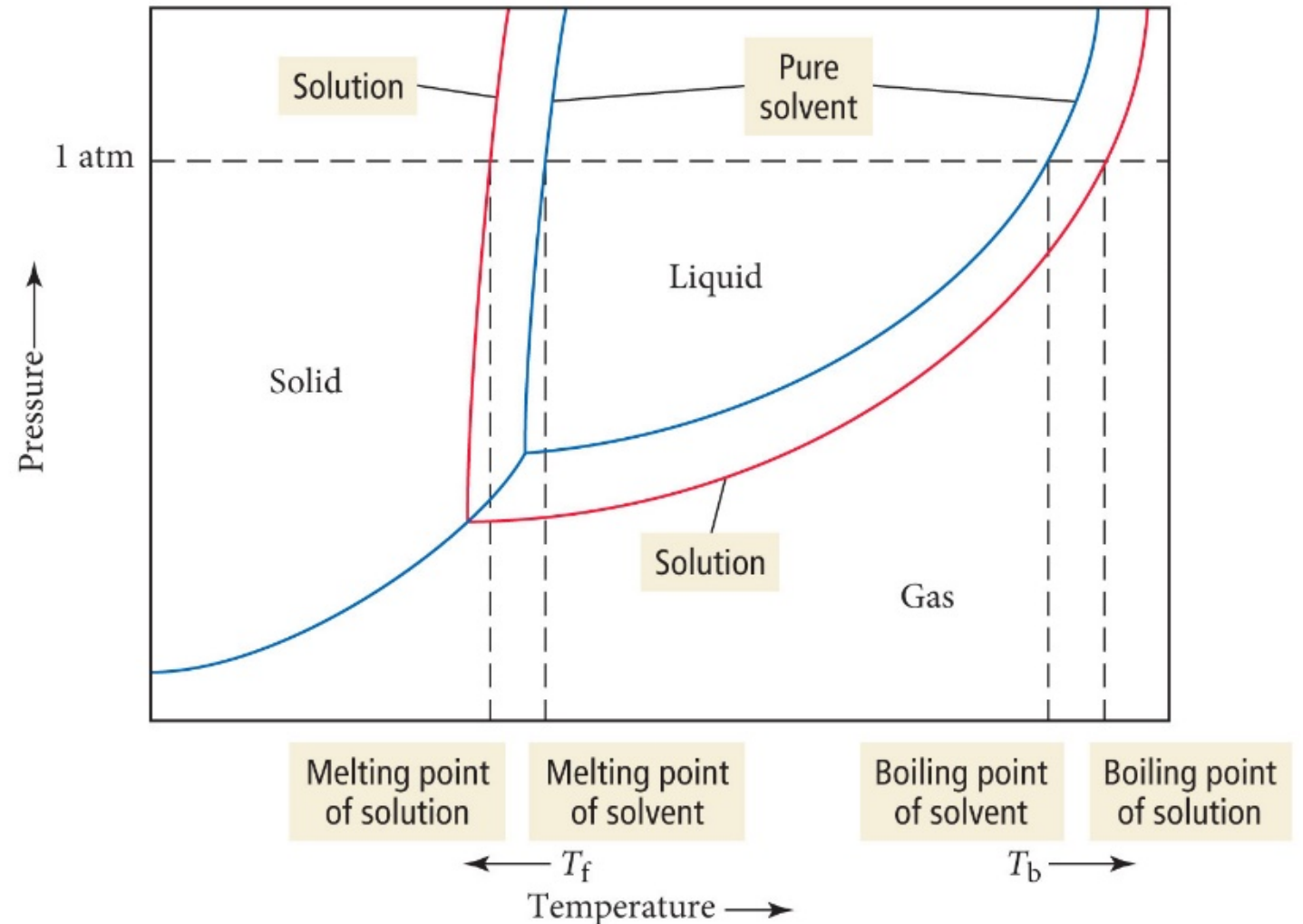
depend on relative number of dissolved solute particles
classification

seen on phase diagram

1. vapor pressure lowering
2. boiling point elevation
3. freezing point depression

not on phase diagram

4. osmosis



Vapor Pressure and Raoult's Law

The vapor pressure of the solvent above a solution containing a nonvolatile solute is proportional to the mole fraction of the solvent present

Raoult's Law: $P_{\text{solvent}} = \chi_{\text{solvent}} P^{\circ}_{\text{solvent}}$ (linear function)

EX 3. The vapor pressure of water at 90°C is 525.8 mm Hg. If a solution of 651 g of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) is dissolved in 1.50 kg of water, what is the solution vapor pressure at 90°C? ($M_{\text{H}_2\text{O}} = 18.02$, $M_{\text{C}_2\text{H}_6\text{O}_2} = 62.07$ g/mol)

$$P_1 = \chi_1 P^{\circ}_1 = (1500/18.002) / (1500/18.02 + 651/62.07) \times 525.8$$

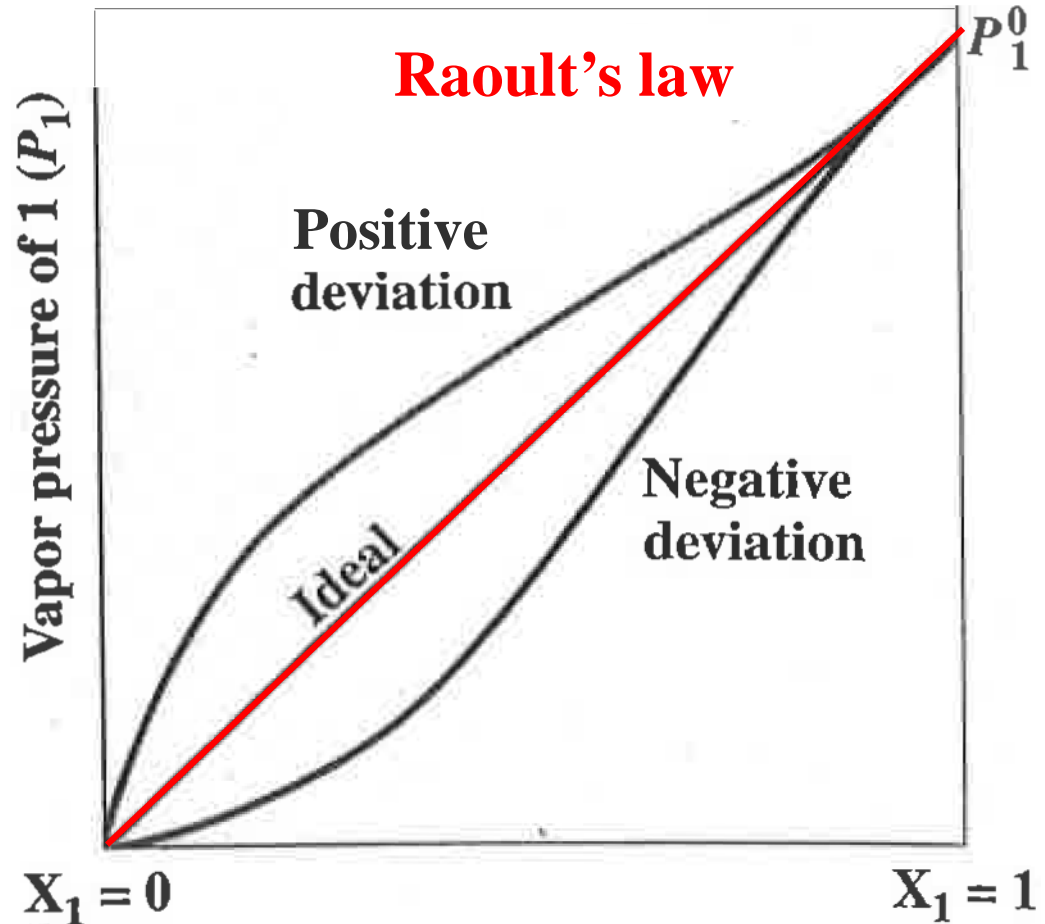
Deviations of Raoult's Law

Nonideal solutions show deviations from Raoult's law

negative deviations – strong solute/solvent interactions

positive deviations – weak solute/solvent interactions (weaker than pure liquids)

$$P_{\text{solvent}} = \chi_{\text{solvent}} P^{\circ}_{\text{solvent}}$$



Raoult's Law for Determining Molar Mass

1 solvent, 2 solute

EX 4. 20.0 g of urea is dissolved in 125 g of water ($M_{\text{H}_2\text{O}} = 18.0148$) at 25°C. The vapor pressure of the solution was observed to be 22.67 mm Hg. The vapor pressure of pure water at 25°C is 23.76 mm Hg. What is the molar mass of urea?

$$M = \text{mass} / n \qquad P_1 = \chi_1 P_1^\circ \Rightarrow \chi_1 = P_1 / P_1^\circ = n_1 / (n_1 + n_2)$$

$$n_1 P_1^\circ = (n_1 + n_2) P_1 \text{ or } n_1 P_1^\circ - n_1 P_1 = n_2 P_1 \Rightarrow$$

$$n_2 = \text{mass} / M = n_1 (P_1^\circ - P_1) / P_1$$

$$M = (\text{mass}) P_1 / [n_1 (P_1^\circ - P_1)]$$

Raoult's Law and a Binary Solution

For an ideal binary solution of A and B the partial pressure of each component above the solution obeys Raoult's law and Dalton's law

$$P_{\text{total}} = P_A + P_B = \chi_A P_A^{\circ} + \chi_B P_B^{\circ}$$

Since both the liquid and gas compositions can be given in terms of mole fractions it is helpful to distinguish between them. The following equations are useful for dealing with binary solutions

$$P_A = \chi_A^L P_A^{\circ} \quad (\chi^{\text{liquid}}) \quad P_A = \chi_A^V P_{\text{tot}} \quad (\chi^{\text{vapor}}) \quad P_{\text{tot}} = P_A + P_B \quad (\text{vapor}) \quad \chi_A + \chi_B = 1$$

(liquid/vapor)

Raoult's Law for a Binary Solution

on Wednesday

EX 5. A mixture of hexane ($P^{\circ}_1 = 0.198$) and heptane ($P^{\circ}_2 = 0.060$) obeys Raoult's law. If the mole fraction of heptane is 0.600, what is the composition of the vapor above the solution?

Strategy:

use Raoult's law to find vapor pressure of each component

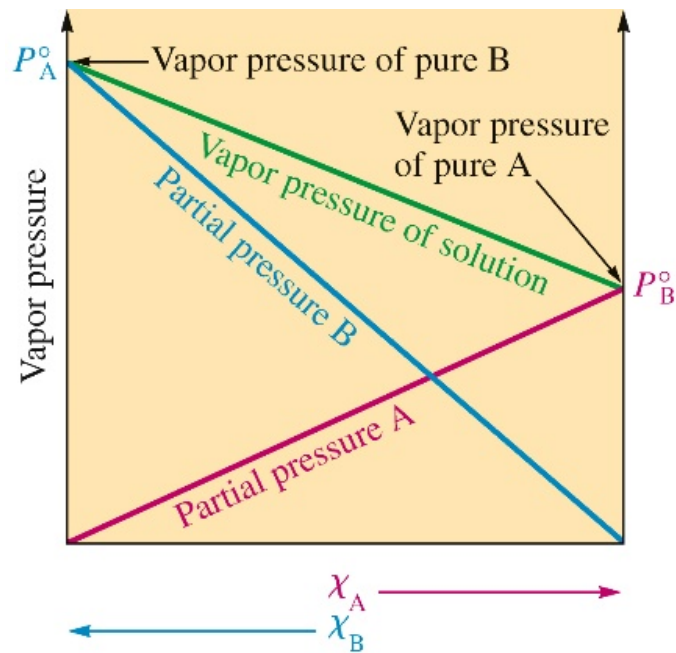
sum to get total vapor pressure

use Dalton's law to get vapor composition

Deviations from Raoult's Law Ideal Behavior

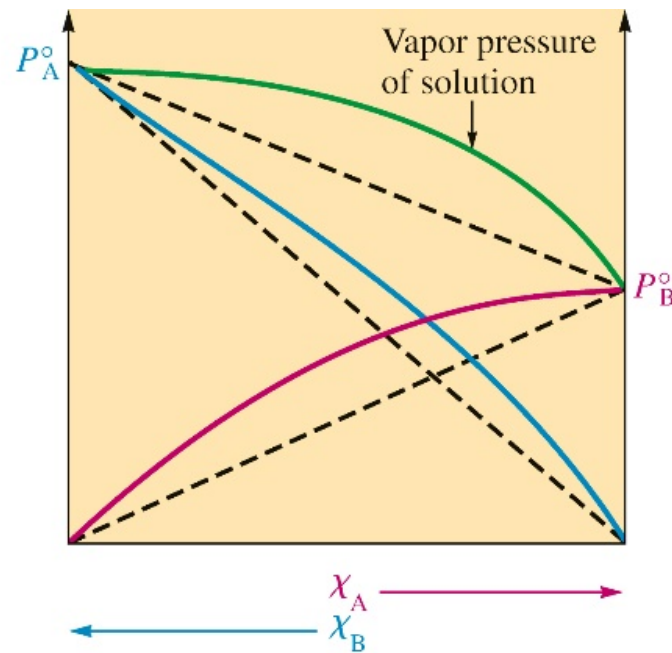
$$P_{\text{total}} = P_A + P_B = \chi_A P_A^\circ + \chi_B P_B^\circ$$

Ideal Solution



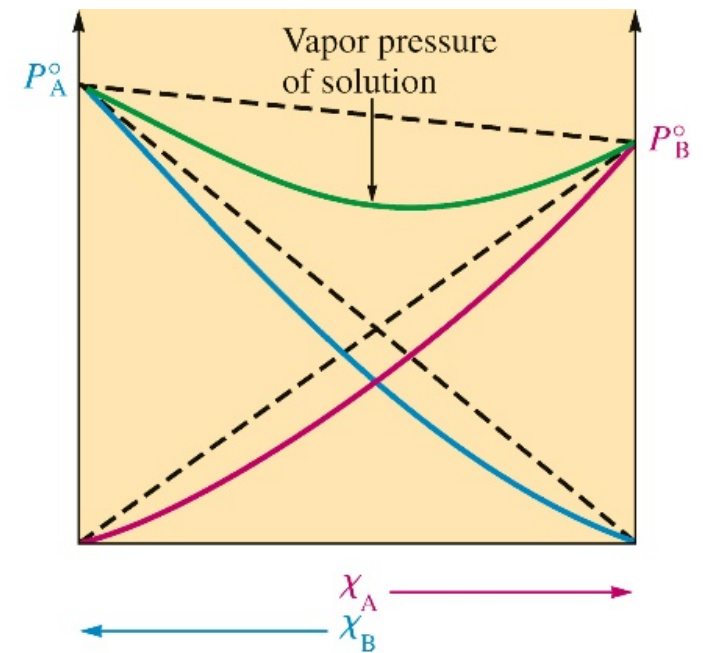
(a)

Weak A/B Interactions
(compared to pure liquids)



(b)

Strong A/B Interactions



(c)

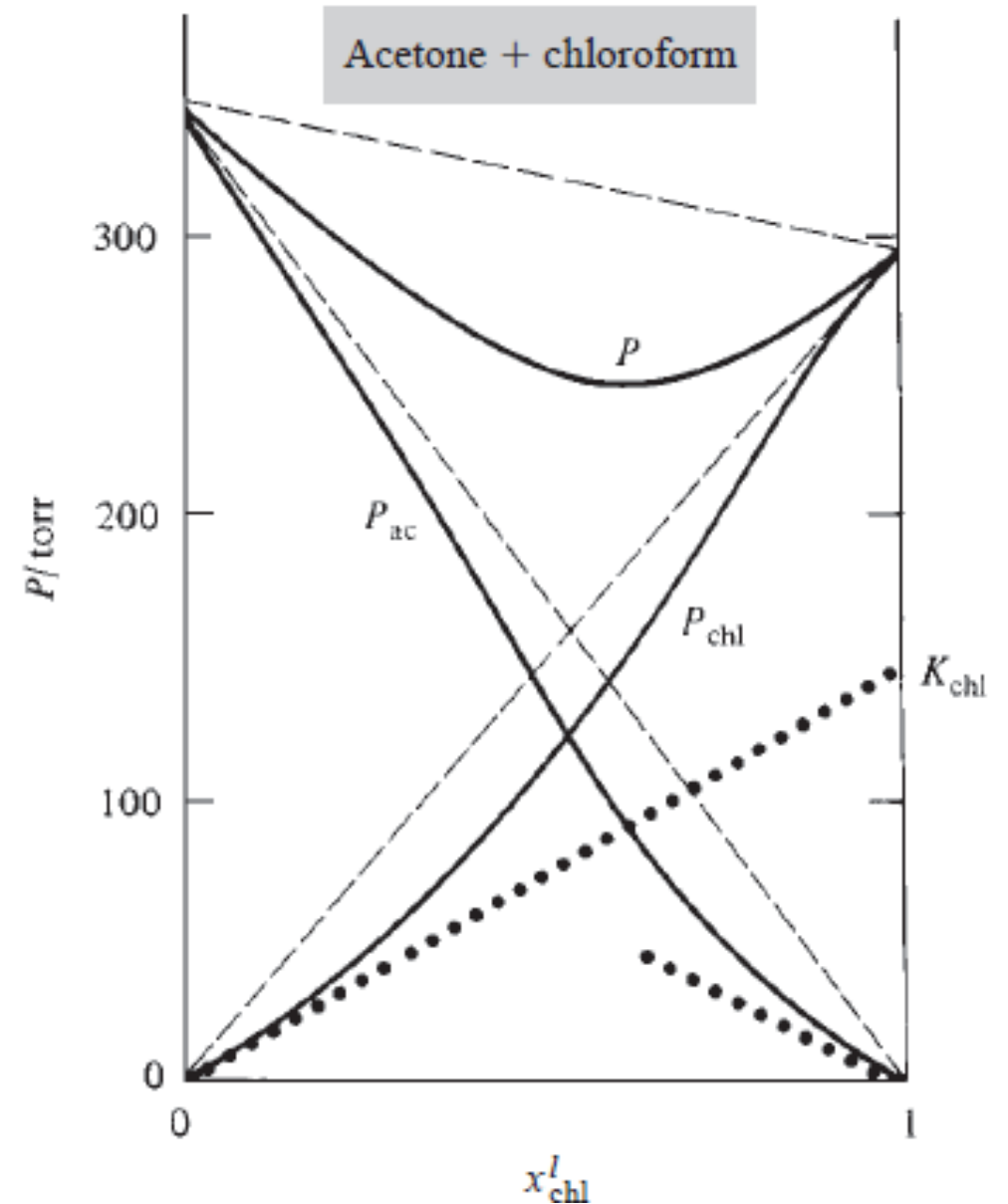
Henry's Law (for Solutes)

It is experimentally found that in the limiting case of a solution very dilute in the solute 2, the partial pressure of 1 in the vapor is directly proportional to the mole fraction of 2 in the liquid.

$$P = \chi_{\text{gas}} k_{\text{H}}$$

where k_{H} is the Henry's law constant for the solution.

Note: this is not Raoult's law behavior where the linear relationship is with the mole fraction of the solvent, 1.



Henry's Law (for Solutes)



Lake Nyos, Cameroon

Table 17.3

The Values of Henry's Law Constants for Several Gases Dissolved in Water at 298 K

Gas	k_H (atm)
CH ₄	4.13×10^2
CO ₂	1.64×10^3
O ₂	4.34×10^4
CO	5.71×10^4
H ₂	7.03×10^4
N ₂	8.57×10^4

