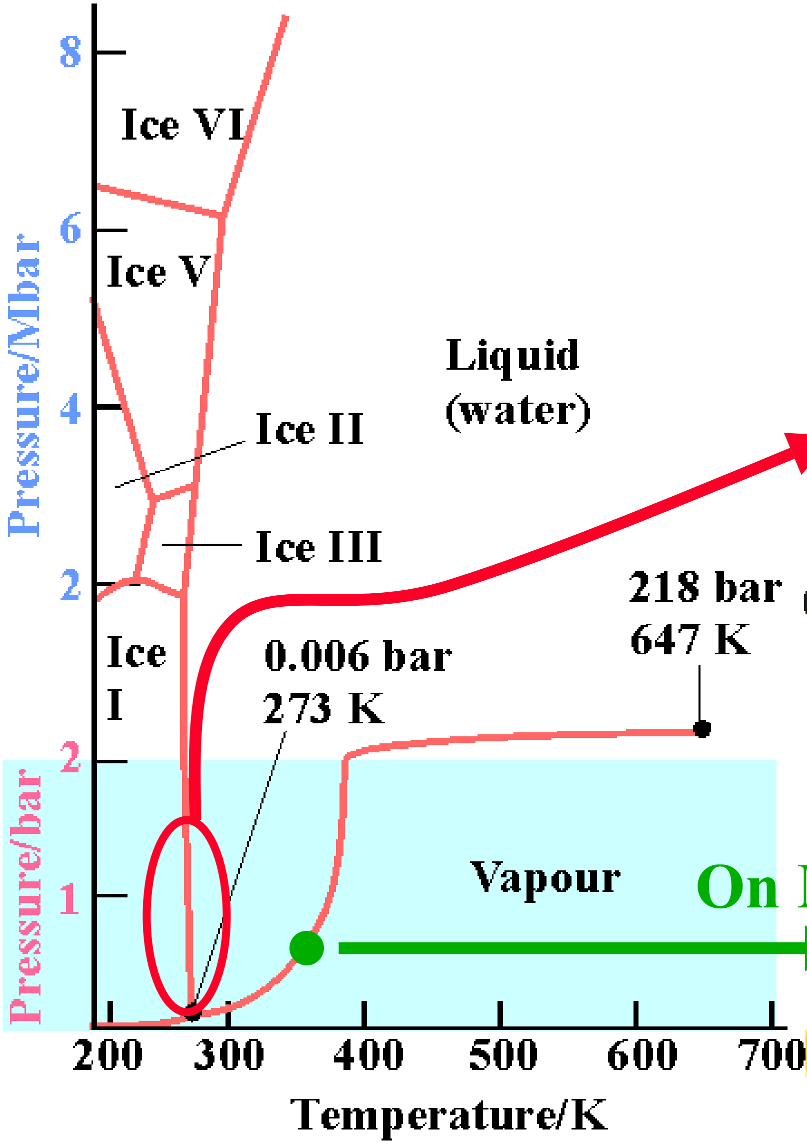
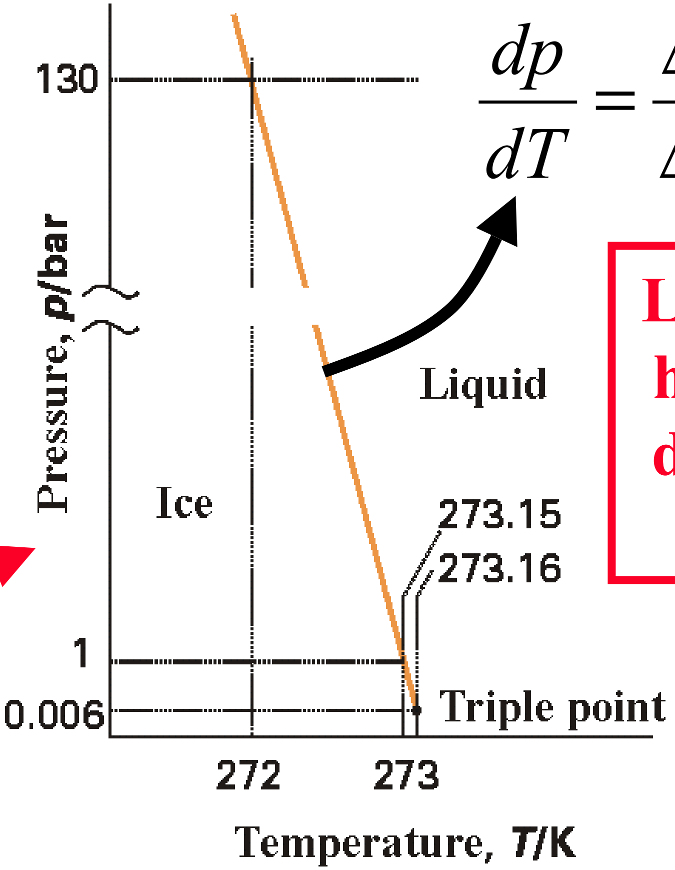
Phase diagrams: Water





$$\frac{dp}{dT} = \frac{\Delta_{trs} S}{\Delta_{trs} V}$$

Liquid water has a higher density than water ice

⇓

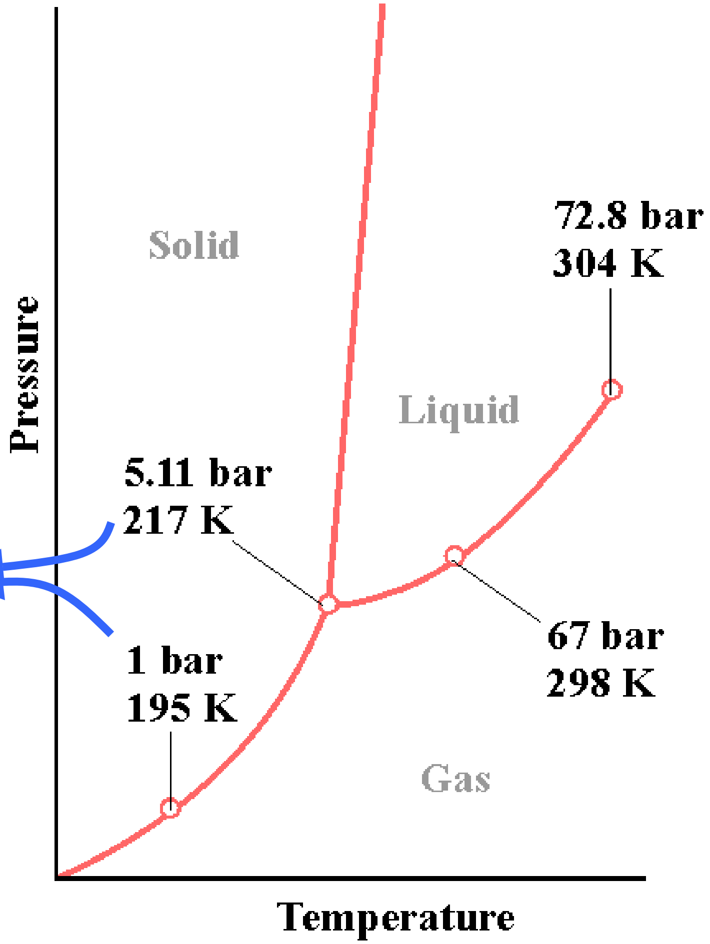
ice skating!

frozen ponds sustain fish!

On Mt. Everest “boiling” eggs becomes easier

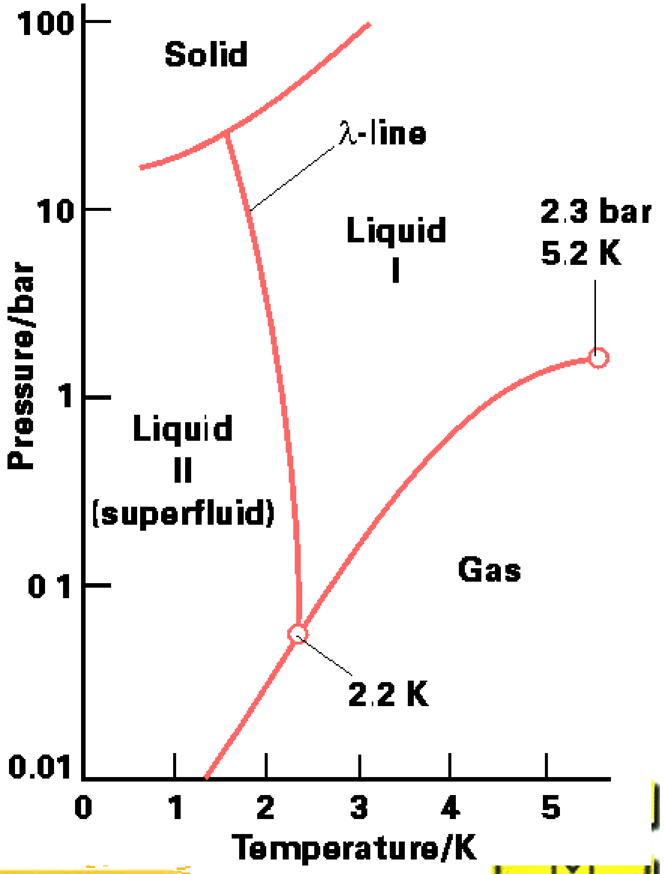
Phase diagrams: CO_2 and Helium

CO_2: quite typical



Sublimes at 1 atm; exists as a liquid only under pressure

He: solid and gas are never in equilibrium; He-II is superfluid



The properties of binary mixtures

Atkins, Chapter 6

Definitions:

solvent: mixture component in excess; solute: other component

molar concentration $$[J] = \frac{\mathit{amount\ of\ solute}}{\mathit{volume\ of\ solution}} = \frac{n_J}{V} (mol\ L^{-1} = M)$$

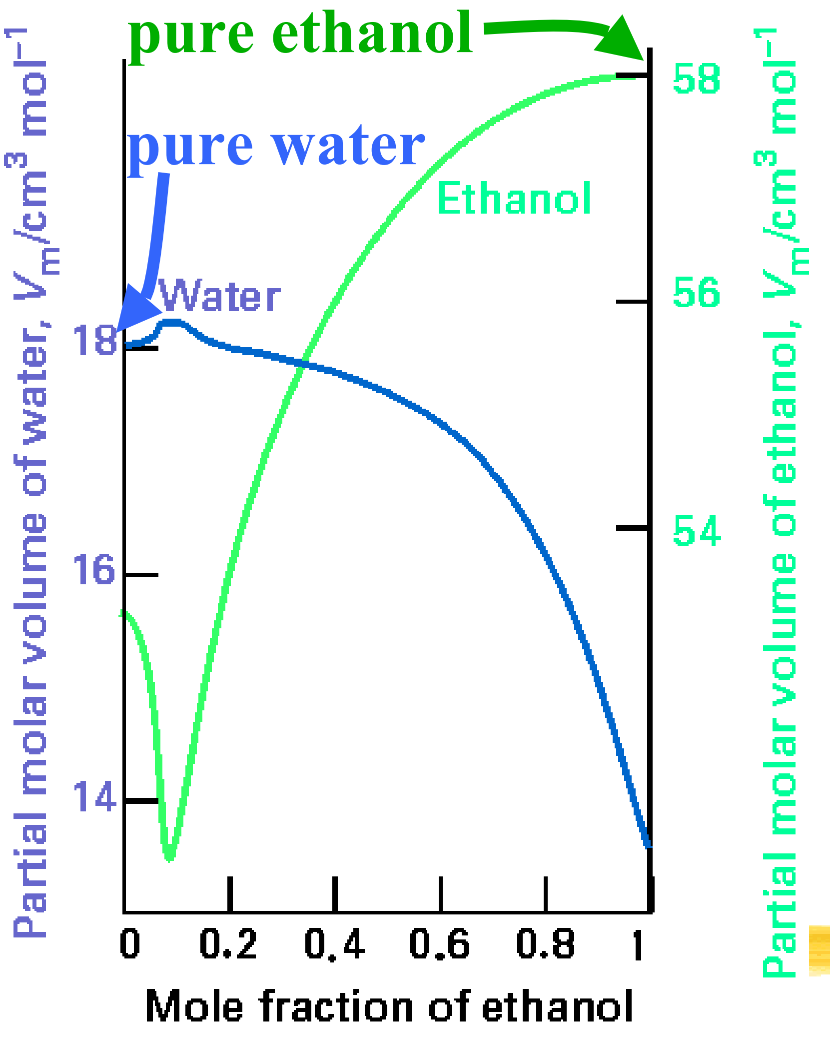
molality $$b_J = \frac{\mathit{amount\ of\ solute}}{\mathit{mass\ of\ solvent}} = \frac{n_J}{m_{solvent}} (mol\ kg^{-1} = m)$$

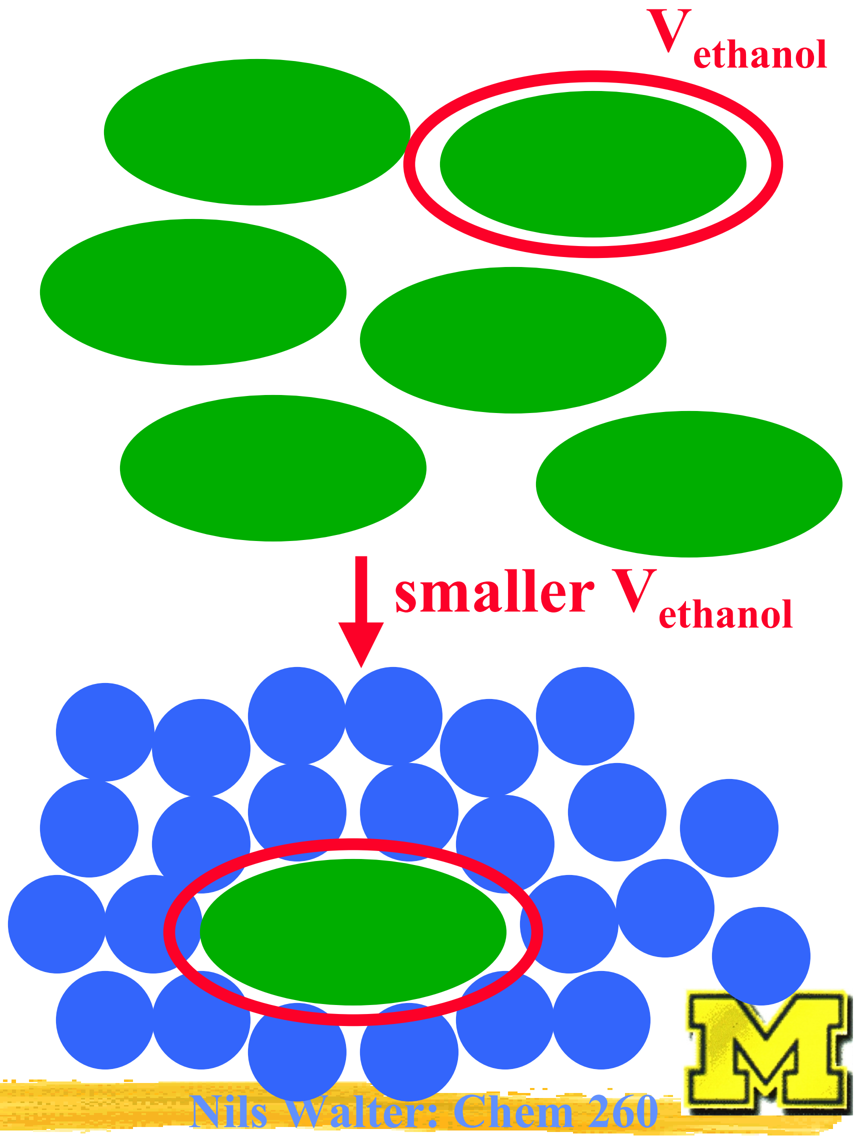
mole fraction $$x_J = \frac{\mathit{amount\ of\ solute}}{\mathit{total\ amount\ of\ molecules}} = \frac{n_J}{n}$$

partial molar volume: volume occupied by a mole of solute or solvent in a mixture

Partial molar volumes: Components in mixtures have altered properties

Total volume: $V = n_A V_A + n_B V_B$





Partial molar Gibbs energies

partial molar Gibbs energy: contribution of substance to the total Gibbs energy of the mixture

$G = n_A G_A + n_B G_B$ → partial molar Gibbs energies also vary with composition!

chemical potentials μ: measure of the ability of a component to bring about physical or chemical change

$\Rightarrow G = n_A \mu_A + n_B \mu_B$

for a perfect gas: $\Delta G_m = G_m(p_f) - G_m(p_i) = \int_{p_i}^{p_f} V_m dp = RT \ln \frac{p_f}{p_i}$

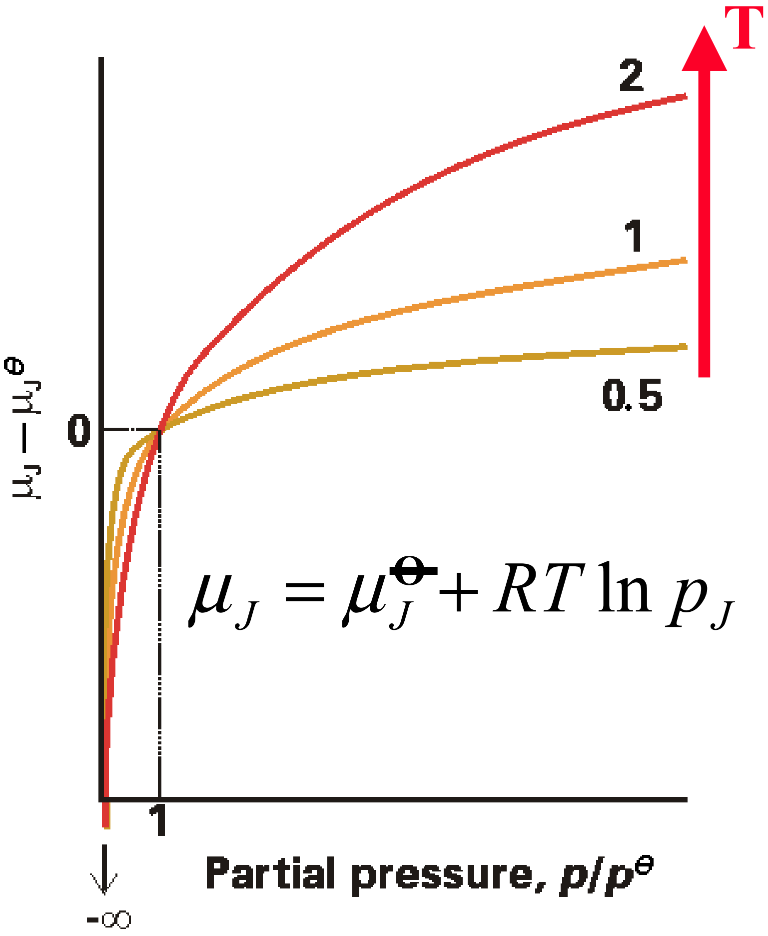
and $p_f = p$; $p_i = p^\ominus$: expressing changes with respect to the standard state $\ominus$ (1 bar)

$$G_m(p) = G_m^\ominus + RT \ln \frac{p}{p^\ominus}$$

$$\boxed{\mu_J = \mu_J^\ominus + RT \ln p_J}$$

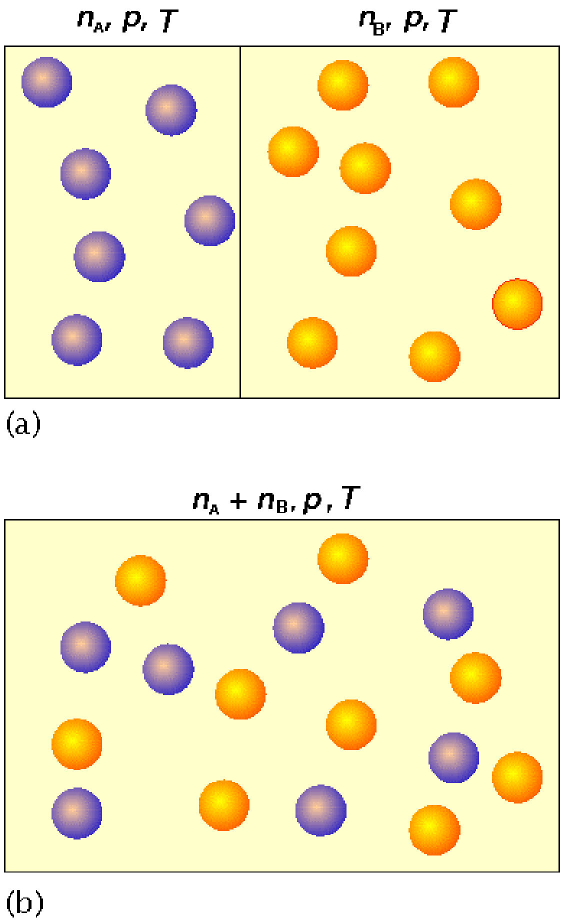
Changes in chemical potential of gases

⇒ for a perfect gas:



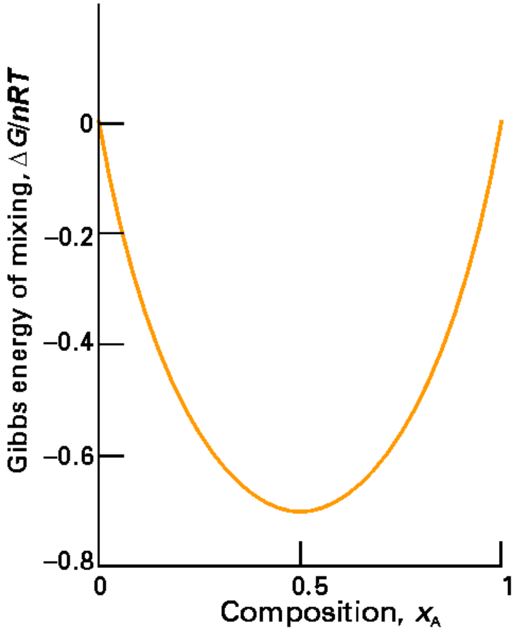
$$\mu_J = \mu_J^{\ominus} + RT \ln p_J$$

Spontaneous mixing



$$\Delta G = RT\{n_A \ln x_A + n_B \ln x_B\} = \Delta H - T\Delta S$$

(purely entropic)

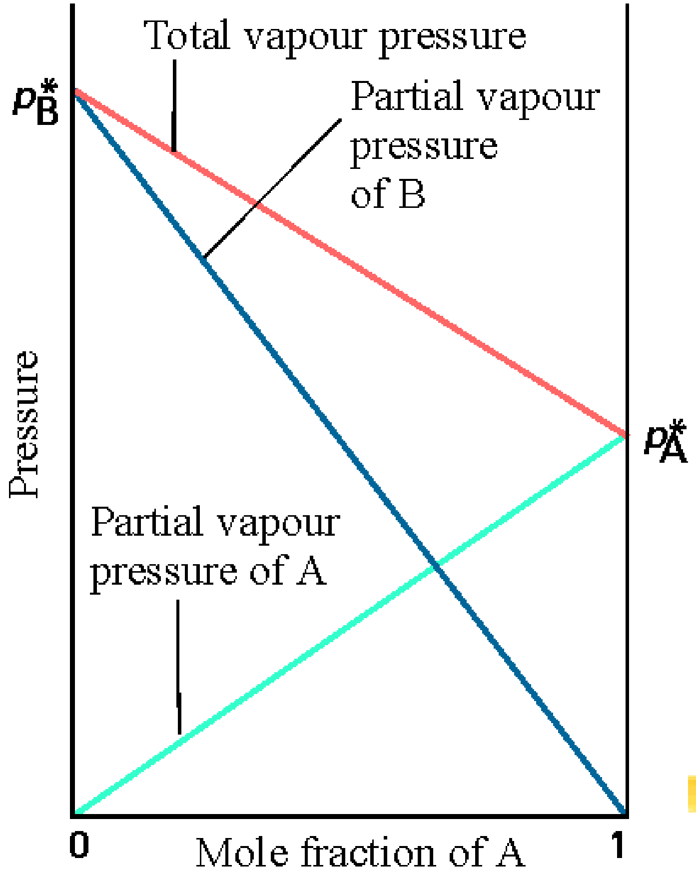


Changes in chemical potential of liquids

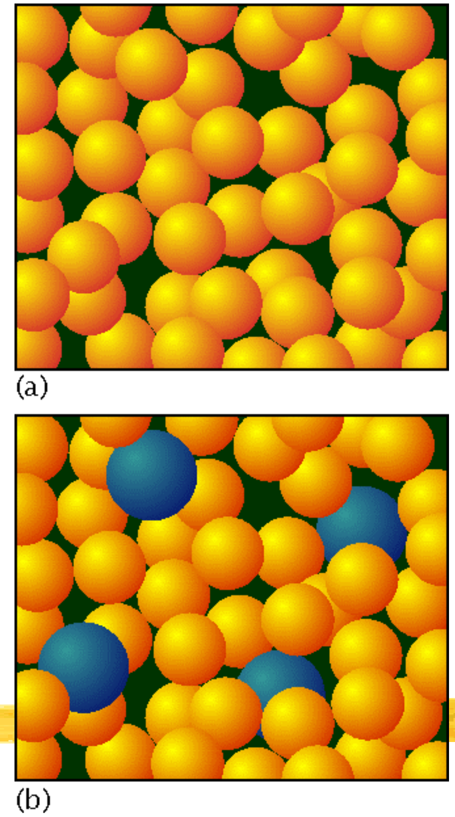
François Raoult (1830-1901) observes <u>Raoult's law</u>: The partial vapor pressure of a substance in a mixture is proportional to its mole fraction in solution x_J and its vapor pressure when pure p_J^*

$$p_J = x_J p_J^*$$

e.g., benzene **toluene**



Why?



$$\mu_{solv}(l) = \mu_{solv}(g)$$
$$= \mu^{\ominus}_{solv}(g) + RT \ln p_{solv}$$
$$= \mu^{\ominus}_{solv}(g) + RT \ln x_{solv} p^*$$
$$= \mu^{\ominus}_{solv}(l) + RT \ln x_{solv}$$

Relation to composition

Solvent has lower molar Gibbs energy