

The properties of binary mixtures

Atkins, Chapter 6

Definitions:

solvent: mixture component in excess; solute: other component

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

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

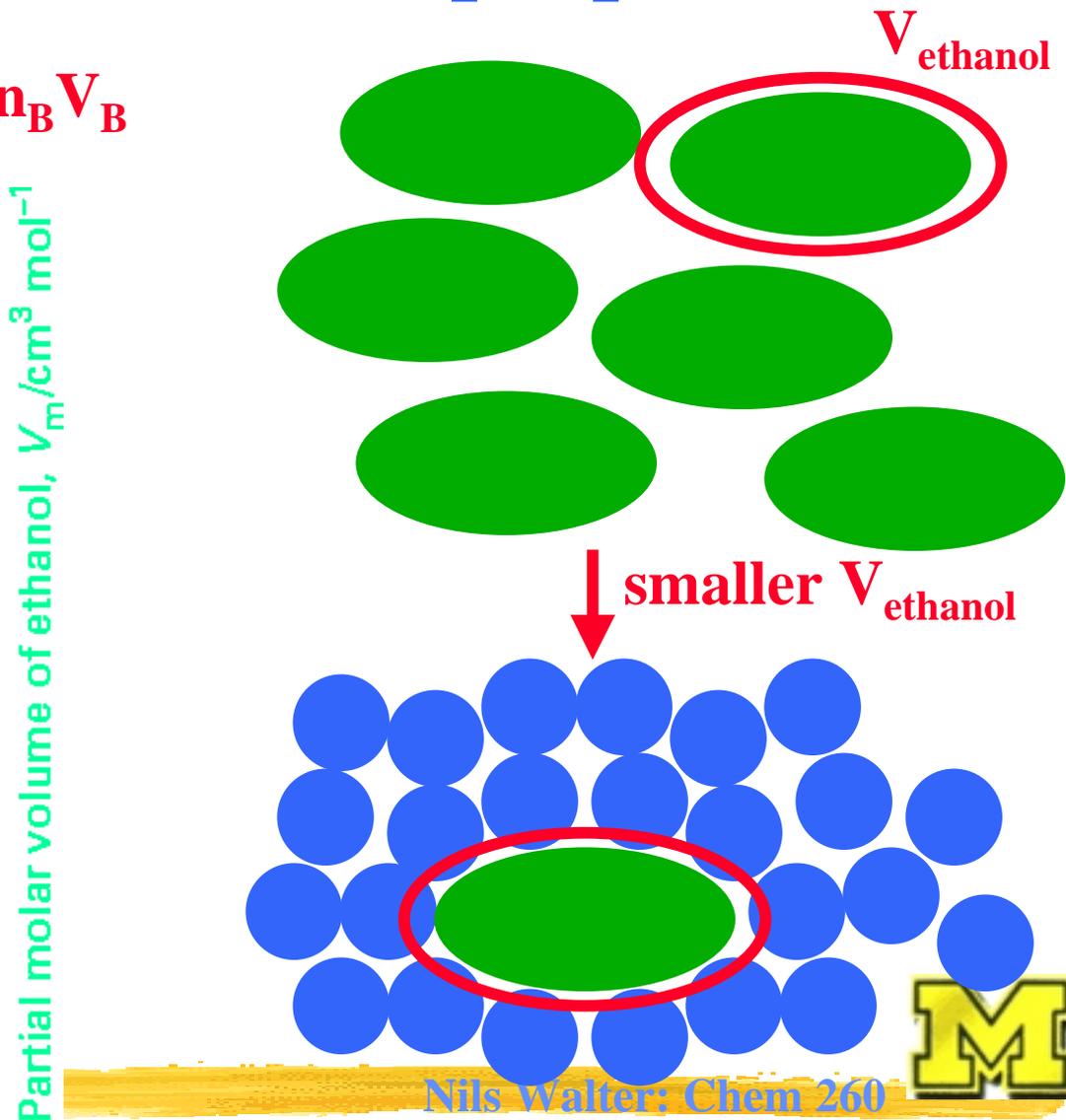
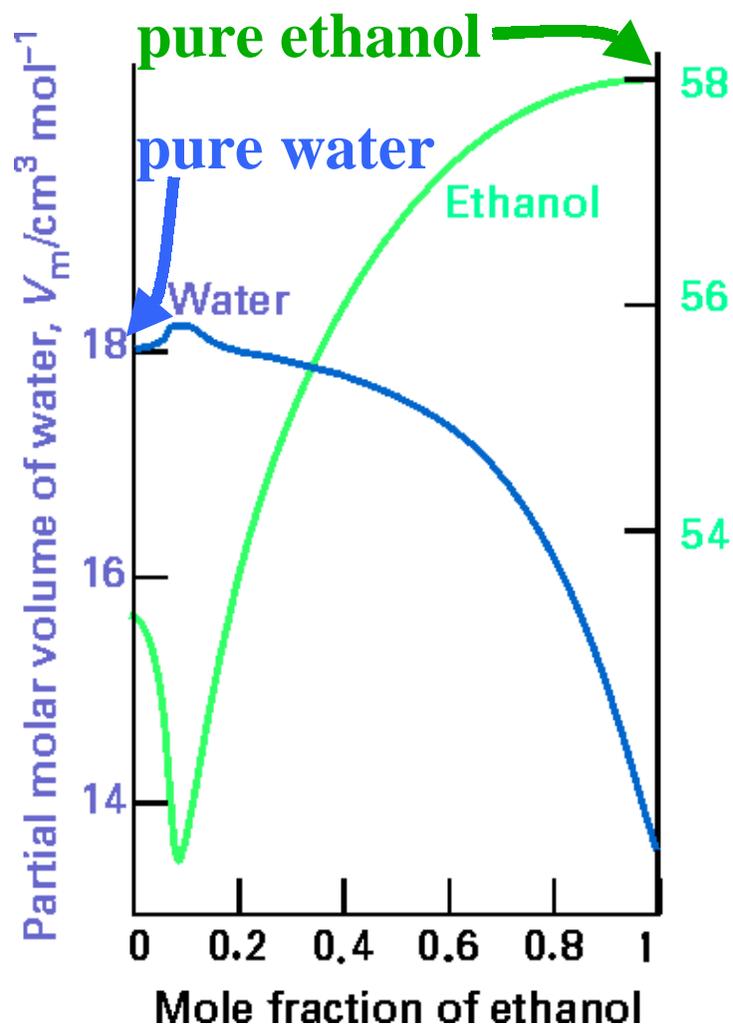
mole fraction $x_J = \frac{\text{amount of solute}}{\text{total amount of molecules}} = \frac{n_J}{n}$

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

$G = n_A G_A + n_B G_B \rightarrow$ **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: $\Delta G_m = G_m(p_f) - G_m(p_i) = \int_{p_i}^{p_f} V_m dp = RT \ln \frac{p_f}{p_i}$

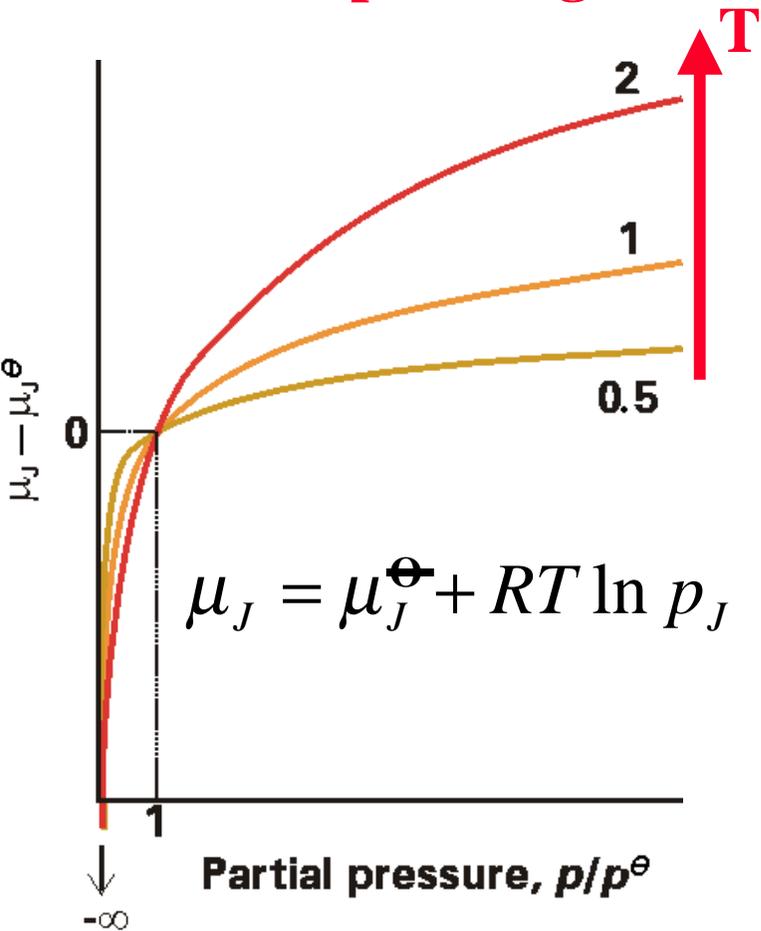
and $p_f = p$; $p_i = p^\ominus$: expressing changes with respect to the standard state \ominus (1 bar)

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

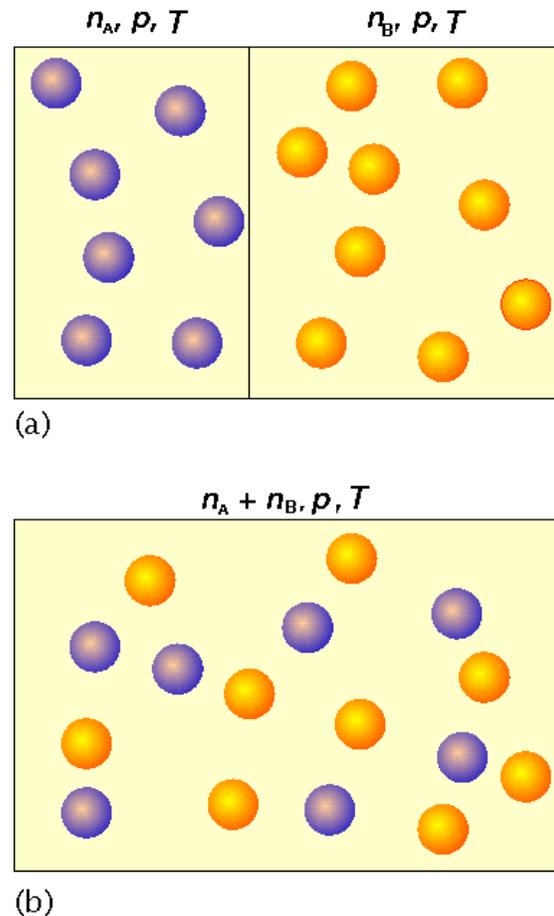


Changes in chemical potential of gases

⇒ for a perfect gas:

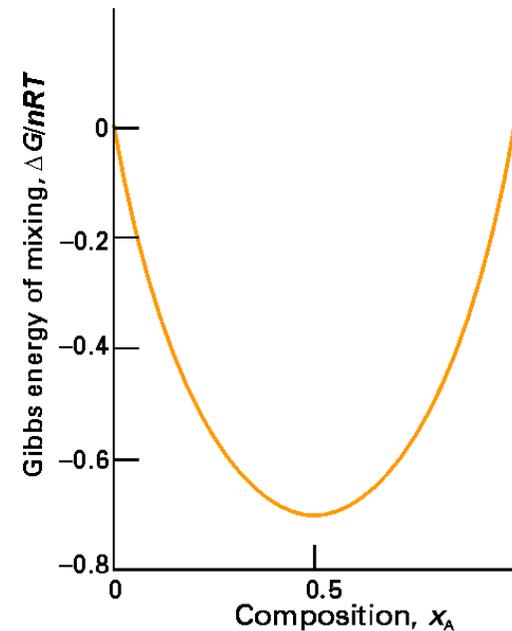


Spontaneous mixing



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

(purely entropic)

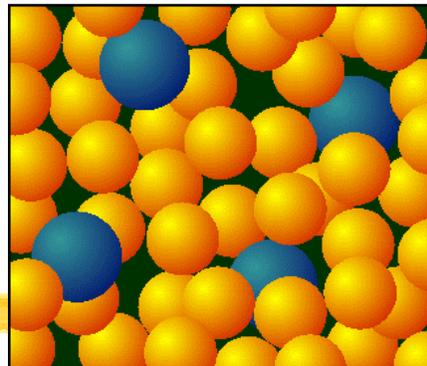
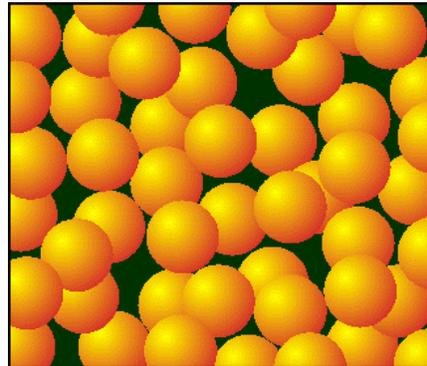
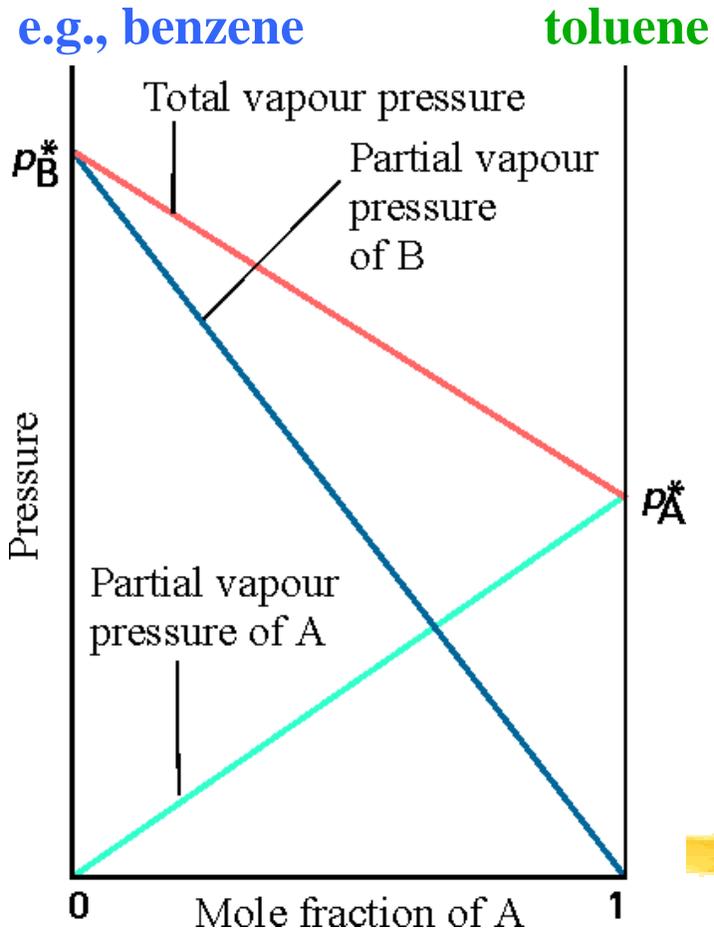


Changes in chemical potential of liquids

François Raoult (1830-1901) observes Raoult's law: 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^*

$$p_J = x_J p_J^*$$

Why?



$$\begin{aligned} \mu_{solv}(l) &= \mu_{solv}(g) \\ &= \mu_{solv}^\ominus(g) + RT \ln p_{solv} \\ &= \mu_{solv}^\ominus(g) + RT \ln x_{solv} p^* \\ &= \mu_{solv}^\ominus(l) + RT \ln x_{solv} \end{aligned}$$

↑
Relation to composition

Solvent has lower molar Gibbs energy

