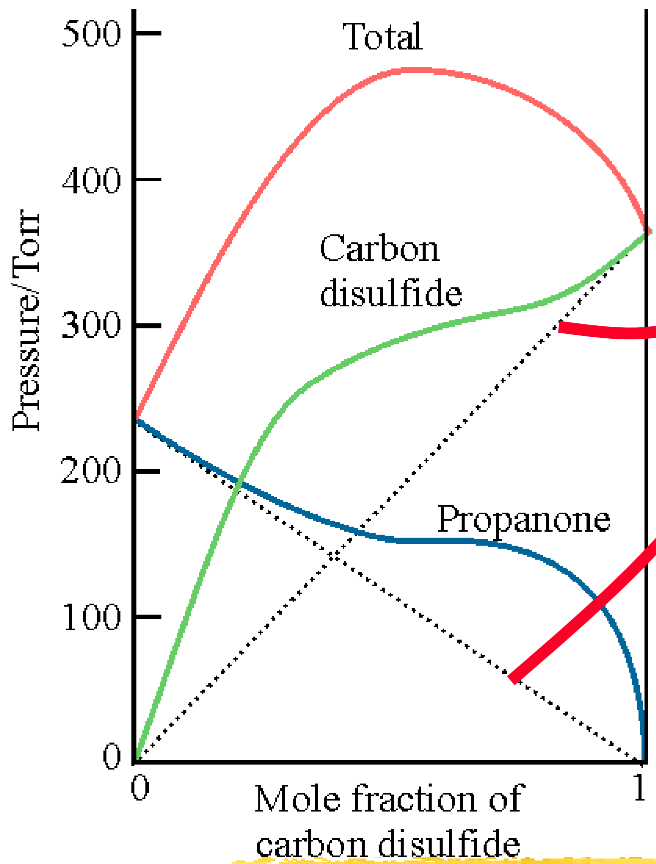
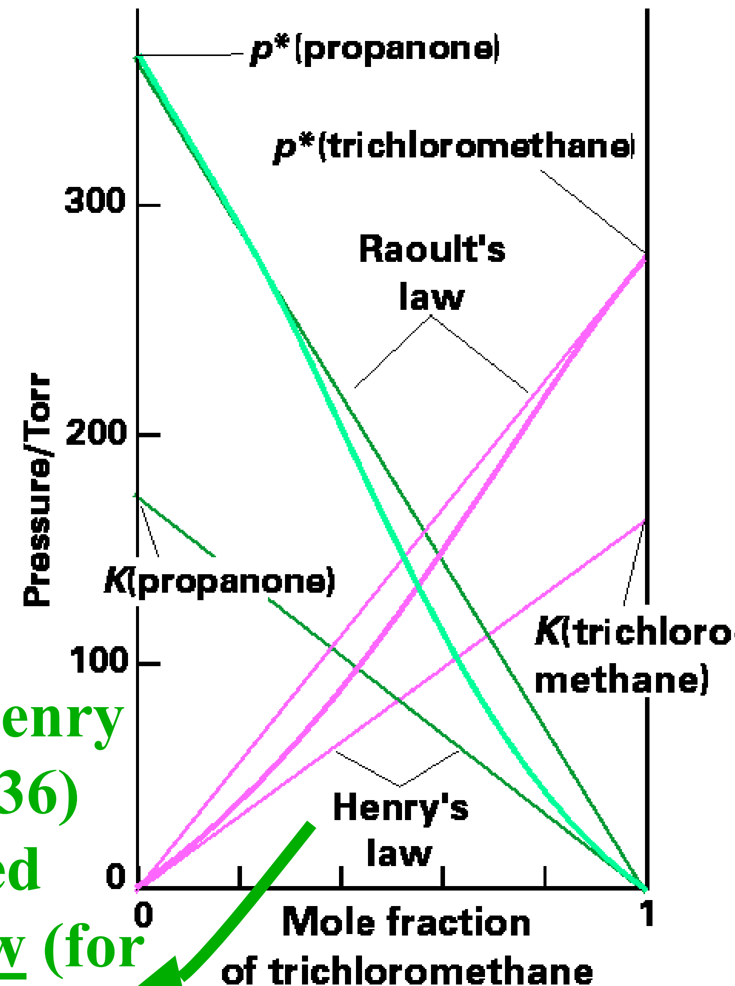
Non-ideal solutions

Strong deviations from ideality are shown by dissimilar substances



Raoult's law obeyed for a close-to-pure solvent



William Henry (1775-1836) observed Henry's law (for a dilute solute):

$p_B = x_B K_B$ (e.g., gas solubility)

Ideal and real solutions: Activities

From both Raoult's (solvent) and Henry's laws (solute) follows:

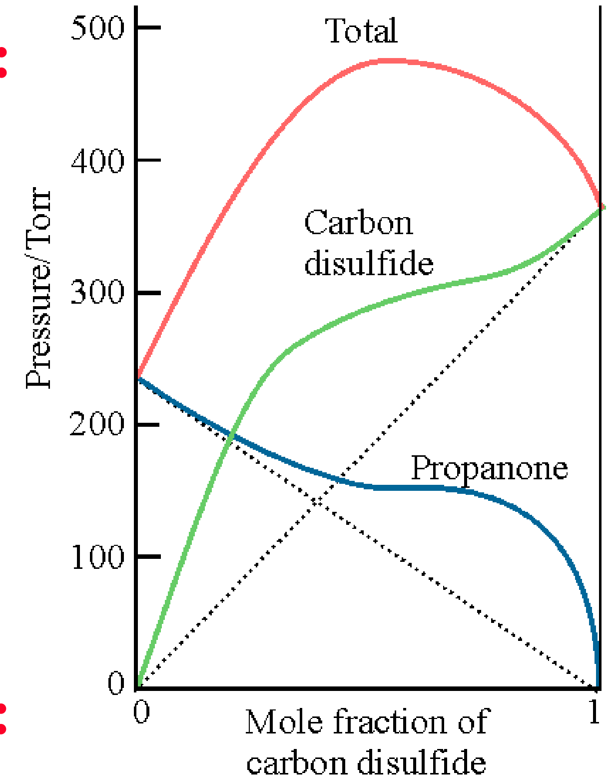
$$\mu_{solv}(l) = \mu^{\ominus}_{solv}(l) + RT \ln x_{solv}$$
$$= \mu^{\ominus}_{solv}(l) + RT \ln C[solv]$$

$$\Rightarrow \mu_J = \mu^{\ominus}_J + RT \ln[J]$$

standard chemical potential @ 1 M

The chemical potential is a measure of the ability of J to bring about physical or chemical change

BUT:



⇓ **to preserve equation for real solutions:**

$$\mu_J = \mu^{\ominus}_J + RT \ln a_J$$

Effective concentration = activity $a_J = \gamma_J[J]$

Consequences of chemical potential changes in mixtures: Colligative properties

Freezing point depression:

$$\Delta T_f = K_f b_B$$

K_f: cryoscopic constant

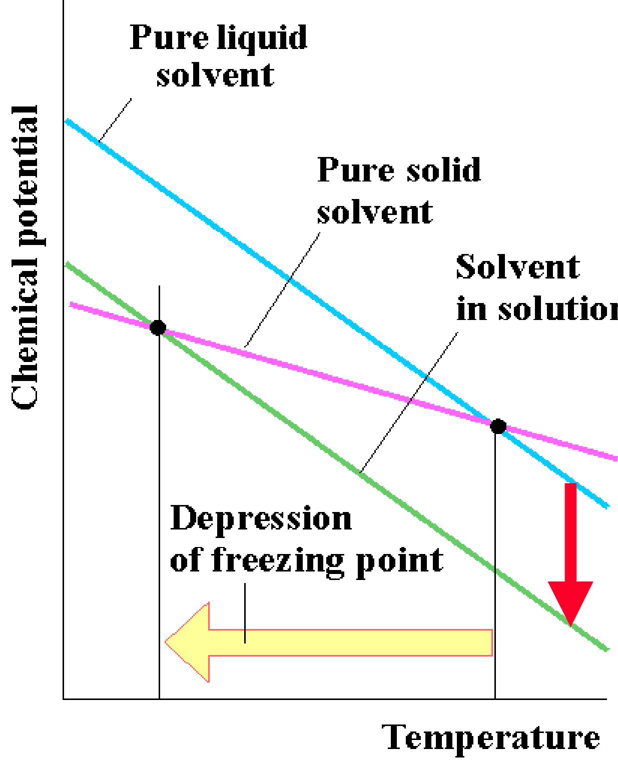
b_B: molality

Boiling point elevation:

$$\Delta T_B = K_B b_B$$

K_B: ebullioscopic constant

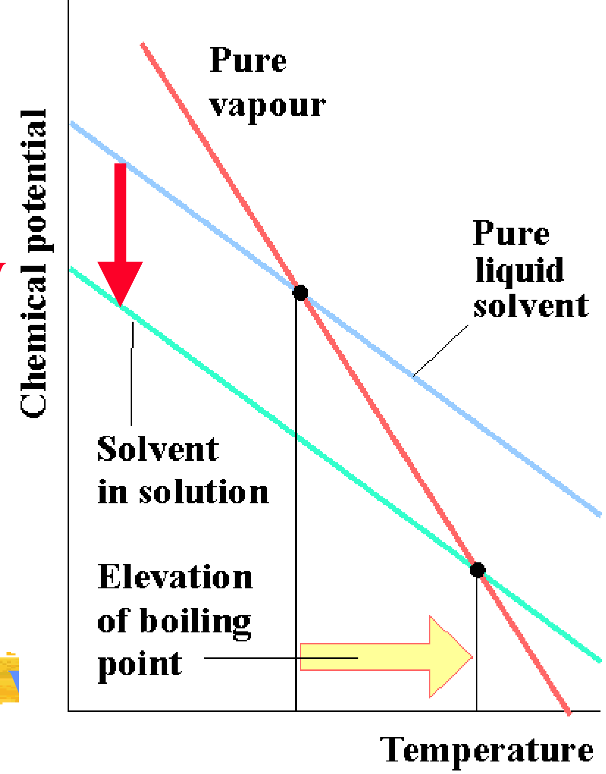
Solute is insoluble in solid solvent:



Chemical Potential lowered by solute

Chemical Potential lowered by solute

Solute is not volatile:

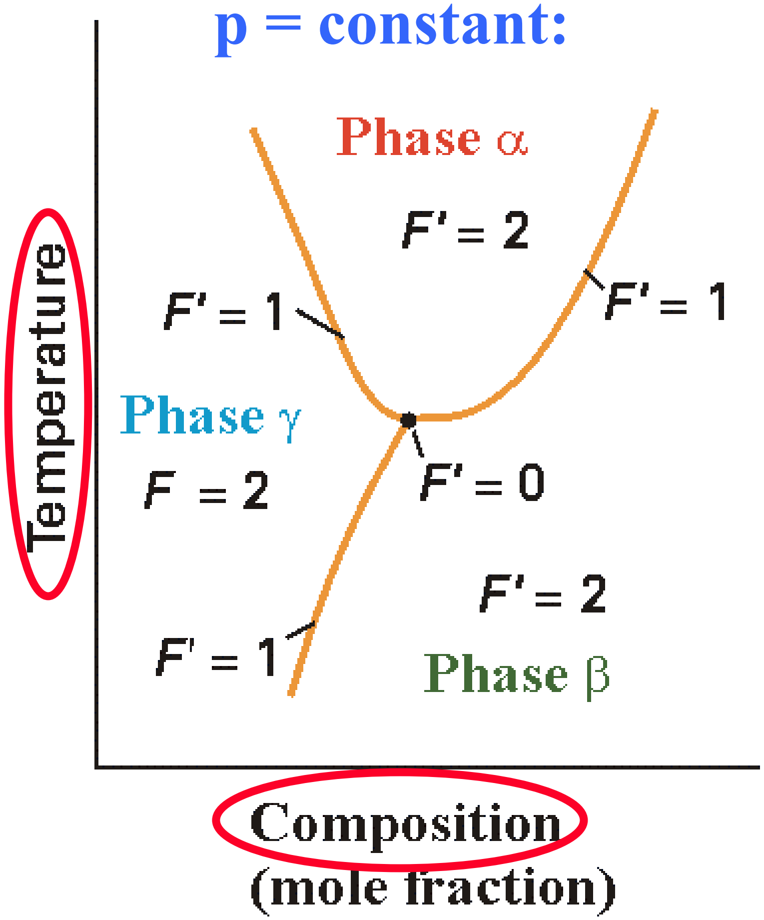


Phase diagrams of binary mixtures

Phase rule: $F = C - P + 2$ → p,T

(C) → for binary mixtures = 2

p = constant:



Temperature-composition diagram
for binary mixture of volatile liquids