

Lecture 15

- Liquid solutions – general considerations
- Ideal solutions
 - Raoult's law
 - Henry's law
 - chemical potential of solvent
 - properties of ideal solution
 - statistical mechanical model for ideal solution
 - solute chemical potential

Read Chs. 10 and 11 Sandler

Objectives

- Definition of ideal solutions in terms of chemical potentials
- Properties of ideal solution
- Understand Raoult's law from chemical potential perspective
- Understand Henry's law from chemical potential perspective
- Understand statistical origin of ideal solution

General Considerations

- Whether two (or more) liquids are fully miscible, and if not what are the coexisting composition?
- How is liquid-vapor equilibrium affected by the presence of another component?
- Solubility of gas or solid in a liquid
- Work of separating mixture into pure components

Start with ideal solution and gradually build in non-ideal effects

Two Empirical Laws for Ideal Solutions

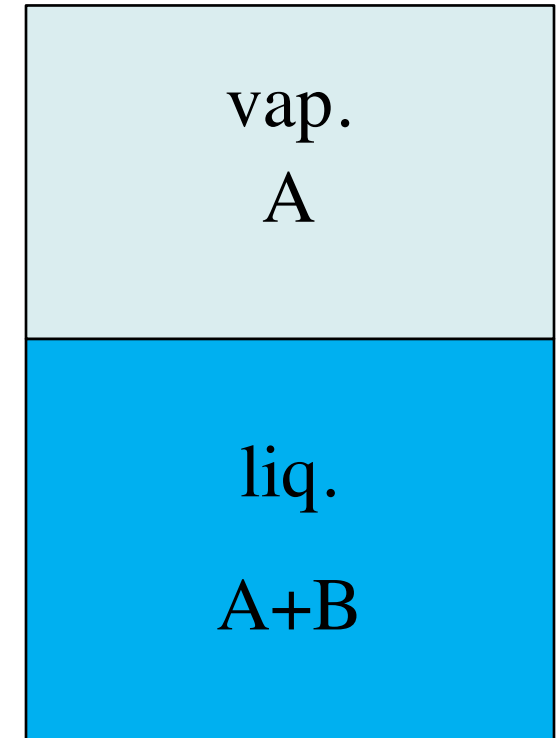
Raoult's law – vapor pressure of a liquid solvent

$$P_A = x_A P_A^{sat}$$

Valid for $x_A \approx 1$

A: solvent

B: solute



Two Empirical Laws for Ideal Solutions

Henry's law – solubility of gas in liquid

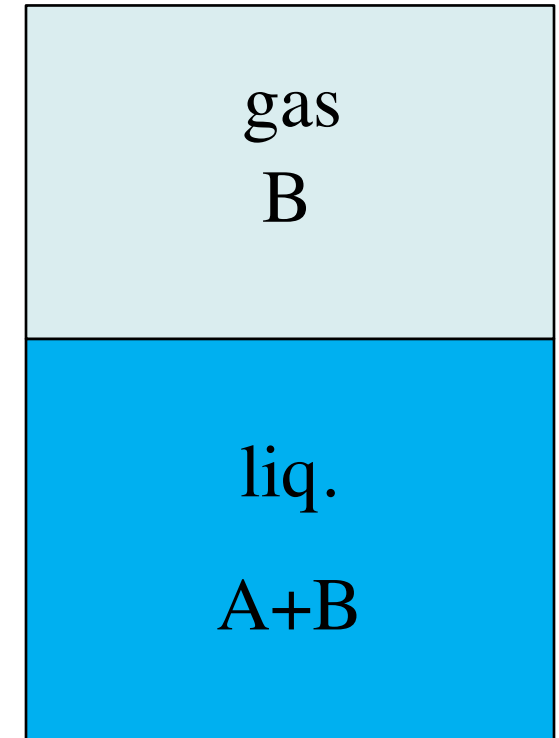
$$x_B = k^{-1}P_B$$

k depends on property of gas/liquid pair

Valid for $x_B \ll 1$

A: solvent

B: solute



Empirical Definition of Ideal Solutions

Raoult's law sense:

- Solvent in a sufficiently dilute solution behaves ideal (obeys Raoult's law); solution is ideal for the solvent
- Solution is ideal if all liquid components obey Raoult's law

Henry's law sense:

- Any solute behaves ideal at sufficient dilute; solution is ideal for the solute

Chemical Potential of Solvent

L-V equilibrium $\mu_A^L(T, P, x_A) = \mu_A^V(T, P_A)$

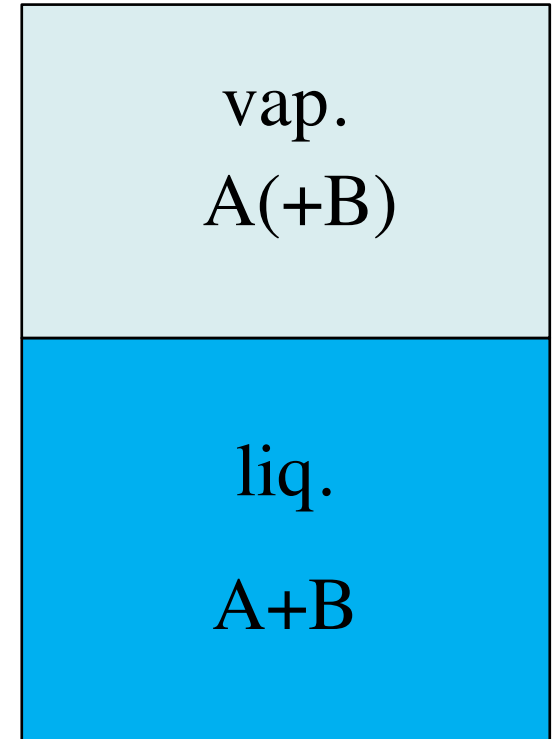
Assume I. G. $\mu_A^V(T, P_A) = \mu_A^\ominus(T) + RT \ln \frac{P_A}{P^\ominus}$

Raoult's law $\mu_A^V(T, P_A) = \mu_A^\ominus(T) + RT \ln \frac{x_A P_A^{sat}}{P^\ominus}$

$$\mu_A^V(T, P_A) = \mu_A^V(T, P_A^{sat}) + RT \ln x_A$$

$$\mu_A^V(T, P_A^{sat}) = \mu_A^L(T, P_A^{sat}) = \mu_A^L(T, P) + \int_{P_A^{sat}}^P v^L \approx \mu_A^{L(0)}(T, P)$$

$$\mu_A^L(T, P, x_A) = \mu_A^{L(0)}(T, P) + RT \ln x_A$$



Formal Definition of Ideal Solutions

All components obey Lewis-Randall Rule

$$\mu_i(T, P, \{x_i\}) = \mu_i^\ominus(T, P) + RT \ln[x_i f_i^{(0)}(T, P)/P^\ominus]$$

$$\mu_i(T, P, \{x_i\}) = \mu_i^\ominus(T, P) + RT \ln \frac{f_i^{(0)}}{P^\ominus} + RT \ln x_i$$

$$\mu_i(T, P, \{x_i\}) = \mu_i^{(0)}(T, P) + RT \ln x_i$$

$\mu_i^{(0)}(T, P)$ Chemical potential of pure component
(liquid or gas) at same T and total P

Consequences of Ideal Solution (Raoult's Law Sense)

$$V^{mix} = 0$$

$$H^{mix} = 0$$

$$S^{mix} = -R \sum_i n_i \ln x_i$$

$$G^{mix} = RT \sum_i n_i \ln x_i$$

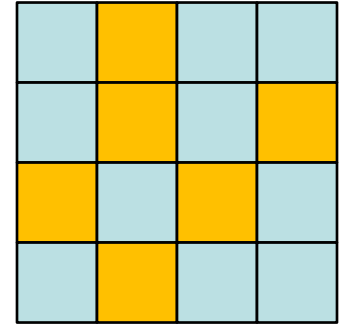
Modified Raoult's law

$$y_i P \phi_i(y_i, P) = x_i \phi_i(P_i^{sat}) P_i^{sat} \exp \left[\frac{v^L (P - P_i^{sat})}{RT} \right]$$

ϕ_i Fugacity coefficient

Lattice Model for Regular Solution

M lattice cells filled with N_A A molecules and N_B B molecules



Nearest neighbor interactions, with coordination # z

$\epsilon_{AA}, \epsilon_{BB}, \epsilon_{AB}$ $\epsilon < 0$ cohesive attraction in liquids

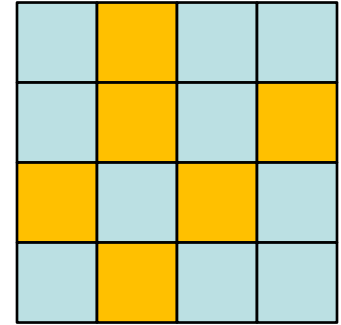
Generally a hard problem, because of correlation effects (e.g., A is more likely to be surrounded by A); no exact solution in 3d

Random mixing approximation: ignore correlations and assume mixing to be completely random

Lattice Model for Regular Solution

Entropy:

M lattice cells filled with N_A identical objects of type A, N_B objects of type B



$$\Omega = \frac{(N_A + N_B)!}{N_A! N_B!}$$

$$S/k = \ln \Omega = \ln(N_A + N_B)! - \ln N_A! - \ln N_B!$$

$$S = -k(N_A + N_B)[x_A \ln x_A + x_B \ln x_B] = -k[N_A \ln x_A + N_B \ln x_B]$$

$$S = S^{mix} = -R[n_A \ln x_A + n_B \ln x_B]$$

Lattice Model for Regular Solution

Energy:

AA interaction pairs: $\frac{1}{2} N_A z \epsilon_{AA} x_A$

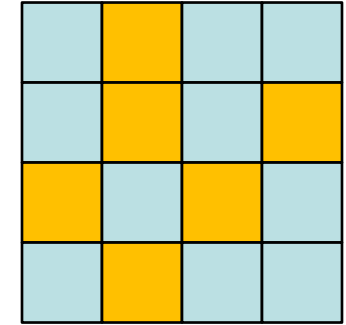
BB interaction pairs: $\frac{1}{2} N_B z \epsilon_{BB} x_B$

AB interaction pairs: $N_A z \epsilon_{AB} x_B = N_B z \epsilon_{AB} x_A = (N_A + N_B) z \epsilon_{AB} x_A x_B$

Energy change upon mixing: $U^{mix} = U(N_A, N_B) - U_A(N_A) - U_B(N_B)$

$$U^{mix} = (N_A + N_B) z \left(\epsilon_{AB} - \frac{\epsilon_{AA} + \epsilon_{BB}}{2} \right) x_A x_B$$

$$U^{mix} = n w x_A x_B \quad w = N_{av} z \left(\epsilon_{AB} - \frac{\epsilon_{AA} + \epsilon_{BB}}{2} \right)$$



Lattice Model of Regular Solution

$$S^{mix} = -R \sum_i n_i \ln x_i$$

$$U^{mix} = H^{mix} = n w x_A x_B$$

$$G^{mix} = F^{mix} = RT \sum_{i=A,B} n_i \ln x_i + n w x_A x_B$$

w is usually positive (Berthelot rule)

$$|\epsilon_{ij}| = (|\epsilon_{ii}| |\epsilon_{jj}|)^{1/2}$$

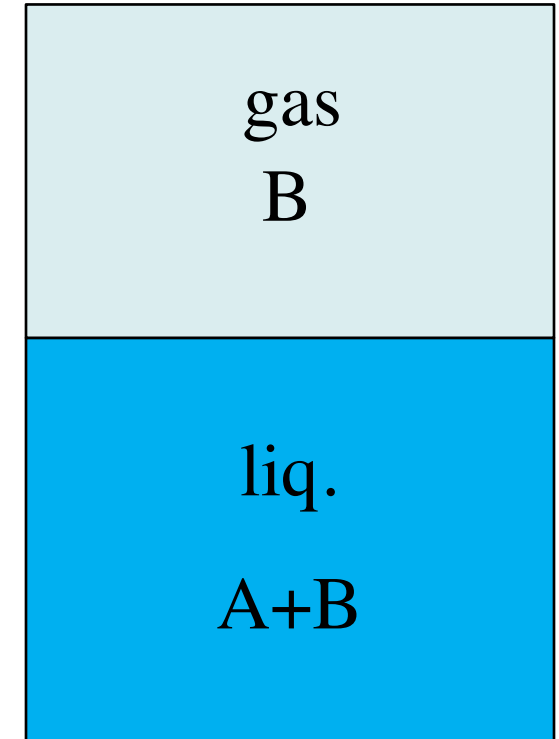
Chemical Potential of Solute in Dilute Solution

Equilibrium $\mu_B^{sol}(T, P, x_B) = \mu_B^G(T, P_B)$

Assume I. G. $\mu_B^G(T, P_B) = \mu_B^\ominus(T) + RT \ln \frac{P_B}{P^\ominus}$

Raoult's law $\mu_B^G(T, P_B) = \mu_B^\ominus(T, P) + RT \ln \frac{kx_B}{P^\ominus}$

$$\mu_B^{sol}(T, P, x_B) = \mu_B^*(T, P) + RT \ln x_B$$



$\mu_B^*(T, P)$ reference chemical potential in hypothetical state when $x_B=1$
depends on solute-solvent pair

Hypothetical Reference State

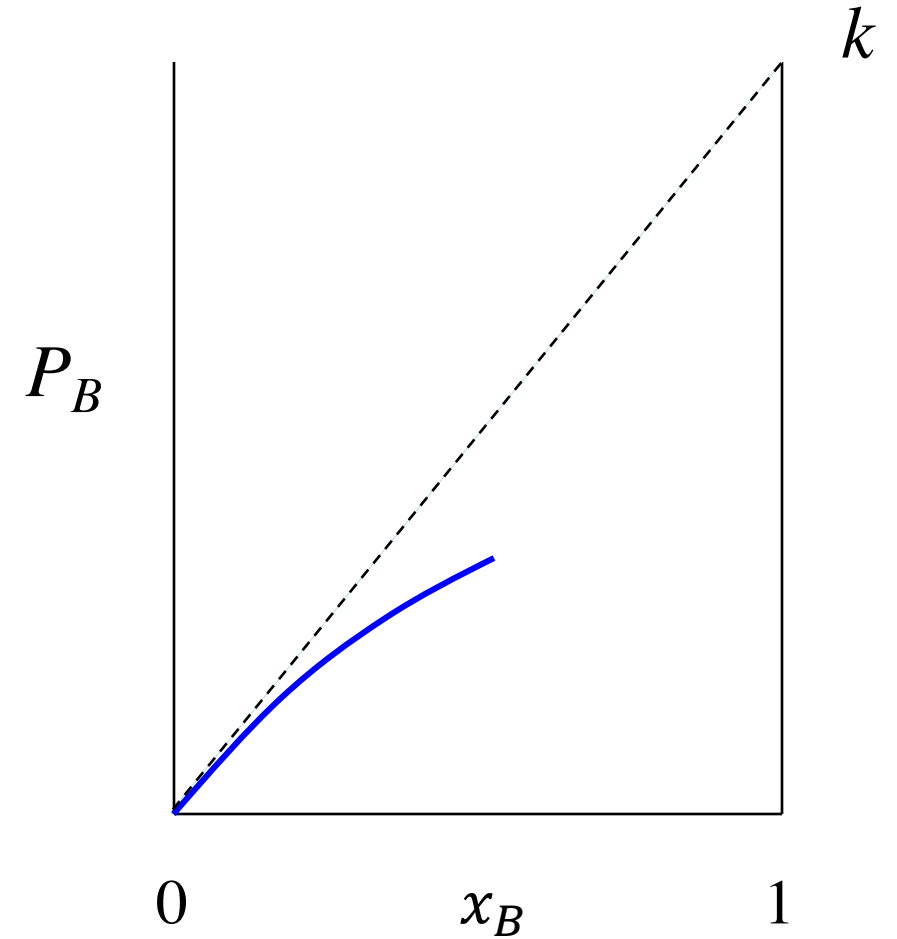
$$\mu_B^G(T, P_B) = \mu_B^\ominus(T) + RT \ln \frac{kx_B}{P^\ominus}$$

$$\mu_B^*(T) = \mu_B^\ominus(T) + RT \ln \frac{k}{P^\ominus}$$

Ideal gas with pressure $P = k$

Hypothetical because $x_B = 1$ may not exist

k can depend on T and P



Relationship between Solute and Solvent Chemical Potential

If solvent is ideal in the Raoult's law sense, then solute is ideal in the Henry's law sense

Proof using Gibbs-Duhem $x_A d\mu_A + x_B d\mu_B = 0$

Questions to Think about

- Prove that if solvent is ideal in the Raoult's law sense, then solute is ideal in the Henry's law sense
- How can we determine the temperature and pressure dependence of the reference chemical potential for solute in dilute solutions?

Lecture 16

- Dilute solutions
 - colligative properties: boiling point elevation, freezing point depression, osmotic pressure
 - distribution law; solubility of gases and solids
- Activity and activity coefficient for non-ideal solutions
- Excess functions
- Non-ideal solution models: Margules and Flory-Huggins models

Read Chs. 12 and 13 Sandler

Objectives

- Understand origin of colligative properties from perspective of solvent chemical potential
- Understand solubility and distribution law from perspective of solute chemical potential
- Understanding meaning of activity
- Know Margules model
- Know how to calculate activity coefficient from model for excess Gibbs free energy

Solvent Properties in Dilute Solution

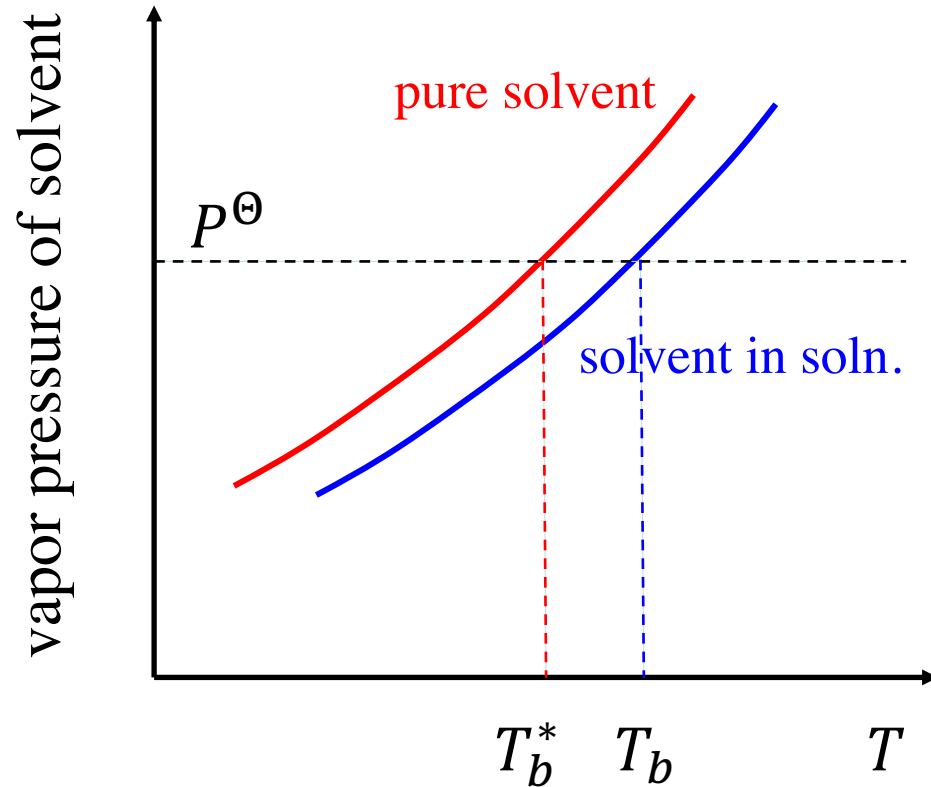
Chemical potential

$$\mu_A(T, P) = \mu_A^{(0)}(T, P) + RT \ln x_A \approx \mu_A^{(0)}(T, P) - RTx_B$$

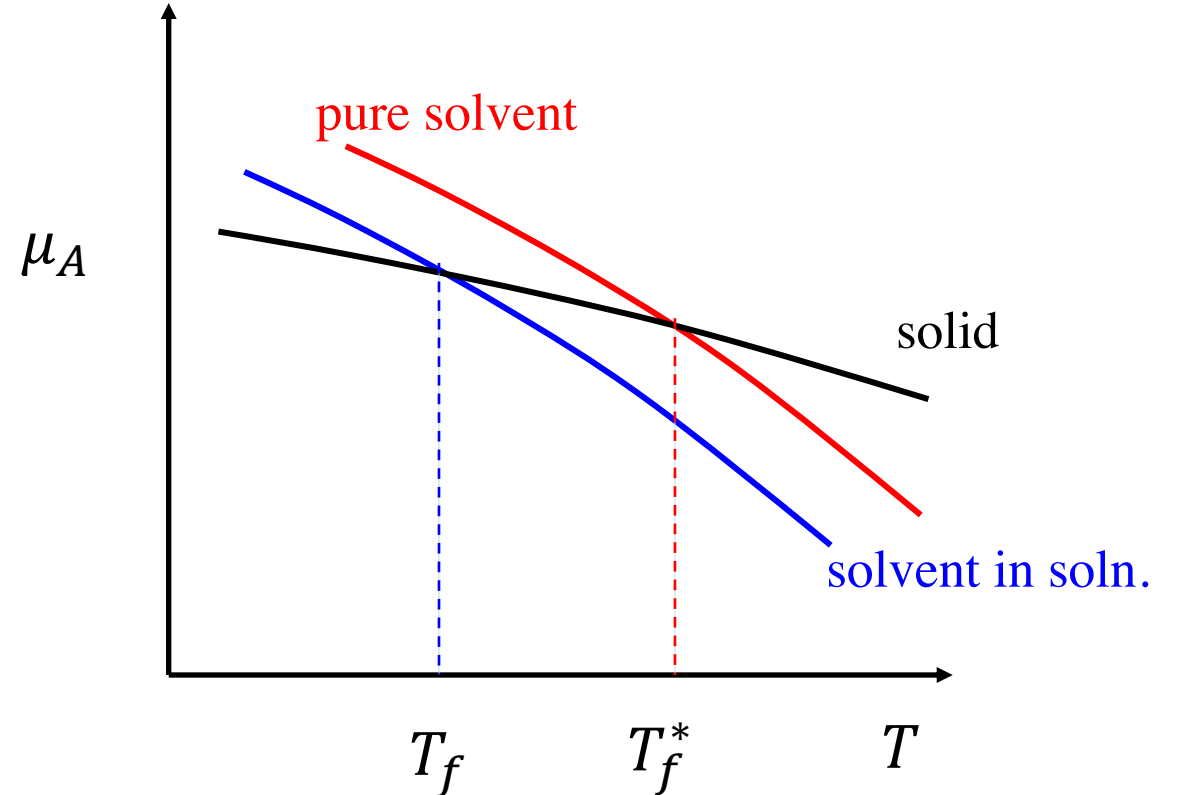
Lower than chemical potential of pure liquid at same T and P by amount of added solute (but not identity) – colligative properties

- Boiling point elevation
- Freezing point depression
- Osmotic pressure

Colligative Properties – Qualitative Understanding



boiling point elevation



freezing point depression

Freezing Point Depression

$$\mu_A^L(T_m) = \mu_A^S(T_m)$$

$$\mu_A^L(T_m - \delta T_m) - R(T_m - \delta T_m)x_B = \mu_A^S(T_m - \delta T_m)$$

$$\delta T_m = \frac{RT_m^2}{\Delta h_m} x_B$$

$$\delta T_m = A \frac{C_B}{M_B}$$

Principle for determining molecular weight
of unknown chemicals

Osmotic Pressure

$$\mu_A(T, P + \Pi, \{x_i\}) = \mu_A^{(0)}(T, P)$$

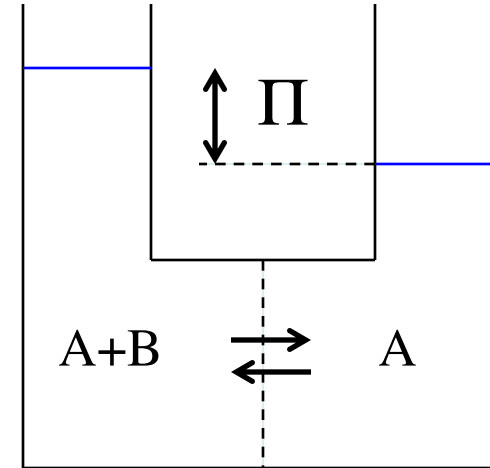
$$\mu_A^{(0)}(T, P + \Pi) + RT \ln a_A = \mu_A^{(0)}(T, P)$$

$$\Pi \nu_A = -RT \ln a_A$$

Dilute solution $a_A \rightarrow x_A = 1 - x_B$

$$\Pi = \frac{n_B}{V}RT$$

van't Hoff's law



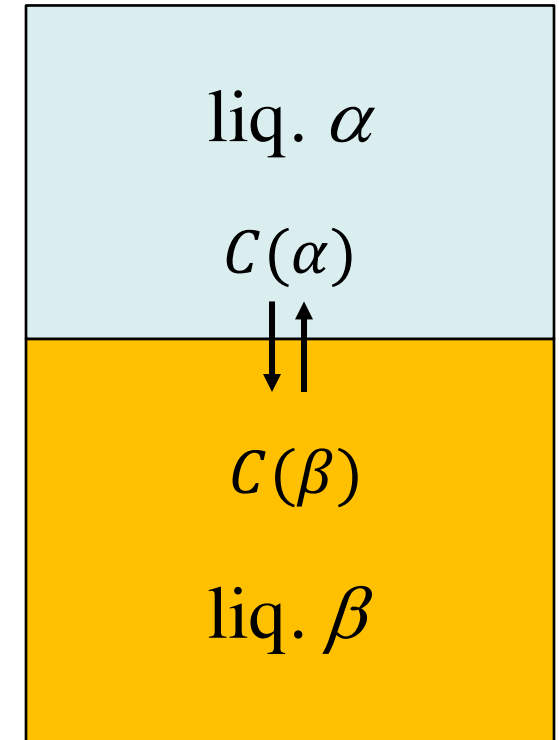
Solute Properties in Dilute Solution

Distribution law $\frac{x_C^\alpha}{x_C^\beta} = K_{\alpha\beta}(T, P)$

$$\mu_C^\alpha(T, P, x_C^\alpha) = \mu_C^\beta(T, P, x_C^\beta)$$

$$\mu_C^{\alpha*}(T, P, x_C^\alpha) + RT \ln x_C^\alpha = \mu_C^{\beta*}(T, P, x_C^\beta) + RT \ln x_C^\beta$$

$$\frac{x_C^\alpha}{x_C^\beta} = \exp \left[-\frac{\mu_C^{\alpha*} - \mu_C^{\beta*}}{RT} \right] \equiv K_{\alpha\beta}(T, P)$$



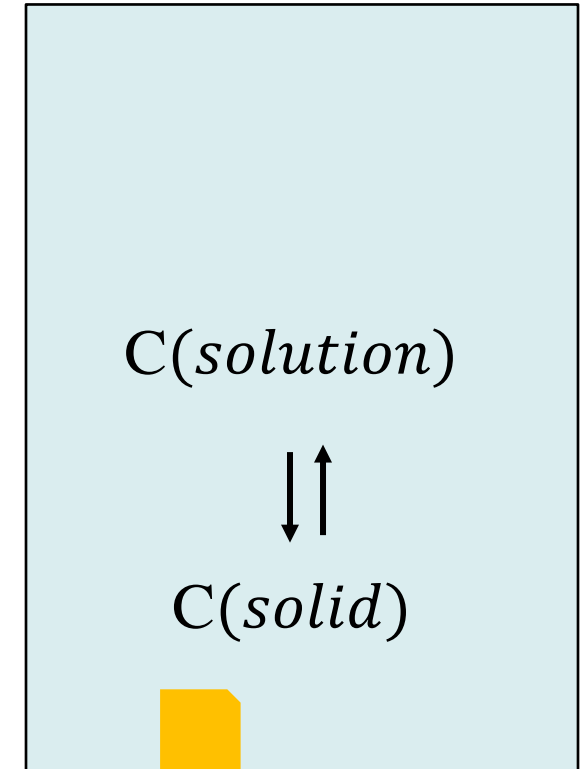
Solute Properties in Dilute Solution

Solubility of solid $x_C = K(T, P)$

$$\mu_C^{solid}(T, P) = \mu_C^{solution}(T, P, x_C)$$

$$\mu_C^{solid}(T, P) = \mu_C^*(T, P) + RT \ln x_C$$

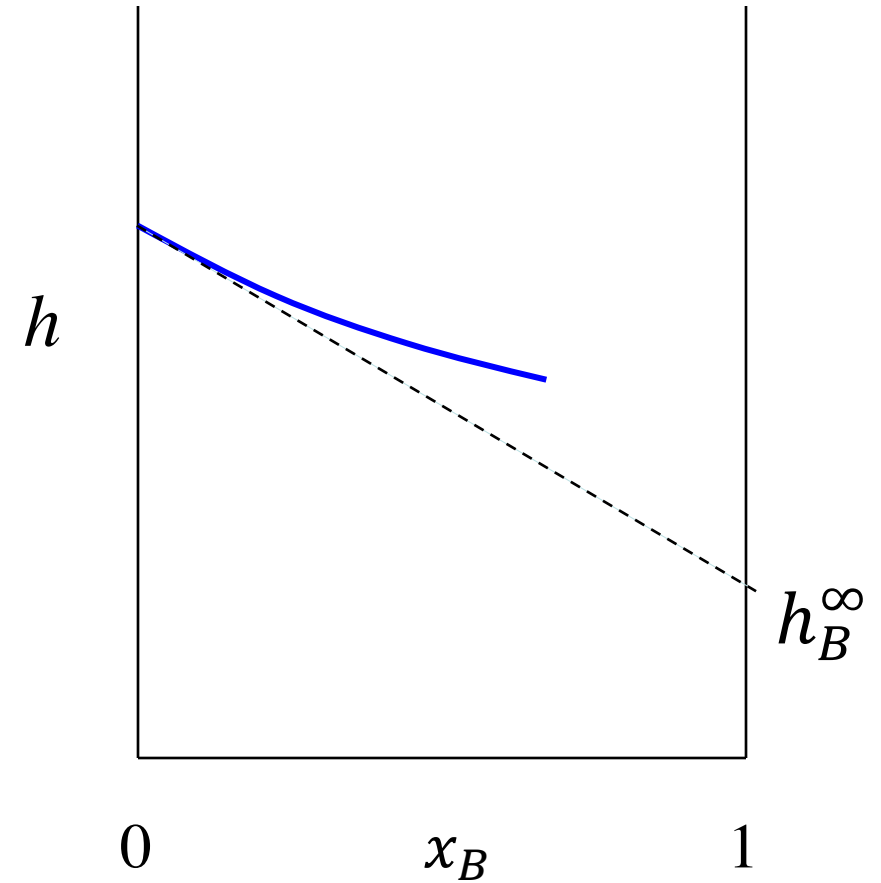
$$x_C = \exp \left[-\frac{\mu_C^* - \mu_C^{solid}}{RT} \right] \equiv K(T, P)$$



Temperature Dependence in Solid Solubility

$$x_B(T_2) = x_B(T_1) \exp \left[\frac{h^\infty}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right]$$

h^∞ partial molar heat of dissolution
at infinite dilution



Non-ideal Solutions: Activity and Activity Coefficient

If all components can exist as pure liquid

$$\mu_i(T, P, x_i) = \mu_i^{(0)}(T, P) + RT \ln a_i$$

$$a_i = \gamma_i x_i \quad \gamma_i = \frac{a_i}{x_i} \quad \lim_{x_i \rightarrow 1} \gamma_i = 1$$

Modified Raoul's law

$$P_A = \gamma_A x_A P_A^{sat}$$

$$P_B = \gamma_B x_B P_B^{sat}$$

Complete modified Raoul's law

$$y_i P \phi_i(y_i, P) = \gamma_i x_i \phi_i(P_i^{sat}) P_i^{sat} \exp \left[\frac{v^L (P - P_i^{sat})}{RT} \right]$$

Gibbs-Duhem

$$\sum_i x_i d \ln \gamma_i = 0$$

In a binary solution, if one component behaves ideal at all composition, then the other component also behaves ideal

Activity Coefficient for Solute in Dilute Solution, or Solute That Cannot Exist as Pure Liquid

$$\mu_B(T, P, x_B) = \mu_B^*(T, P) + RT \ln a_B$$

$$a_B = \gamma_B x_B \quad \gamma_B = \frac{a_B}{x_B}$$

$$\lim_{x_B \rightarrow 0} \gamma_B = 1$$

Gibbs-Duhem still holds

Modified Henry's law

$$P_B = \gamma_B x_B k$$

Excess Functions

Measures deviations from ideal solution

$$B^E = B^{mix} - B^{mix,ID}$$

$$G^E = RT \sum_i n_i \ln \gamma_i$$

$$RT \ln \gamma_i = \left(\frac{\partial G^E}{\partial n_i} \right)_{T,P,n_{j \neq i}}$$

Basis for calculating activity coefficients from theoretical models for excess Gibbs free energy

Excess Properties

From excess Gibbs free energy, can get

$$V^E = \left(\frac{\partial G^E}{\partial P} \right)_{T, \{n\}}$$

$$S^E = - \left(\frac{\partial G^E}{\partial T} \right)_{P, \{n\}}$$

$$H^E = G^E + TS^E = -T^2 \left[\frac{\partial \left(\frac{G}{T} \right)}{\partial T} \right]_{P, \{n\}}$$

Margules Model

$$G^E = nwx_Ax_B$$

$$RT \ln \gamma_A = wx_B^2 \qquad \gamma_A = \exp\left(\frac{w}{RT}x_B^2\right)$$

$$RT \ln \gamma_B = wx_A^2 \qquad \gamma_B = \exp\left(\frac{w}{RT}x_A^2\right)$$

Modified Raoult's law

$$P_A = x_A \exp\left(\frac{w}{RT}x_B^2\right) P_A^{sat}$$

$$P_B = x_B \exp\left(\frac{w}{RT}x_A^2\right) P_B^{sat}$$

Flory-Huggins Model for Polymer Solutions

Free energy of mixing per unit volume (assuming incompressibility)

$$\frac{\Delta_{mix}G}{V} = RT \left[\frac{\phi_A}{N_A v_A} \ln \phi_A + \frac{\phi_B}{N_B v_B} \ln \phi_B + \frac{\chi}{v_0} \phi_A \phi_B \right]$$

Special case: polymer solution (monomeric solvent)

$$\frac{\Delta_{mix}G}{V} = \frac{RT}{v_0} \left[\frac{\phi}{N} \ln \phi + (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi) \right]$$

$$\phi_c = (1 + N^2)^{-1}$$

$$\chi_c = \frac{1}{2} (1 + N^{-1/2})^2$$

Questions to Think about

- For solute that can exist as pure solvent, one can define the activity coefficient using either the ideal solution in Raoult's law sense, or the ideal solution in Henry's law sense, as the reference. Use the Margules model to show the relationship between these two activity coefficients and between the two reference chemical potentials
- Show the temperature dependence of solid solubility is related to the partial molar heat of dissolution at infinite dilution