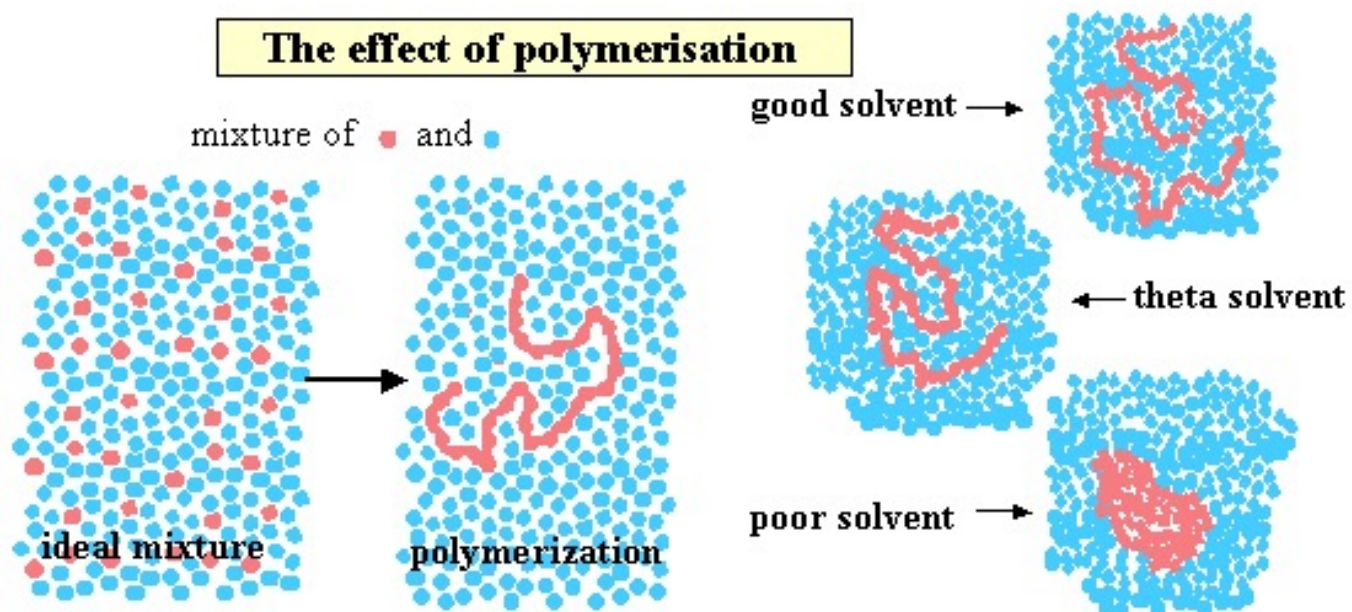


# Chemical Engineering Thermodynamics

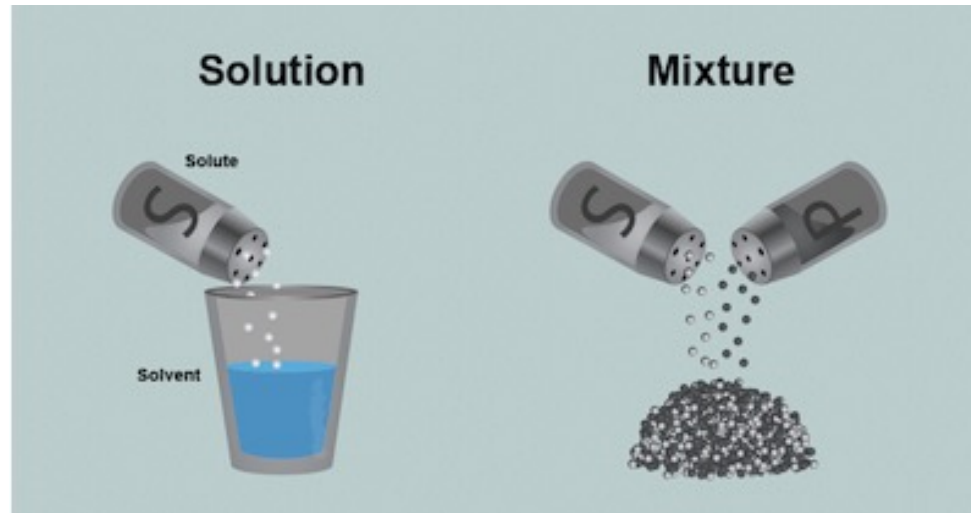
## Lecture 8 Solution Thermodynamics

Xiaofei Xu



# Solutions and Mixtures

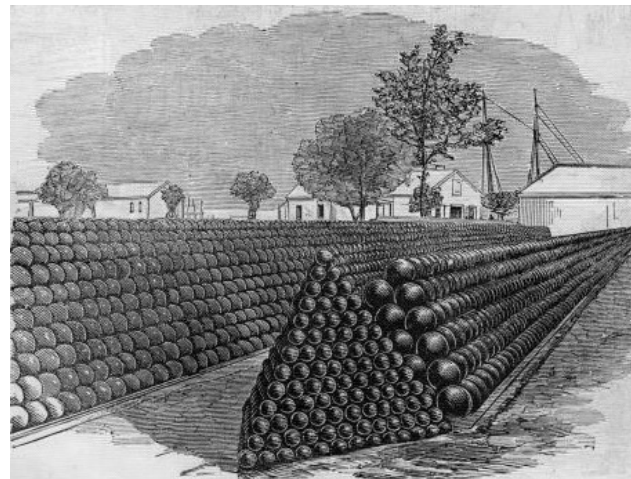
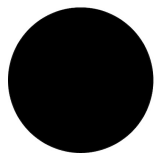
- Solutions are homogeneous mixtures



Solution Type	Example
gas-gas	air
gas-liquid	carbon dioxide in soda
gas-solid	hydrogen gas in palladium metal
liquid-liquid	gasoline
solid-liquid	sugar in water
liquid-solid	mercury dental amalgam
solid-solid	sterling silver

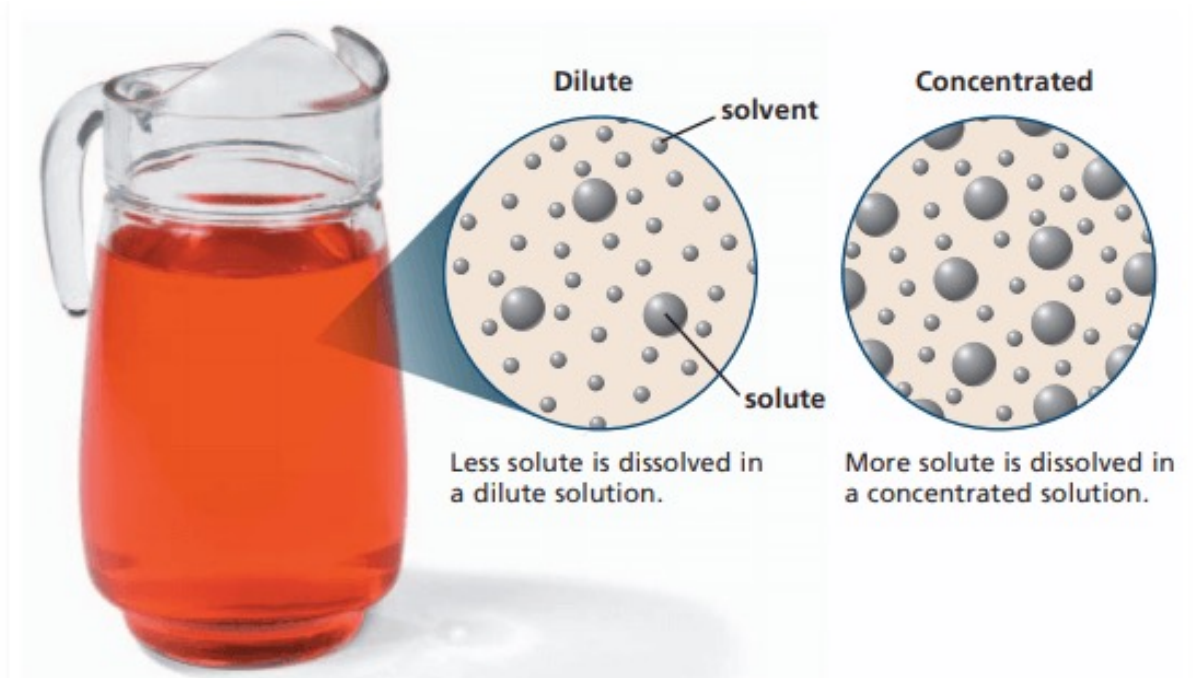
# Measures of Composition

- Mass fraction:  $x_i = \frac{m_i}{m}$
- Molar fraction:  $x_i = \frac{n_i}{n}$
- Molar concentration:  $C_i = \frac{x_i}{V}$
- Volume fraction:  $\phi_i = \frac{V_i}{V}$
- Packing fraction:  $\eta_i = \frac{\pi}{6} \rho_i \sigma_i^3$



# Dilute and Concentrated Solution

Concentrated solution	Dilute solution
A liquid with a high solute concentration is called a concentrated solution.	A liquid with a less solute concentration is called a dilute solution.
The solution becomes more concentrated as more solute is applied to a solution	The dissolved salt from a well in the drinking water is a dilute solution.
There is a significant amount of water in a concentrated solution.	By adding more water, the concentration of a solution can be further decreased and diluted



# Fundamental Property Relation

- $dG = VdP - SdT + \sum_i \mu_i dn_i$
- Chemical potential:  $\mu_i = \left[ \frac{\partial G}{\partial n_i} \right]_{P,T,n_j}$
- $dG_n = V_n dP - S_n dT + \sum_i \mu_i dx_i$

# Partial Properties

- Partial molar properties:  $\bar{M}_i \equiv \left[ \frac{\partial M}{\partial n_i} \right]_{P,T,n_j}$
- A measure of the response of total property to the addition of an infinitesimal amount of species i.

Total properties	Molar properties	Partial properties	Pure-species properties
V	$V_n$	$\bar{V}_i$	$V_i$
U	$U_n$	$\bar{U}_i$	$U_i$
H	$H_n$	$\bar{H}_i$	$H_i$
S	$S_n$	$\bar{S}_i$	$S_i$
G	$G_n$	$\bar{G}_i$	$G_i$

# Some Important Formulas

- Summability:  $M = \sum_i n_i \bar{M}_i$

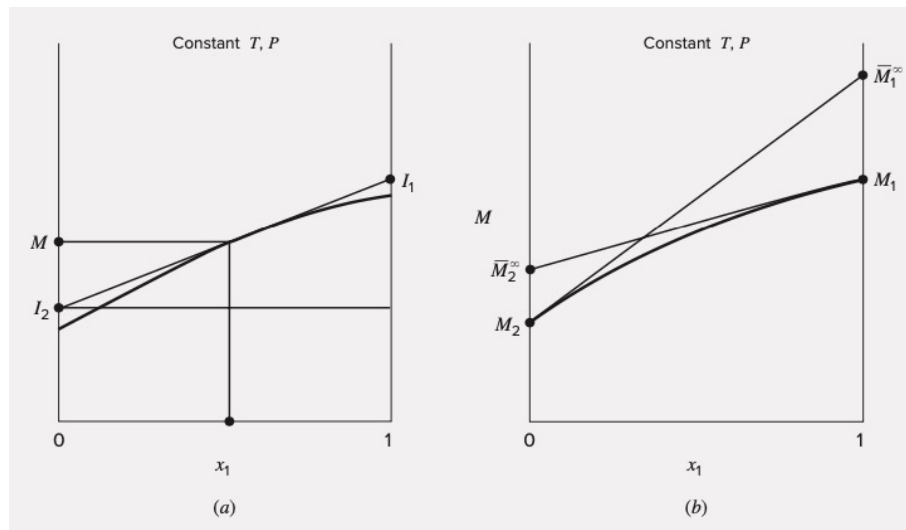
- $\bar{M}_i = M_n - \sum_{k \neq i} x_k \frac{\partial M_n}{\partial x_k}$

- Gibbs-Duhem equation:

$$\left( \frac{\partial M_n}{\partial P} \right)_{T,x} dP + \left( \frac{\partial M_n}{\partial T} \right)_{P,x} dT - \sum_i x_i d\bar{M}_i = 0$$

- In binary system:

$$x_1 \frac{d\bar{M}_1}{dx_1} + x_2 \frac{d\bar{M}_2}{dx_1} = 0$$



# Example

## Molar enthalpy

The enthalpy of a binary liquid system of species 1 and 2 at fixed  $T$  and  $P$  is represented by the equation:

$$H = 400x_1 + 600x_2 + x_1x_2(40x_1 + 20x_2)$$

where  $H$  is in  $\text{J}\cdot\text{mol}^{-1}$ . Determine expressions for  $\bar{H}_1$  and  $\bar{H}_2$  as functions of  $x_1$ , numerical values for the pure-species enthalpies  $H_1$  and  $H_2$ , and numerical values for the partial enthalpies at infinite dilution  $\bar{H}_1^\infty$  and  $\bar{H}_2^\infty$ .



# Partial Properties

Original Properties	Partial Properties
$H = U + pV$	$\bar{H}_i = \bar{U}_i + p\bar{V}_i$
$F = U - TS$	$\bar{F}_i = \bar{U}_i - T\bar{S}_i$
$G = H - TS$	$\bar{G}_i = \bar{H}_i - T\bar{S}_i$
$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p$	$\left(\frac{\partial \bar{H}_i}{\partial p}\right)_T = \bar{V}_i - T\left(\frac{\partial \bar{V}_i}{\partial T}\right)_p$
$c_p = \left(\frac{\partial H}{\partial T}\right)_p$	$\bar{c}_{p_i} = \left(\frac{\partial \bar{H}_i}{\partial T}\right)_p$

# The Ideal-Gas-State Mixture Model

- $\bar{V}_i^{id} = V_{n,i}^{id} = V_n^{id}$
- Partial pressure:  $p_i = y_i P$
- Gibbs' s theorem:  $\bar{M}_i^{id}(T, P) = M_{n,i}^{id}(T, p_i)$
- Entropy:  $\bar{S}_i^{id} = S_{n,i}^{id} - R \ln y_i$
- Gibbs free energy:  $\bar{G}_i^{id} = G_{n,i}^{id} + RT \ln y_i$

# Mixing in ideal-gas state

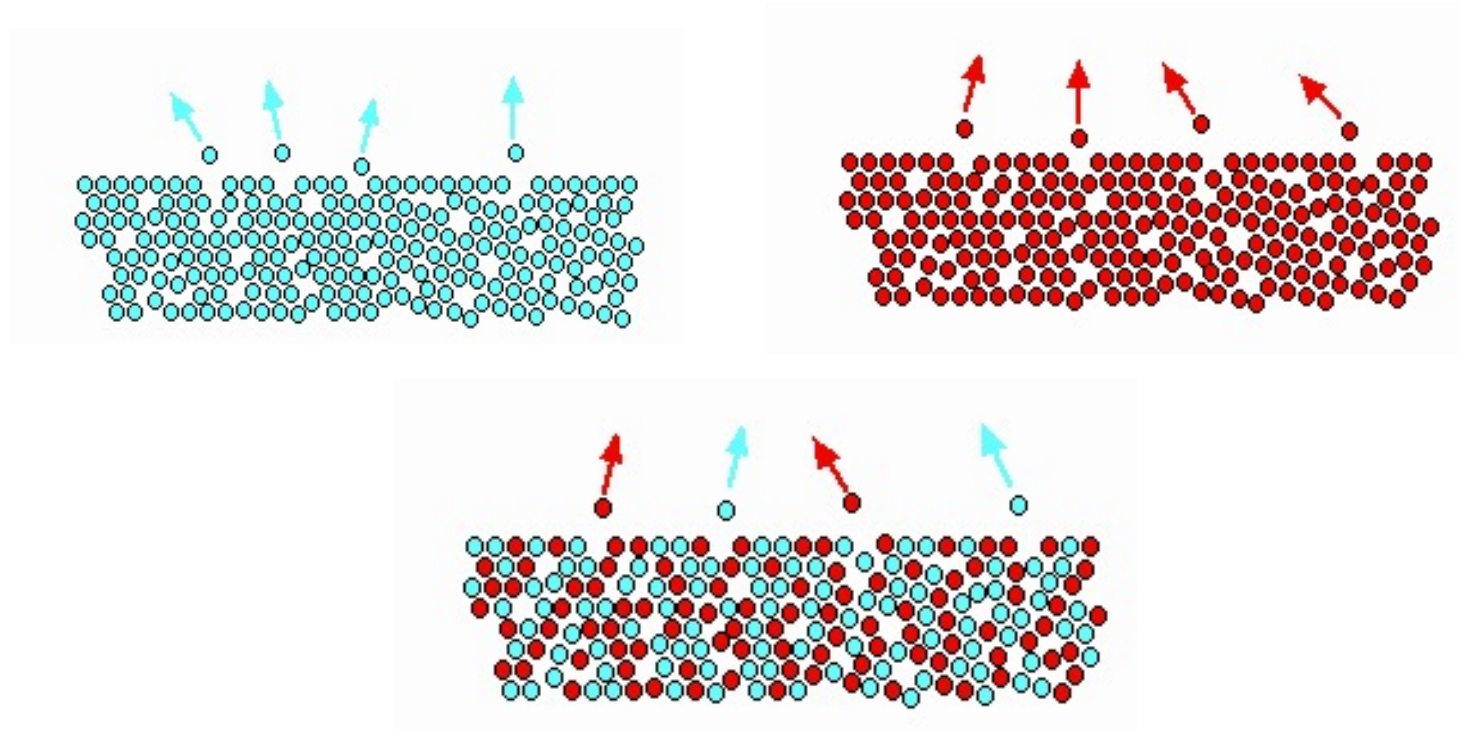
$$H_n^{id} = \sum_i y_i H_{n,i}^{id}$$

$$S_n^{id} = \sum_i y_i S_{n,i}^{id} - R \sum_i y_i \ln y_i$$

$$G_n^{id} = \sum_i y_i G_{n,i}^{id} + RT \sum_i y_i \ln y_i$$

- $\Delta H_{mix} = 0$
- $\Delta S_{mix} = -nR \sum y_i \ln y_i$
- $\Delta G_{mix} = nRT \sum y_i \ln y_i$

# Fugacity



**In an ideal mixture, the tendency of the two types of molecules to escape is the same as that in pure species.**

**In a real mixture, the tendency depends on the interaction between molecules.**

# Fugacity

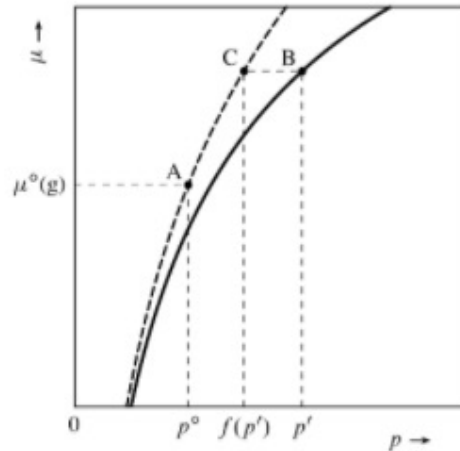
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- A measure of the tendency of a fluid to escape or expand
- Measure the behaviors deviating from ideal-gas
- Depends on molecular interactions
- The pressure value needed at a given  $T$  to make the properties of a non-ideal gas satisfy the equation for an ideal gas

# Fugacity of Pure Species

- Ideal gas:  $d\mu = RT d \ln P$
- Real fluid:  $d\mu = RT d \ln f$
- Residual Gibbs free energy:  $G_n^R = RT \ln \frac{f}{P}$
- Fugacity coefficient:  $\phi \equiv \frac{f}{P}$
- $\ln \phi = \int_0^P (Z - 1) \frac{dP}{P}$

# Fugacity



**Figure 7.6** Chemical potential as a function of pressure at constant temperature, for a real gas (solid curve) and the same gas behaving ideally (dashed curve). Point A is the gas standard state. Point B is a state of the real gas at pressure  $p'$ . The fugacity  $f(p')$  of the real gas at pressure  $p'$  is equal to the pressure of the ideal gas having the same chemical potential as the real gas (point C).

# Fugacity of a Pure Liquid

$$f_i^l(P) = \underbrace{\frac{f_i^v(P_i^{\text{sat}})}{P_i^{\text{sat}}}}_{(A)} \underbrace{\frac{f_i^l(P_i^{\text{sat}})}{f_i^v(P_i^{\text{sat}})}}_{(B)} \underbrace{\frac{f_i^l(P)}{f_i^l(P_i^{\text{sat}})} P_i^{\text{sat}}}_{(C)}$$

- A: vapor-phase fugacity coefficient
- B: Ratio of liquid-phase fugacity to vapor-phase fugacity
- C: The effect of pressure on the fugacity
- Evaluate the fugacity of compressed liquid by using the data at saturation



# Example

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For  $\text{H}_2\text{O}$  at a temperature of  $300^\circ\text{C}$  and for pressures up to  $10,000\text{ kPa}$  ( $100\text{ bar}$ ) calculate values of  $f_i$  and  $\phi_i$  from data in the steam tables and plot them vs.  $P$ .

# Fugacity of Species in Solution

- Fugacity in solution:  $d\mu_i = RT d \ln \hat{f}_i$
- Fugacity residual:  $\mu_i - \mu_i^{ig} = RT \ln \frac{\hat{f}_i}{y_i P}$
- Fugacity coefficient:  $\hat{\phi}_i = \frac{\hat{f}_i}{y_i P}$

# Some Important Formulas

- $\frac{V_n^R}{RT} = \left[ \frac{\partial \left( \frac{G_n^R}{RT} \right)}{\partial P} \right]$
- $\frac{H_n^R}{RT} = -T \left[ \frac{\partial \left( \frac{G_n^R}{RT} \right)}{\partial T} \right]$
- $\ln \hat{\phi}_i = \left[ \frac{\partial \left( \frac{G^R}{RT} \right)}{\partial n_i} \right]$
- $\ln \hat{\phi}_i = \int_0^P (\bar{Z}_i - 1) \frac{dP}{P}$

# Fugacity Coefficients from the Virial EOS

- $Z = 1 + \frac{BP}{RT}$
- $B = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22}$
- $\delta_{12} = 2B_{12} - B_{11} - B_{22}$
- $\ln \hat{\phi}_1 = \frac{P}{RT} (B_{11} + y_2^2 \delta_{12})$
- $\ln \hat{\phi}_2 = \frac{P}{RT} (B_{22} + y_1^2 \delta_{12})$

# Generalized Correlations for the Fugacity Coefficient

- $\ln \phi_i = \int_0^{P_r} (Z_i - 1) \frac{dP_r}{P_r}$
- $\ln \phi = \int_0^{P_r} (Z^0 - 1) \frac{dP_r}{P_r} + \omega \int_0^{P_r} Z^1 \frac{dP_r}{P_r}$

# Ideal Gases versus Ideal Solutions

- Ideal gas: molecules occupy no volume; no intermolecular interactions; real gas at low pressure
- Ideal solution: molecules exhibit the same intermolecular interactions between all constituents; dilute solution or mixtures of molecularly-similar materials

ideal gas

$$\Delta v_{mix}^{ig} = 0$$

$$\Delta h_{mix}^{ig} = 0$$

$$\Delta s_{mix}^{ig} = -R \sum_i y_i \ln[y_i]$$

$$\Delta g_{mix}^{ig} = RT \sum_i y_i \ln[y_i]$$

ideal solution

$$\Delta v_{mix}^{is} = 0$$

$$\Delta h_{mix}^{is} = 0$$

$$\Delta s_{mix}^{is} = -R \sum_i x_i \ln[x_i]$$

$$\Delta g_{mix}^{is} = RT \sum_i x_i \ln[x_i]$$

# Ideal Solution

- The gas phase of the solution exhibits properties analogous of ideal gas mixtures
- Ideal gas:  $\mu_i^{ig} \equiv \bar{G}_i^{ig} = G_{n,i}^{ig}(T, P) + RT \ln y_i$
- Ideal solution:  $\mu_i^{id} \equiv \bar{G}_i^{id} = G_{n,i}(T, P) + RT \ln x_i$
- $\bar{V}_i^{id} = V_{n,i}$
- $\bar{S}_i^{id} = S_{n,i} - R \ln x_i$
- $\bar{H}_i^{id} = H_{n,i}$

# Ideal Solution

- $G_n^{id} = \sum_i x_i G_{n,i} + RT \sum_i x_i \ln x_i$
- $S_n^{id} = \sum_i x_i S_{n,i} - R \sum_i x_i \ln x_i$
- $V_n^{id} = \sum_i x_i V_{n,i}$
- $H_n^{id} = \sum_i x_i H_{n,i}$



# Lewis/Randall Rule

- $\mu_i = \Gamma_i(T) + RT \ln \hat{f}_i$
- $G_i = \Gamma_i(T) + RT \ln f_i$
- $\hat{f}_i^{id} = x_i f_i$
- $\hat{\phi}_i^{id} = \phi_i$

The fugacity of each species in an ideal solution is proportional to its mole fraction.

# Excess Properties

- Excess properties:  $M^E \equiv M - M^{id}$
- Residual properties:  $M^R \equiv M - M^{ig}$
- $M^E = M^R - \sum_i x_i M_i^R$
- $d \left( \frac{G^E}{RT} \right) = \frac{V^E}{RT} dP - \frac{H^E}{RT^2} dT + \sum_i \frac{\bar{G}_i^E}{RT} dn_i$

# Typical Solution Models

- Regular solution:  $S^E = 0$
- Athermal solution:  $H^E = 0$
- Ideal solution

	Ideal solution	Regular solution	Athermal solution
$\Delta H_{mix}$	0	$\neq 0$	0
$\Delta S_{mix,m}$	$-k_B(x_1 \ln \phi_1 + x_2 \ln \phi_2)$	$-k_B(x_1 \ln \phi_1 + x_2 \ln \phi_2)$	$-k_B(x_1 \ln \phi_1 + \frac{x_2}{N} \ln \phi_2)$

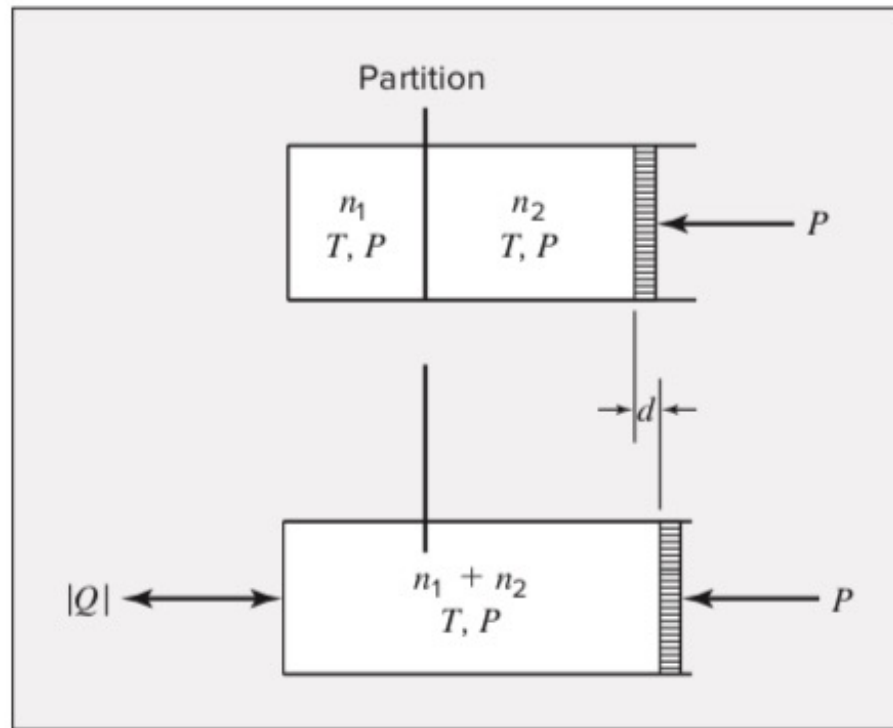
$x_1, x_2$  : molar fraction

$\phi_1, \phi_2$  : volume fraction

$$\left\{ \begin{array}{l} x_1 = \frac{\phi_1 V_A}{\phi_1 V_A + \phi_2 V_B} \\ x_2 = \frac{\phi_2 V_B}{\phi_1 V_A + \phi_2 V_B} \end{array} \right.$$

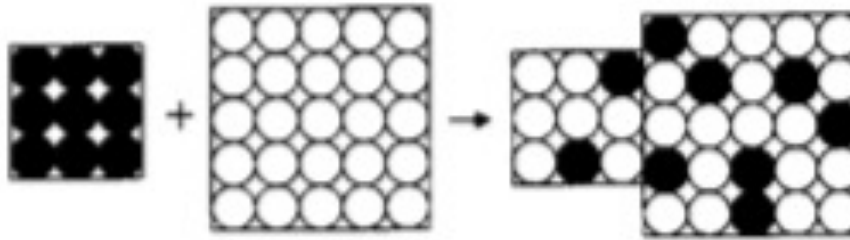
# Mixing Processes

- Standard mixing process: mixing at constant  $T$  and  $P$ .



# Entropy of Binary Random Mixing

- $\Delta \bar{S}_{\text{mix}} = -k \left[ \frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B \right]$
- $\Delta \bar{F}_{\text{mix}} = kT \left[ \frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B \right]$



# Energy of Binary Mixing

- Flory interaction parameter:

$$\chi \equiv \frac{z}{2kT} (2u_{AB} - u_{AA} - u_{BB})$$

- Free energy of mixing

$$\Delta \bar{F}_{mix} = kT \left[ \frac{\phi}{N_A} \ln \phi + \frac{1 - \phi}{N_B} \ln(1 - \phi) + \chi \phi(1 - \phi) \right]$$

# $\chi$ parameter

- $\chi(T) \approx A + \frac{B}{T}$

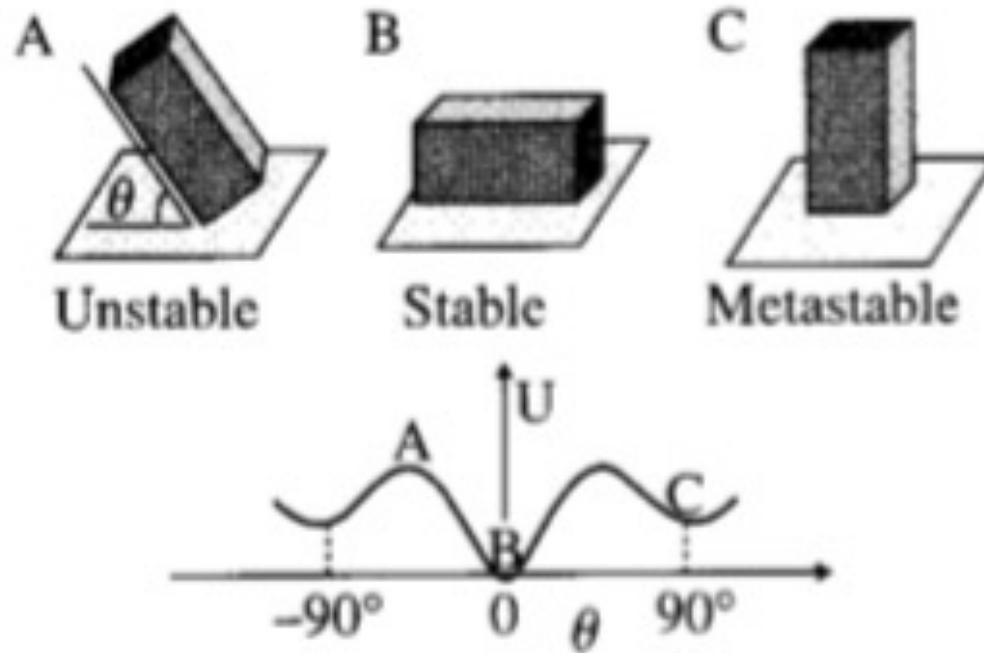
**Table 4.3** Temperature dependence of the Flory interaction parameters of polymer blends [Eq. (4.31)] with  $v_0 = 100 \text{ \AA}^3$

Polymer blend	$A$	$B$ (K)	$T$ range ( $^{\circ}\text{C}$ )
$d\text{PS}/\text{PS}$	-0.00017	0.117	150–220
$d\text{PS}/\text{PMMA}$	0.0174	2.39	120–180
$\text{PS}/d\text{PMMA}$	0.0180	1.96	170–210
$\text{PS}/\text{PMMA}$	0.0129	1.96	100–200
$d\text{PS}/d\text{PMMA}$	0.0154	1.96	130–210
$\text{PVME}/\text{PS}$	0.103	-43.0	60–150
$d\text{PS}/\text{PPO}$	0.059	-32.5	180–330
$d\text{PS}/\text{TMPC}$	0.157	-81.3	190–250
$\text{PEO}/d\text{PMMA}$	-0.0021	–	80–160
$\text{PP}/\text{hhPP}$	-0.00364	1.84	30–130
$\text{PIB}/d\text{hhPP}$	0.0180	-7.74	30–170

$d\text{PS}$ —deuterated polystyrene;  $\text{PS}$ —polystyrene;  $\text{PMMA}$ —poly(methyl methacrylate);  $d\text{PMMA}$ —deuterated poly(methyl methacrylate);  $\text{PVME}$ —poly(vinyl methyl ether);  $\text{PPO}$ —poly(2,6-dimethyl 1,4-phenylene oxide);  $\text{TMPC}$ —tetramethylpolycarbonate;  $\text{PEO}$ —poly(ethylene oxide);  $\text{PP}$ —polypropylene;  $\text{hhPP}$ —head-to-head polypropylene;  $\text{PIB}$ —polyisobutylene;  $d\text{hhPP}$ —deuterium labelled head-to-head polypropylene (after N. P. Balsara, *Physical Properties of Polymers Handbook*, AIP Press, 1996, Chapter 19).

# Stability

- Unstable, stable, metastable



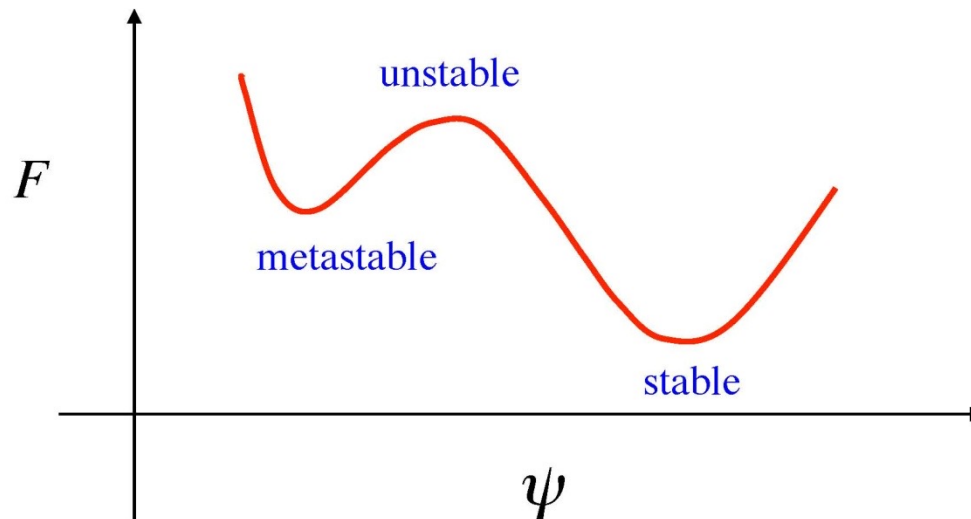


# Stable, Metastable and Unstable States

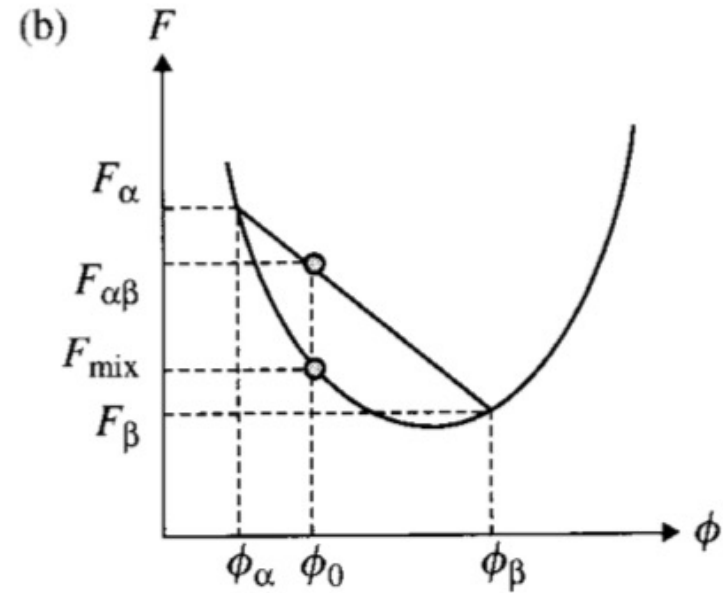
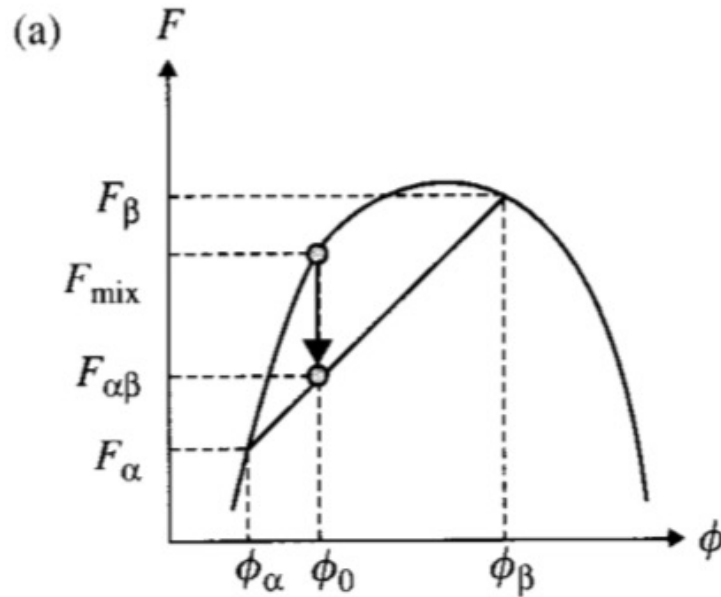
Equilibrium condition:  $\frac{\partial F}{\partial \psi} = 0$

Thermodynamic stability (under isothermal condition):

$$\frac{\partial^2 F}{\partial \psi^2} > 0 \quad (\text{a local condition})$$



# Stability



$$\frac{\partial^2 F_{\text{mix}}}{\partial \phi^2} < 0 \quad \text{unstable,}$$

$$\frac{\partial^2 F_{\text{mix}}}{\partial \phi^2} > 0 \quad \text{locally stable.}$$

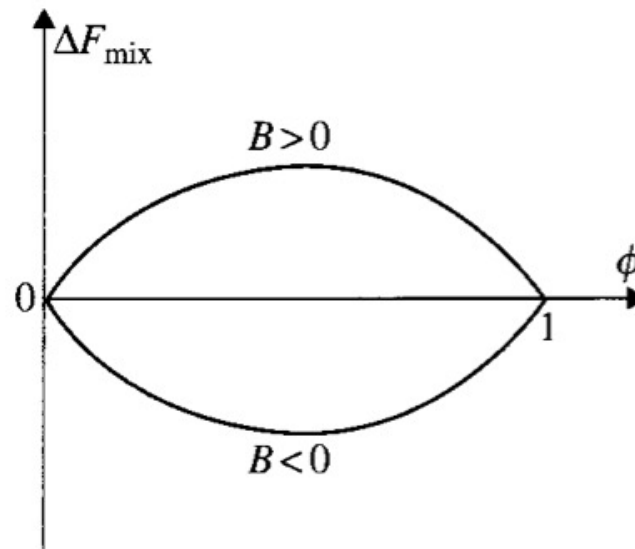
# Ideal mixture

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- Ideal mixture are stable always
- Entropy always acts to promote mixing
- Principle of entropy increase

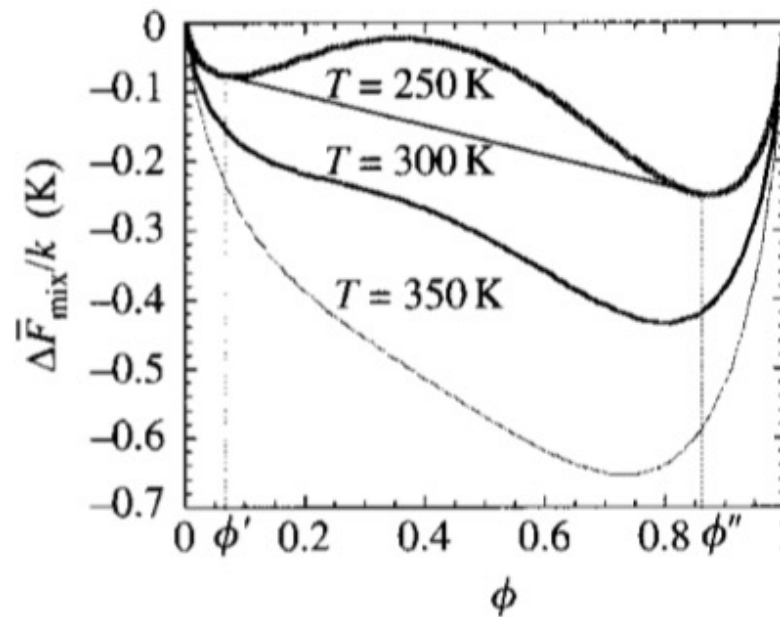
# Mixing at $T=0$ K

- The mixing free energy is determined by the energy of mixing
- $\chi = A + \frac{B}{T}$
- $B > 0$ : mixing is unfavorable
- $B < 0$ : mixing is favorable



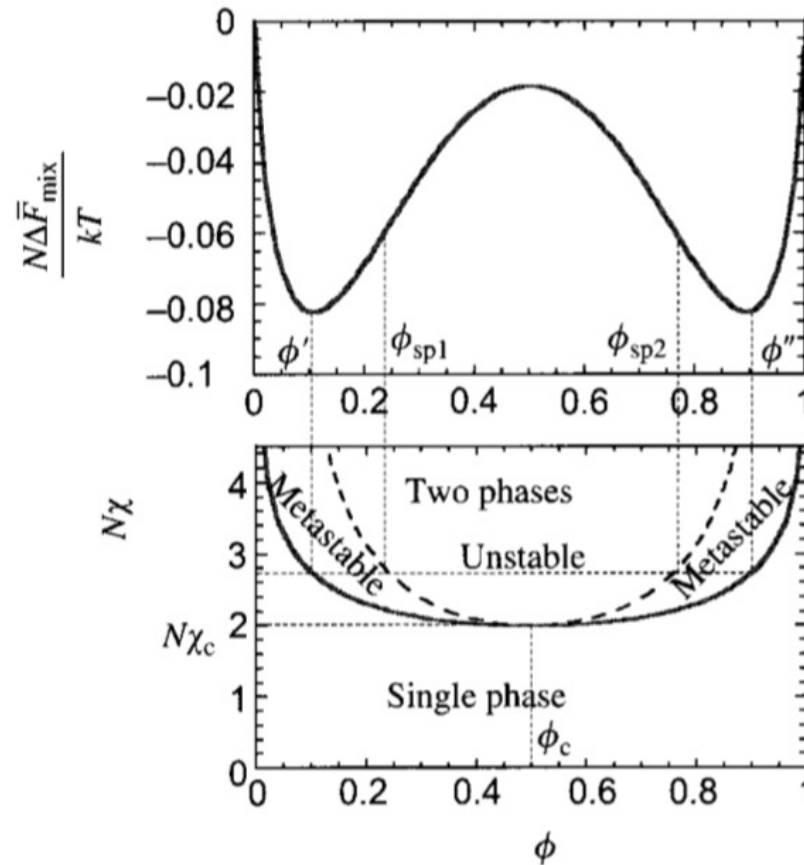
# Real Mixture

- Common tangent rule
- Chemical potentials are balanced at equilibrium

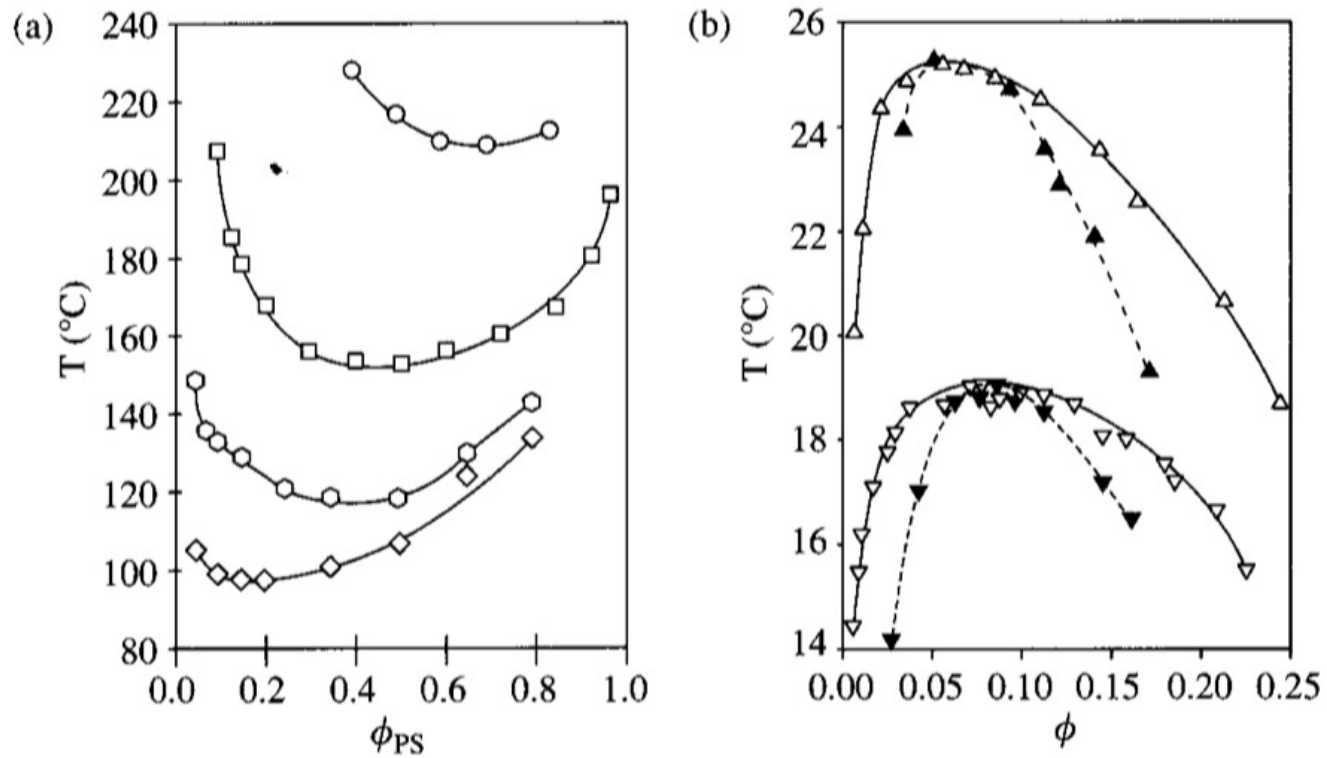


# Phase diagram

- Binodal
- Spinodal
- Critical point



# UCST and LCST



# Summary Points

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- Partial properties
- Fugacity
- Ideal solution
- Excess properties
- Flory-Huggins theory
- Metastability