

Chapter 10



Polymers in Solution

Solution thermodynamics

□ solution = mixing solvent (1) and solute (2)

□ $\Delta G_m = G_{12} - (G_1 + G_2)$

□ $\Delta G_m = \Delta H_m - T \Delta S_m$

□ $\Delta S_m > 0$ always

□ $\Delta H_m > 0$ almost always

■ "like dissolves like"

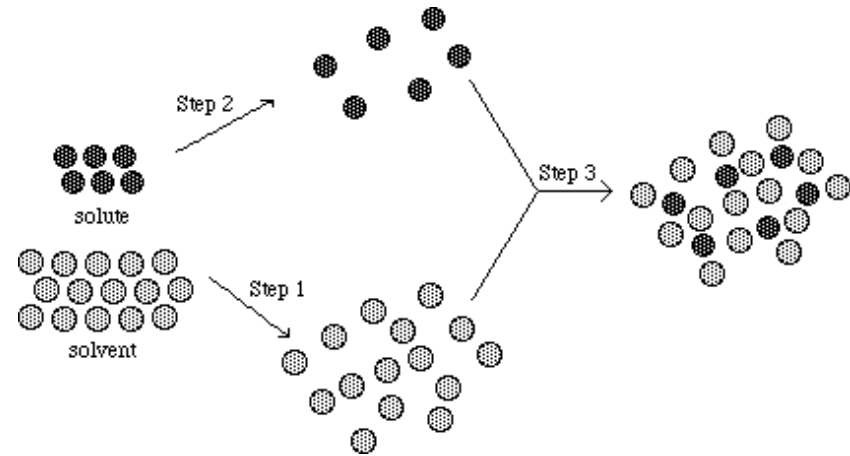
■ $\Delta H_m = 0$ at best (when solute is the same to solvent)

■ if not, $\Delta H_m > 0$

■ $\Delta H_m < 0$ only when specific interaction like H-bonding exists

□ For solution, $\Delta H_m < T \Delta S_m$

■ $G_{12} < (G_1 + G_2)$

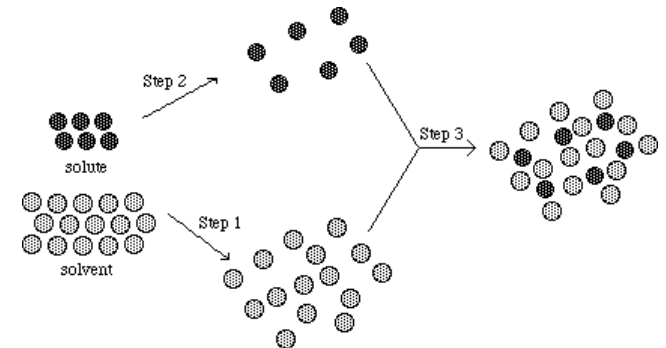


Solubility parameter $\leftarrow \Delta H_m$

$$\begin{aligned}\square \Delta H_m &= V_m [(\Delta E_1/V_1)^{1/2} - (\Delta E_2/V_2)^{1/2}]^2 \phi_1\phi_2 \\ &= V_m [\delta_1 - \delta_2]^2 \phi_1\phi_2\end{aligned}$$

Eqn (10.58) p250

- $\phi \sim$ volume fraction
- $\Delta E \sim$ cohesive energy \sim energy change for vaporization
 - $\Delta E = \Delta H_{\text{vap}} - P\Delta V \approx \Delta H_{\text{vap}} - RT$ [J]
- $\Delta E/V \sim$ cohesive energy density [J/cm³ = MPa]
- $\delta \sim$ **solubility parameter** [MPa^{1/2}] = [(J/cm³)^{1/2}] \approx [(1/2)(cal/cm³)^{1/2}]
- δ (ΔE , CED) depends on intermolecular interaction
 - dispersion force
 - polar interaction
 - H-bonding



- For solution,
 - $\Delta H_m < T \Delta S_m$
 - without specific interaction
 - $\delta_1 = \delta_2 \rightarrow \Delta H_m = 0 \rightarrow \Delta G_m < 0$
 - $\Delta\delta < 20 \text{ MPa}^{1/2}$ for solvent/solvent solution
 - $\Delta\delta < 2 \text{ MPa}^{1/2}$ for solvent/polymer solution
 - Why? smaller ΔS_m
 - $\Delta\delta \approx 0$ for polymer/polymer solution

TABLE 10.2
Solubility Parameters for Common Solvents and Polymers

Solvent	$\delta / \text{J}^{1/2} \text{cm}^{-3/2}$	Polymer	$\delta / \text{J}^{1/2} \text{cm}^{-3/2}$
Acetone	20.3	Polyethylene	16.4
Carbon tetrachloride	17.6	Polystyrene	18.5
Chloroform	19.0	Poly(methyl methacrylate)	19.0
Cyclohexane	16.8	Polypropylene	17.2
Methanol	29.7	Poly(vinyl chloride)	20.0
Toluene	18.2		
Water	47.9		
Xylene	18.0		

for amorphous state at 25 °C

□ PP soluble in cx? No.

Semicrystalline polymers are not soluble at RT.

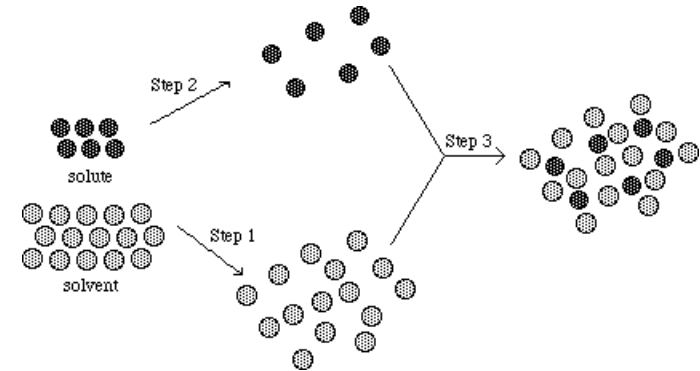
■ positive $\Delta H_{\text{fusion}} \rightarrow \Delta H_{\text{fusion}} + \Delta H_{\text{m}} > T \Delta S_{\text{m}}$

■ soluble at higher temperature ~ PP in p-xylene at above 100 °C

■ solubilize using specific interaction ~ PET in formic acid (H-bonding)

Ideal solution

- ideal solution $\sim \Delta H_m = 0$
 - size of 1 and 2 the same
 - interaction energy, $h_{1-1} = h_{2-2} = h_{1-2}$



- ΔG_m of ideal solution
 - $\Delta G_1 = \mu_1 - \mu_1^0 = RT \ln X_1$
 $\Delta G_2 = \mu_2 - \mu_2^0 = RT \ln X_2$
 - $\Delta G_m = n_1 \Delta G_1 + n_2 \Delta G_2$
 $= RT (n_1 \ln X_1 + n_2 \ln X_2)$

μ ~ chemical potential
 n ~ number of moles
 X ~ mole fraction
 $X_1 = n_1 / (n_1 + n_2)$

- ΔS_m of ideal solution
 - $\Delta H_m = 0 \rightarrow \Delta S_m = -R (n_1 \ln X_1 + n_2 \ln X_2)$

ΔS_m from statistical thermodynamics

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- lattice model
 - filling N_1 and N_2 molecules in $N_1 + N_2 = N_0$ cells
 - volume of 1 \approx volume of 2 (for small molecules)
- Boltzmann relation, $S = k \ln \Omega$
 - $S \sim$ combinatorial [configurational] entropy
 - $\Omega \sim$ number of (distinguishable) ways

- $$\Delta S_m^{\text{comb}} = S_{12} - S_1 - S_2$$

$$= k[\ln \Omega_{12} - (\ln \Omega_1 + \ln \Omega_2)]$$
 - $S_1 = k \ln \Omega_1 = k \ln (N_1! / N_1!) = 0 = S_2$
 - $S_{12} = k \ln \Omega_{12} = k \ln [(N_1 + N_2)! / N_1! N_2!]$

Stirling's approximation, $\ln N! = N \ln N - N$ (for large N)

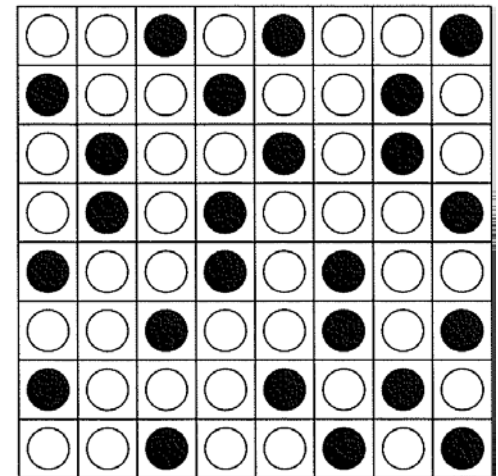


Fig 10.1 p230

$$\Delta S_m^{\text{comb}} = -R[n_1 \ln X_1 + n_2 \ln X_2]$$

ΔS_m of polymer solution

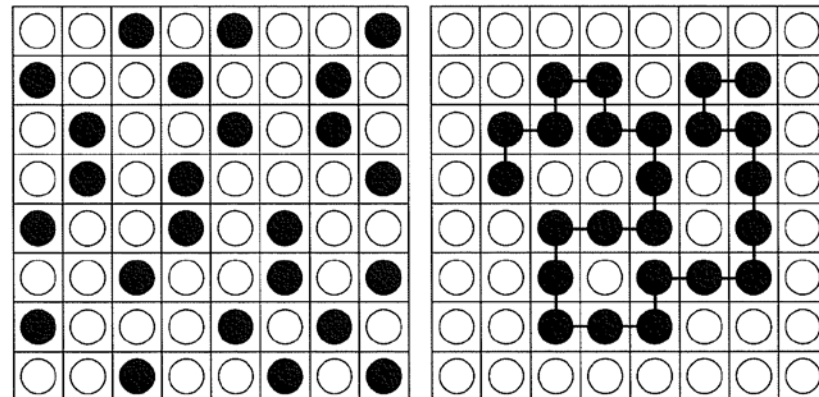
- ❑ developed by Flory and Huggins
- ❑ lattice model
 - ❑ filling N_1 solvents and N_2 polymers in $N_1 + xN_2 = N_0$ cells
 - volume of 1 \ll volume of 2 (by x ; $x \sim$ deg of polym'n)
 - ❑ $\Delta S_m = S_{12} - S_1 - S_2 = k \ln [\Omega_{12}/\Omega_1\Omega_2] = k \ln [\Omega_{12}/\Omega_2]$
 - $\Omega_1 = 0$; $\Omega_2 \neq 0$ (connected)

$$\Delta S_m^{\text{comb}} = -R[n_1 \ln \phi_1 + n_2 \ln \phi_2]$$

n ~ number of moles
 ϕ ~ volume fraction
 $\phi_1 = N_1/(N_1 + xN_2)$

pp239-243
 for derivation

- ❑ $x \uparrow$ (mol wt \uparrow) $\rightarrow n_2 \downarrow \rightarrow \Delta S_m \downarrow$
- ❑ for polymer/polymer soln,
 ΔS_m even smaller (n_1 & $n_2 \downarrow$)



$$\square \Delta G_m = \Delta H_m - T \Delta S_m$$

\square in original F-H theory

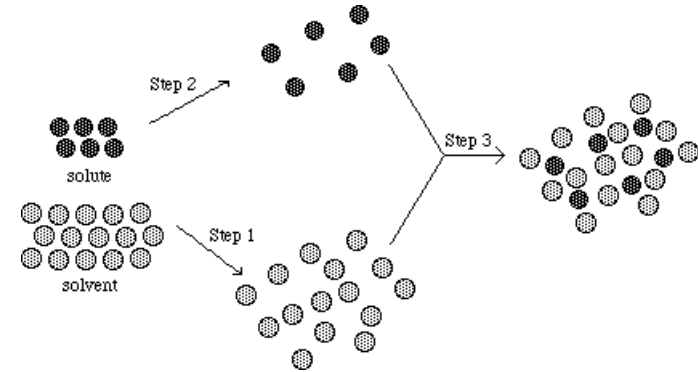
$$\begin{aligned} \Delta H_m &= N_1 z X_2 [h_{12} - \frac{1}{2}(h_{11} + h_{22})] \\ &= kT N_1 \phi_2 \chi \end{aligned}$$

\square modified \leftarrow entropy change with interaction

$$\Delta G_m^{\text{contact}} = RT n_1 \phi_2 \chi$$

\square $\chi \sim$ (F-H polymer-solvent) **interaction parameter**

\square $\chi \downarrow \rightarrow \Delta H_m \downarrow \rightarrow$ solvent power \uparrow



$$\begin{aligned} \chi &= \chi_1 = \chi_{12} \\ \chi &= \chi_H + \chi_S \end{aligned}$$

$$\square \Delta H_m = V_m [\delta_1 - \delta_2]^2 \phi_1 \phi_2 \rightarrow \chi_H = \frac{V_1 (\delta_1 - \delta_2)^2}{RT}$$

Flory-Huggins equation

$$\square \Delta G_m = \Delta H_m - T \Delta S_m$$

$$\Delta G_m = \Delta G_m^{\text{contact}} - T \Delta S_m^{\text{comb}}$$

$$\Delta S_m^{\text{comb}} = -\mathbf{R}[n_1 \ln \phi_1 + n_2 \ln \phi_2]$$

$$\Delta G_m^{\text{contact}} = \mathbf{RT}n_1\phi_2\chi$$

$$\Delta G_m = \mathbf{RT}[n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1\phi_2\chi]$$

- F-H theory predicts polymer solution property,
 - solubility, miscibility, phase separation, fractionation, ---
 - vapor pressure, boiling point, ---
- but not that precisely.
 - due to drawbacks of theory like
 - no volume change, self-intersection, changing χ
 - especially for dilute polymer solution
 - Chains are separated in dilute soln.