

Scan Table 3.3 here

Table 3.3 Group molar attraction constants at 25°C (according to Small; derived from measurement of heat of evaporation)¹

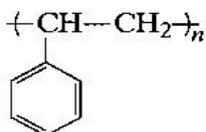
| Group | G° | Group | G | Group | G |
|----------------------------------|------|------------------------------------|---------|---|------|
| -CH ₃ | 214 | Ring 5-membered | 105-115 | Br single | 340 |
| -CH ₂ - single-bonded | 133 | Ring 6-membered | 95-105 | I single | 425 |
| -CH< | 28 | Conjugation | 20-30 | CF ₂ } n-fluorocarbons only | 150 |
| >C< | -93 | H (variable) | 80-100 | CF ₃ } | 274 |
| CH ₂ = | 190 | O ethers | 70 | S sulfides | 225 |
| -CH= double-bonded | 111 | CO ketones | 275 | SH thiols | 315 |
| >C= | 19 | COO esters | 310 | ONO nitrates | -440 |
| -CH=C< | 285 | CN | 410 | NO ₂ (aliphatic nitro-compounds) | -440 |
| -C=C- | 222 | Cl (mean) | 260 | PO ₄ (organic phosphates) | -500 |
| Phenyl | 735 | Cl single | 270 | Si (in silicones) | -38 |
| Phenylene (o, m, p) | 658 | Cl twinned as in >CCl ₂ | 260 | | |
| Naphthyl | 1146 | Cl triple as in -CCl ₃ | 250 | | |

Source: P. A. Small, *J. Appl. Chem.*, 3, 71 (1953).

¹Units of G = (cal-cm³)^{1/2}/mol.

²The solubility parameter can be calculated via $\delta = \rho \Sigma G/M$, where M is the mer molecular weight.

For example, the solubility parameter of polystyrene may be estimated from Table 3.3. The structure is



which contains -CH₂- with a G value of 133, a -CH- with G equal to 28, and a phenyl group with G equal to 735. The density of polystyrene is 1.05 g/cm³, and the mer molecular weight is 104 g/mol. Then equation (3.5) gives

$$\delta = \frac{1.05}{104} (133 + 28 + 735) \quad (3.6)$$

$$\delta = 9.05 (\text{cal/cm}^3)^{1/2} \quad (3.7)$$

Table 3.2 gives a value of 9.1 (cal/cm³)^{1/2} for polystyrene.

HW Problem 1

Calculate the sp's for TMPTA, and two isocyanurates in Supplement.

3.3 Thermodynamics of mixing

3.3.1 Types of solutions

3.3.1.1 The Ideal solution

In 3.2, **solubility** of a **polymer** in a **solvent** was examined in terms of their respective ΔG_M , which was governed by heat of mixing. **The entropy of mixing is entirely ignored.**

Ideal solution (See the Supplement)

Interactions between **A-A = B-B = A-B**

$$\Delta V_M = 0, \Delta H_M = 0$$

Ideal solution follows Raoult's law.

$$p_i = p_i^\circ n_i \quad (3.8)$$

p_i = Partial pressure of component, i

p_i° = Vapor pressure of pure i

n_i = Mole fraction of component, i in the solution

The free energy of mixing (ΔG_M) = \sum Free energies of dilution per molecule (Incompressibility assumed)

$$\Delta G_M = N_1 \Delta G_1 + N_2 \Delta G_2 \quad (3.9)$$

$$\Delta G_M = kT \left[N_1 \ln \left(\frac{p_1}{p_1^0} \right) + N_2 \ln \left(\frac{p_2}{p_2^0} \right) \right] \quad (3.10)$$

k =Boltzmann constant, T =Absolute temperature

N_1, N_2 , = Number of molecules for component, 1 and 2.

From Section 3.9 (E&R) (*italic*)

$$\Delta G_{mix} = n \text{ (moles)} RT \sum x_j \ln x_j = n' \text{ (molecules)} kT \sum x_i \ln x_i = kT \sum n_i \ln x_i = (3.11)$$

$$\langle nk = (n/N_A) N_A k = NR \text{ (Note } k=R/N_A) \rangle$$

Plug 3.8 into 3.10,

$$\Delta G_M = kT [N_1 \ln n_1 + N_2 \ln n_2] \quad (< \mathbf{0}) \quad (3.11)$$

$\Delta G_M < 0$: Necessary, but not sufficient condition for miscibility

Since $\Delta H_M = 0$ for ideal solution ($\Delta G_M = \Delta H_M - T\Delta S_M$),
entropy of mixing becomes

$$\Delta S_M = -k [N_1 \ln n_1 + N_2 \ln n_2] \quad (> \mathbf{0}) \quad (3.12)$$

$\Delta S_M > 0 \rightarrow$ Mixing always occurs spontaneously for ideal solution.

3.3.1.2 Statistical thermodynamics of mixing

Eq (3.12) can be derived from the statistical thermodynamics as follow.

Boltzmann Eq.

$$\Delta S_M = k \ln \Omega \quad (13)$$

Ω = Total number of ways of arranging N_2 identical solute molecules in

$N_0 = N_1 + N_2$ lattice slots and N_1 solvent molecules in N_0 (Figure 3.3).

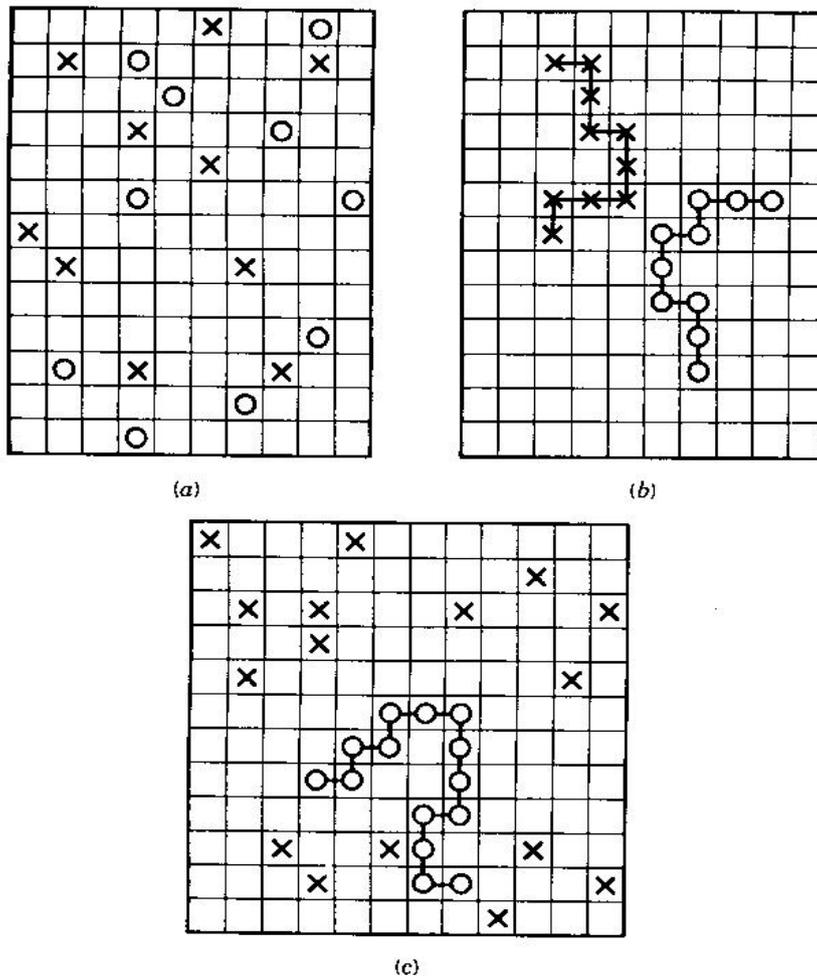


Figure 3.3 Illustration of two types of molecules on quasilattice structures. (a) Two types of molecules; (b) a blend of two types of polymer molecules; (c) a polymer dissolved in a solvent. The entropy of mixing decreases from (a) to (c) to (b) because the number of different ways of arranging the molecules in space decreases. Note that the mers of the polymer chains are constrained to remain in juxtaposition with their neighbors.

The total number of arrangement is given by,

$$\Omega = N_o! / (N_1! N_2!) \quad (a)$$

Make use of String's approximation:

$$\ln N! = N \ln N - N \quad (3.14)$$

Plug (a) into (13), and apply String's formula,

$$\Delta S_M = k \ln \Omega = k \ln N_o! / (N_1! N_2!) = k[(N_o \ln N_o - N_o) - (N_1 \ln N_1 - N_1) - (N_2 \ln N_2 - N_2)]$$

$$= k [(N_1 + N_2) \ln N_o - N_1 - N_2 - N_1 \ln N_1 + N_1 - N_2 \ln N_2 + N_2]$$

$$= k [(N_1 + N_2) \ln(N_1 + N_2) - N_1 \ln N_1 - N_2 \ln N_2] \quad (3.15)$$

$$= k[(N_1 + N_2) \ln N_o - N_1 \ln N_1 - N_2 \ln N_2]$$

Rearrange this to get (12)

$$= -k [N_1(\ln N_1 - \ln N_o) + N_2(\ln N_2 - \ln N_o)]$$

$$= -k [N_1 \ln N_1 / N_o + N_2 \ln N_2 / N_o]$$

$$= -k [N_1 \ln n_1 + N_2 \ln n_2] \quad (12)$$

Above was driven for low molecular weight solute and solvent where one molecule occupies one lattice slot)

When the polymer has x chain segments (mers) the total entropy of mixing is given by

$$\Delta S_M = -k(N_1 \ln v_1 + N_2 \ln v_2) \quad (3.16)$$

For unit volume,

$$\frac{\Delta S_M}{kV} = - \frac{\sum_i N_i \ln v_i}{\sum_i V_i} \quad (3.16a) \quad \langle \text{For ideal solution } V = \sum_i V_i \rangle$$

v_1 = Volume fraction of solvent

v_2 = Volume fraction of polymer

For polymer – solvent solution:

$$v_1 = \frac{N_1}{N_1 + xN_2} \quad (3.17)$$

$$v_2 = \frac{xN_2}{N_1 + xN_2} \quad (3.18)$$

For polymer-polymer solution:

$$v_1 = \frac{x_1 N_1}{x_1 N_1 + x_2 N_2} \quad (3.19)$$

$$v_2 = \frac{x_2 N_2}{x_1 N_1 + x_2 N_2} \quad (3.20)$$

ΔS_M is the combinatorial entropy computed by considering the possible arrangements of the molecules on the lattice (Figure 3.3).

The number of ways that the system can be rearranged is reduced when one or both of the species exist as long chains.

3.1.3.3 Other types of solutions

Ideal solution ($\Delta V=0$)

$$\Delta H_M = 0, \quad \Delta S_M = -k(N_1 \ln v_1 + N_2 \ln v_2)$$

► Athermal solution; $\Delta H_M=0$,
$$\Delta S_M \neq -k(N_1 \ln v_1 + N_2 \ln v_2) \quad (3.16)$$

► Regular solution (Close to ideal solution)

$$\Delta S_M=0, \quad \Delta H_M = \text{Finite}$$

► Nonideal solutions; $\Delta S_M \neq 0$, $\Delta H_M \neq 0$

Note Hildebrand's use of **ideal as a good solvent** is different from \ominus **temperature** (3.5), which involves a thermodynamically poor solvent.

3.3.2 Dilute Solutions (P J Flory)

Flory-Huggins theory introduced the dimensionless parameter χ_1 to represent the **heat of mixing**;

$$\chi_1 = \frac{\Delta H_M}{kTN_1v_2} \quad (3.21)$$

Subing (21, ΔH_M) and (16, ΔS_M) in ($\Delta G_M = \Delta H_M - T\Delta S_M$) gives

$$\Delta G_M = kT[N_1 \ln v_1 + N_2 \ln v_2 + \chi_1 N_1 v_2] \quad (3.22)$$

Entropy terms < 0 Enthalpy term > 0

$\Delta G_M > 0 \rightarrow$ Phase separation

$\Delta G_M < 0 \rightarrow$ Molecular solution (Necessary condition for miscibility)

Eq (22) is the starting point of many eqs

► The partial molar free energy of mixing:

Differentiate (22) wrt N_1 , and use n (molecules) $k=N$ (moles) $R \rightarrow$

$$\overline{\Delta G_1} = RT \left[\ln(1 - v_2) + \left(1 - \frac{1}{x}\right) v_2 + \chi_1 v_2^2 \right] \quad (3.23)$$

The osmotic pressure is given by

$$\pi = -\frac{\overline{\Delta G_1}}{V_1} \quad (3.24), \text{ Then}$$

$$\text{► } \pi = -\frac{RT}{V_1} \left[\ln(1 - v_2) + \left(1 - \frac{1}{x}\right) v_2 + \chi_1 v_2^2 \right] \quad (3.25)$$

$V_1 =$ Molar volume of the solvent

► Expand (25) using $\ln(1+x) = x - x^2/2 + \dots$ to give the second virial coefficient as

$$A_2 = \frac{\bar{v}_2^2}{N_A V_1} \left(\frac{1}{2} - \chi_1 \right) \quad (3.26) \quad \text{in} \quad \frac{\pi}{c} = RT \left(\frac{1}{M_n} + A_2 c + A_3 c^2 + \dots \right) \quad (3.41)$$

$\bar{v}_2 =$ Specific volume of the polymer.

► Flory θ temperature can now be seen as the point where $\chi_1 = 1/2$, and $A_2 = 0$.