

### Flory- Huggins theory

From the thermodynamic point of view, dissolution of a polymer into a solvent is favourable when Gibbs free energy of mixing is negative. This can happen when either  $\Delta H_{\text{mix}}$  is negative or the product ( $T\Delta S_{\text{mix}}$ ) of the temperature and the entropy of mixing is greater than the enthalpy of mixing ( $\Delta H_{\text{mix}}$ ). The amount of change for entropy of mixing ( $\Delta S_{\text{mix}}$ ) of polymer solution is always positive and relatively smaller than small molecules. Anyhow you have to calculate the values of  $\Delta H_{\text{mix}}$  and  $\Delta S_{\text{mix}}$  for the determination of  $\Delta G_{\text{mix}}$ . The Flory–Huggins theory uses the lattice model to arrange the polymer chains and solvent molecules for the determination of  $\Delta H_{\text{mix}}$  and  $\Delta S_{\text{mix}}$ . The simplest version of this lattice chain theory is generally referred to as Flory–Huggins mean-field theory. It is assumed that there is no volume change for polymer solution mixing ( $\Delta V_{\text{mix}} = 0$ ). Thus the expression of  $\Delta S_{\text{mix}}$  for polymer in solution will be (using the Flory-Huggins theory)

$$\Delta S_{\text{mix}} = -R \left[ \phi_1 \ln \phi_1 + \frac{\phi_2}{n} \ln \phi_2 \right]$$

where  $\phi_1, \phi_2$  are the volume fractions or number fractions of the component 1 and 2.  $n$  is the lattice sites occupied per polymer or degree of polymerization. The expression of  $\Delta H_{\text{mix}}$  for polymer in solution will be

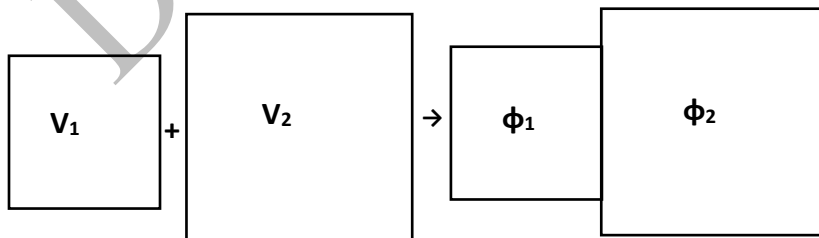
$$\Delta H_{\text{mix}} = RT \chi_{12} \phi_1 \phi_2$$

where  $\chi_{12}$  is the Flory-Huggins binary interaction parameter,  $R$  is the universal gas constant and  $T$  is the absolute temperature. Thus the expression of  $\Delta G_{\text{mix}}$  for polymer in solution will be

$$\Delta G_{\text{mix}} = RT \left[ \phi_1 \ln \phi_1 + \frac{\phi_2}{n} \ln \phi_2 + \chi_{12} \phi_1 \phi_2 \right]$$

**Entropy of polymer mixing:** Now consider step by step to determine the entropy of polymer mixing. For simplicity first consider regular solutions and then will move to polymer solutions. The Flory–Huggins theory uses the lattice model to arrange the two components in lattice sites. When two or more components (chemical species) are mixed together mixtures are formed. In case of two components mixing it is termed binary mixtures, for three components it is termed ternary mixtures. Whatever be the situation entropy always favours mixing. See the schematic presentation below to understand the entropy of mixing.

Consider two components having volume  $V_1$  and  $V_2$  respectively and the total volume  $V$  ( $V = V_1 + V_2$ ).



Thus volume fraction of component 1 will be

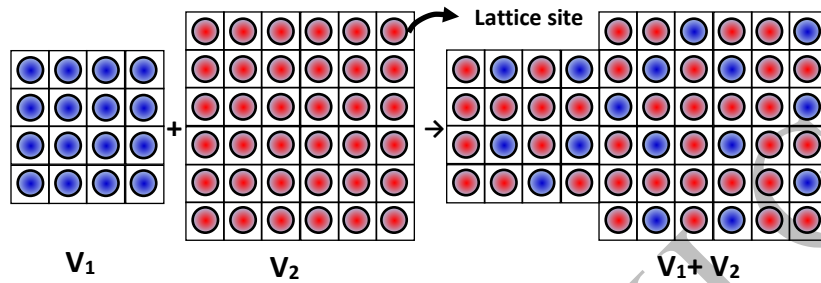
$$\phi_1 = \frac{V_1}{V_1 + V_2} = \frac{V_1}{V}$$

Similarly volume fraction of component 2 will be

$$\phi_2 = \frac{V_2}{V_1 + V_2} = \frac{V_2}{V} = 1 - \phi_1$$

[For better understanding take the help of an example. Suppose two components having volume 10L and 40L respectively. Total volume (10+40 = 50L). Then volume fraction of component 1 is 10/50 = 0.2 and the volume fraction of component 2 is 0.8.]

Now consider the following schematic presentation.



The volumes of two components are still  $V_1$  and  $V_2$  but  $V_1$  &  $V_2$  are made by  $n_1$  &  $n_2$  number of lattice sites. Again the volume of each sites is  $v_0$  and total sites are  $n$  ( $n_1 + n_2 = n$ ). Thus  $V_1 = n_1 v_0$ ,  $V_2 = n_2 v_0$  and  $V = n v_0$ . This is an assumption that components 1 and 2 both have the same volume of their lattice site. Clearly the volume of blue circle and red circle is equal and that is  $v_0$ . Keep in mind that it is a 2D presentation, in 3D presentation circle will be sphere. Thus volume fraction can be replaced by number fraction.

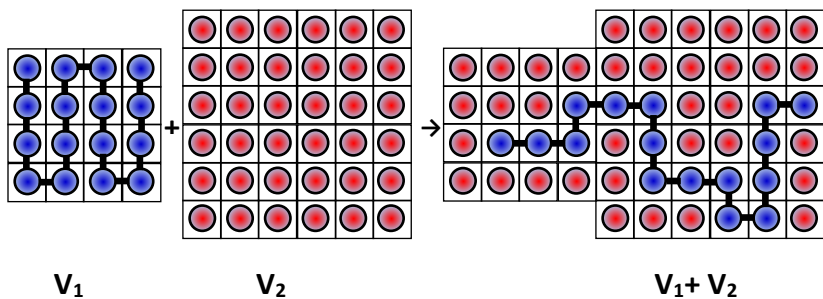
Thus number fraction of component 1 will be

$$\phi_1 = \frac{V_1}{V_1 + V_2} = \frac{V_1}{V} = \frac{n_1 v_0}{n v_0} = \frac{n_1}{n}$$

and the number fraction of component 2 will be

$$\phi_2 = \frac{V_2}{V_1 + V_2} = \frac{V_2}{V} = 1 - \phi_1 = \frac{n_2}{n}$$

Now consider the polymer solution which means polymer mixed with solvent. See the following schematic presentation.



A polymer chain is formed by combining many lattice sites which depend on the monomer units. Each monomer unit occupies one lattice site. Let one polymer chain is formed by combining  $n_m$  number of monomer units and there are  $n_p$  number of polymer chains. But each solvent molecule occupies one lattice site.  $\phi_p$  is the volume fraction of polymer and  $n$  is the total sites Thus

Number of polymer chains = total lattice sites  $\times$  volume fraction of polymer / lattice sites occupied by single polymer chain i.e.

$$n_p = n \frac{\phi_p}{n_m} \quad \text{or} \quad \phi_p = \frac{n_p n_m}{n}$$

- ❖ It will be easier to understand with mathematical examples. Let mixed polymer [polymer contain 10 ( $n_p$ ) polymer chains, each chain has 200 ( $n_m$ ) monomer units. Thus it will occupy 2000 lattice sites] with solvent molecules (occupy 8000 lattice sites). Total lattice site  $n=10000$ , then  $10 = 10000 \times \frac{0.2}{200}$  as  $\phi_p(0.2) = \frac{2000}{10000}$ .

And the number of solvent molecules is

$$n_s = n(1 - \phi_p) \quad \text{or} \quad \phi_s = \frac{n_s}{n}$$

where  $n_s$  and  $\phi_s$  are the number of lattice sites occupied by solvent molecules and volume fraction of solvent respectively.

Once we have number of polymer chains and solvent molecules, entropy can be calculated using the equation

$$S = k \ln \Omega$$

where  $S$  is entropy,  $k$  is Boltzmann constant and  $\Omega$  is the arrangement (possible distribution or number of states) of polymer chains and solvent molecules on the lattice. These two equations needed to calculate  $S$

$$\Omega = \frac{N!}{n_p! n_s!} \text{ and Stirling's approximation } \ln x! \approx x \ln x - x$$

There are four states, entropy of polymer before mixing and after mixing, entropy of solvent before mixing and after mixing. Therefore, we can write down the entropy per molecule as

$$S_p^B = \text{entropy of one polymer chain before mixing}$$

$$= k \ln(n_p n_m v_0)$$

$$S_s^B = \text{entropy of one solvent molecule before mixing}$$

$$= k \ln(n_s v_0), \text{ as each solvent molecule occupy one site}$$

$$S_p^A = \text{entropy of one polymer chain after mixing}$$

$$= k \ln[(n_p n_m + n_s) v_0]$$

$$S_s^A = \text{entropy of one solvent molecule after mixing}$$

$$= k \ln[(n_p n_m + n_s) v_0]$$

Thus total entropy change due to polymer mixing with solvents

$$\Delta S_{\text{mix}} = n_p S_p^A + n_s S_s^A - n_p S_p^B - n_s S_s^B$$

$$= -k \left[ n_p \ln \left( \frac{n_p n_m}{n_p n_m + n_s} \right) + n_s \ln \left( \frac{n_s}{n_p n_m + n_s} \right) \right]$$

$$= -k [n_p \ln \phi_p + n_s \ln \phi_s]$$

Divided by N, the equation become

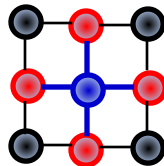
$$\frac{\Delta S_{\text{mix}}}{n} = -k \left[ \frac{n_p}{n} \ln \phi_p + \frac{n_s}{n} \ln \phi_s \right]$$

$$= -k \left[ \frac{\phi_p}{n_m} \ln \phi_p + \phi_s \ln \phi_s \right]$$

**Enthalpy of polymer mixing:** Enthalpy of polymer mixing can be calculated by following steps  
 i) counting total number of interactions of polymer–solvent system before and after mixing ii) values of their interaction energies.

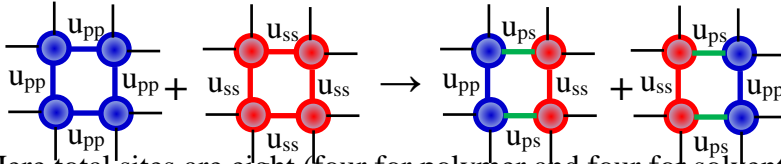
Let  $u_{ss}$ ,  $u_{pp}$ , and  $u_{ps}$  are the interaction energies between adjacent lattice sites for a solvent–solvent (S–S) contact, a polymer–polymer (P–P) contact, and a polymer–solvent (P–S) contact respectively. Each lattice site has a definite coordination number (Z) depending on the lattice. For square lattice the coordination number Z = 4 and for cubic lattice the coordination number Z = 6 respectively. Z also denotes the number of adjacent lattice sites.

This is a square lattice



Each lattice site (shown as blue circle) has 4 interactions (shown as blue bold line) with adjacent lattice sites (shown as red circle). There are no interactions if they are not adjacent (shown as black circle).

The square lattice of polymer-solvent interaction can be shown as



Here total sites are eight (four for polymer and four for solvents). Before mixing there are four P–P contacts and four S–S contacts and after mixing there are two P–P contacts, two S–S contacts and four P–S contacts. Let the interaction energies of P–P contact, S–S contact and P–S contact are  $u_{pp}$ ,  $u_{ss}$  and  $u_{ps}$  respectively.

The interaction energy before mixing =  $4u_{pp} + 4u_{ss}$

The interaction energy after mixing =  $2u_{pp} + 2u_{ss} + 4u_{ps}$

Total energy change =  $2u_{pp} + 2u_{ss} + 4u_{ps} - (4u_{pp} + 4u_{ss})$   
 $= 4u_{ps} - 2(u_{pp} + u_{ss})$

There are **eight** sites or eight bonds from which **two** P–S contacts or bonds formed. Thus for each newly created P–S contact, the energy change is

$$\begin{aligned} &= \frac{\text{two}}{\text{eight}} [4u_{ps} - 2(u_{pp} + u_{ss})] \\ &= \frac{2}{8} [4u_{ps} - 2(u_{pp} + u_{ss})] \\ &= u_{ps} - \frac{(u_{pp} + u_{ss})}{2} \end{aligned}$$

The  $\chi$  (chi) parameter, also called Flory's  $\chi$  parameter or Flory–Huggins  $\chi$  parameter, is expressed as

$$\chi = \frac{Z \left[ u_{ps} - \frac{(u_{pp} + u_{ss})}{2} \right]}{kT}$$

where  $Z$  is coordination number,  $k$  is Boltzmann constant and  $T$  is absolute temperature. When  $\chi = (-)$ ve, P–S contacts are favoured and for  $\chi = (+)$ ve, P–P & S–S contacts are favoured.

Probability of adjacent contacts are

contact	Interaction energies	Probability before mixing	Probability after mixing
P-P	$u_{pp}$	$\phi_p$	$(\phi_p)^2$
S-S	$u_{ss}$	$\phi_s = 1 - \phi_p$	$(\phi_s)^2 = (1 - \phi_p)^2$
P-S	$u_{ps}$	0	$2\phi_p\phi_s = 2\phi_p(1 - \phi_p)$

Now we will count the total number of interactions of polymer-solvent system before and after mixing with the help of probability. The probability for formation of a P-P contact, S-S contact and P-S contact are  $(\phi_p)^2$ ,  $(\phi_s)^2$  or  $(1 - \phi_p)^2$  and  $2\phi_p\phi_s$  or  $2\phi_p(1 - \phi_p)$  respectively.

Total interaction energy before mixing

For polymer =  $(Zn/2)u_{pp}\phi_p$

For solvent =  $(Zn/2)u_{ss}\phi_s = (Zn/2)u_{ss}(1 - \phi_p)$

For both polymer and solvent =  $(Zn/2)u_{pp}\phi_p + (Zn/2)u_{ss}(1 - \phi_p) = (Zn/2) [u_{pp}\phi_p + u_{ss}(1 - \phi_p)] = H_B$

And total interaction energy after mixing

$$H_A = (Zn/2) [\{u_{pp}\phi_p + u_{ps}(1 - \phi_p)\} \phi_p + \{u_{ps}\phi_p + u_{ss}(1 - \phi_p)\}(1 - \phi_p)]$$

$$= (Zn/2)[u_{pp}(\phi_p)^2 + 2u_{ps}\phi_p(1 - \phi_p) + u_{ss}(1 - \phi_p)^2]$$

Thus, total interaction energy for mixing is

$$\Delta H_{mix} = H_A - H_B$$

$$= (Zn/2)[u_{pp}(\phi_p)^2 + 2u_{ps}\phi_p(1 - \phi_p) + u_{ss}(1 - \phi_p)^2] - (Zn/2) [u_{pp}\phi_p + u_{ss}(1 - \phi_p)]$$

$$= (Zn/2)[u_{pp}(\phi_p)^2 + 2u_{ps}\phi_p(1 - \phi_p) + u_{ss}(1 - \phi_p)^2 - u_{pp}\phi_p - u_{ss}(1 - \phi_p)]$$

$$= (Zn/2) [u_{pp}\{(\phi_p)^2 - \phi_p\} + 2u_{ps}\phi_p(1 - \phi_p) + u_{ss}\{1 - 2\phi_p + (\phi_p)^2 - 1 + \phi_p\}]$$

$$= (Zn/2) [u_{pp}\phi_p(\phi_p - 1) + 2u_{ps}\phi_p(1 - \phi_p) + u_{ss}\phi_p(\phi_p - 1)]$$

$$= (Zn/2) [-u_{pp}\phi_p(1 - \phi_p) + 2u_{ps}\phi_p(1 - \phi_p) - u_{ss}\phi_p(1 - \phi_p)]$$

$$= (Zn/2) \phi_p(1 - \phi_p)(2u_{ps} - u_{pp} - u_{ss})$$

Hence interaction energy for mixing per lattice site is

$$= (\Delta H_{mix} / n) = [(Zn/2) \phi_p(1 - \phi_p)(2u_{ps} - u_{pp} - u_{ss})] / n$$

$$= (Z/2) \phi_p(1 - \phi_p)(2u_{ps} - u_{pp} - u_{ss}) = \chi\phi_p(1 - \phi_p)kT$$

Where

$$\chi = \frac{Z \left[ u_{ps} - \frac{(u_{pp} + u_{ss})}{2} \right]}{kT}$$

$\chi$  (chi) is Flory's  $\chi$  parameter or Flory–Huggins  $\chi$  parameter.

It was assumed in Flory–Huggins theory that there is no volume change after mixing, again the monomer units of polymer chain and solvent molecule have fit on the same lattice sites. But in reality, volume changes after mixing and also packing mismatch in lattice sites. These volume effects lead to deviation from lattice site model and sum up into the interaction parameter  $\chi$  which have nontrivial dependency on composition, chain length and temperature. Thus  $\chi(T)$  can be written as

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

where A is temperature independent entropic part and B/T is enthalpic part.

The expression of Flory–Huggins equation for polymer in solution is

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}}$$

$$\begin{aligned} &= kT \chi \phi_p (1 - \phi_p) - T \left[ -k \left( \frac{\phi_p}{n_m} \ln \phi_p + \phi_s \ln \phi_s \right) \right] \\ &= kT \left[ \frac{\phi_p}{n_m} \ln \phi_p + \phi_s \ln \phi_s + \chi \phi_p (1 - \phi_p) \right] \end{aligned}$$

### Lower and Upper critical solution temperatures

There are varieties of Flory Huggins phase diagram depending on the nature of solute and solvent molecules. In the solute-solvent systems, solute can be small molecule or polymer and solvent can be liquid molecule or another polymer. Thus the systems are small molecule-solvent, polymer-solvent (polymer solution) and polymer-polymer (blend) system. Though polymer solutions phase diagram is of main interest but other systems will also be shown. Flory–Huggins interaction parameter  $\chi(T)$  can be written as

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

When  $B > 0$ , with increasing temperature  $\chi$  decreases and the highest temperature of the two-phase region is termed as upper critical solution temperature (UCST),  $T_c$ . When the solution temperature is more than  $T_c$ , it makes a stable homogeneous solution.

When  $B < 0$ , with increasing temperature  $\chi$  increases and the lowest temperature of two-phase region is termed as lower critical solution temperature (LCST),  $T_c$ . When the solution temperature is less than  $T_c$ , it makes a stable homogeneous solution.

The schematic presentations of different Flory Huggins phase diagrams are shown below.

