Introduction to Polymer Science
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Lecture - 24
Polymers in Solution: Applications of Flory - Huggins Theory

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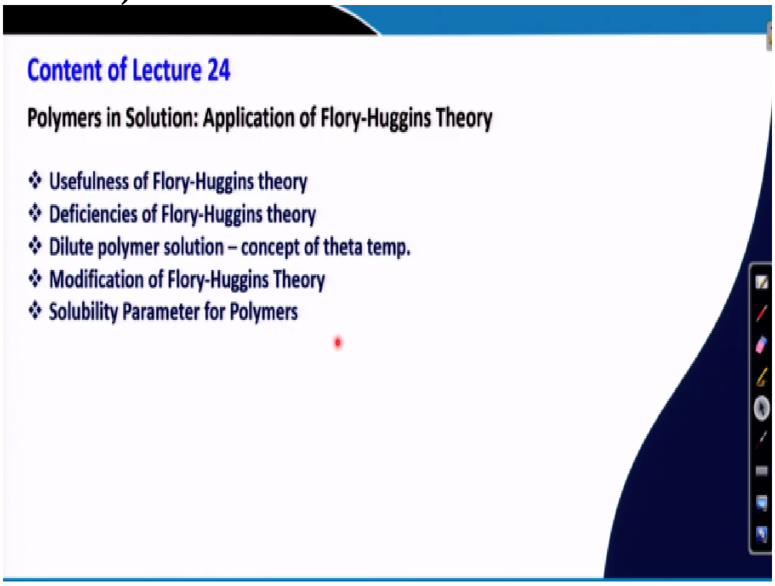

Content of Lecture 24

Polymers in Solution: Application of Flory-Huggins Theory

- ❖ Usefulness of Flory-Huggins theory
- ❖ Deficiencies of Flory-Huggins theory
- ❖ Dilute polymer solution – concept of theta temp.
- ❖ Modification of Flory-Huggins Theory
- ❖ Solubility Parameter for Polymers

Welcome back in this lecture 24. We will continue our discussion on polymers in solution and few applications of Flory Huggins theory.

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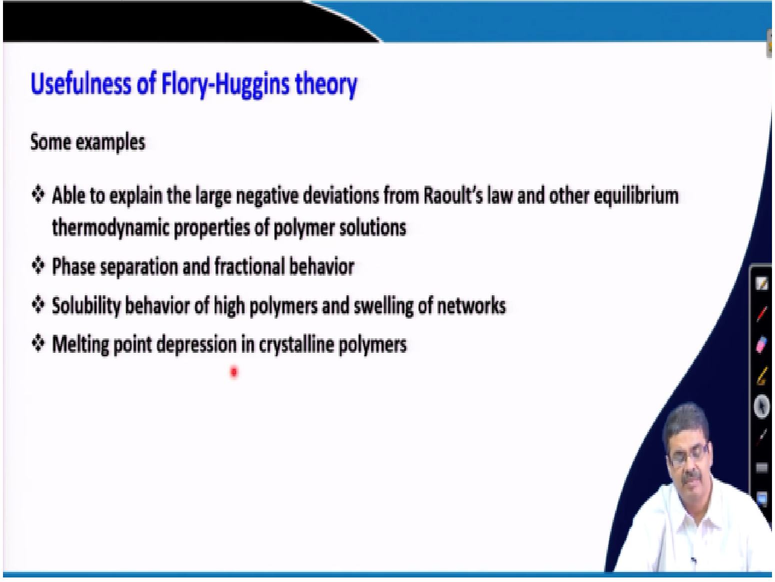

Usefulness of Flory-Huggins theory

Some examples

- ❖ Able to explain the large negative deviations from Raoult's law and other equilibrium thermodynamic properties of polymer solutions
- ❖ Phase separation and fractional behavior
- ❖ Solubility behavior of high polymers and swelling of networks
- ❖ Melting point depression in crystalline polymers

We derived Flory Huggins theory in the last lecture, now some of the usefulness of Flory Huggins theory will be discussed here. For example, we will be able to explain large negative deviations from Raoult’s law and other equilibrium thermodynamic properties of polymer solutions using Flory Huggins theory. We can also explain phase separation and fractional behavior of polymer solutions. We can explain solubility behavior of high polymers and swelling of polymer networks in different solvents using Flory Huggins theory and we can also explain melting point depression in crystalline polymers.

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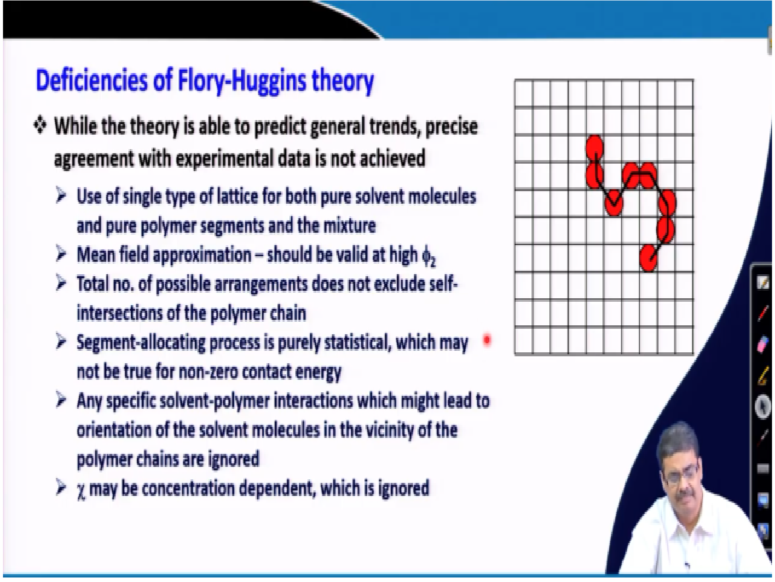

Deficiencies of Flory-Huggins theory

- While the theory is able to predict general trends, precise agreement with experimental data is not achieved
  - Use of single type of lattice for both pure solvent molecules and pure polymer segments and the mixture
  - Mean field approximation – should be valid at high ϕ_2
  - Total no. of possible arrangements does not exclude self-intersections of the polymer chain
  - Segment-allocating process is purely statistical, which may not be true for non-zero contact energy
  - Any specific solvent-polymer interactions which might lead to orientation of the solvent molecules in the vicinity of the polymer chains are ignored
  - χ may be concentration dependent, which is ignored

Now, there are deficiencies in Flory Huggins theory. This theory, while it is able to predict general trends and several thermodynamic properties can be explained but precise agreement with experimental data is not achieved. Now, this is because, there are several assumptions made during the derivation of Flory Huggins theory, e.g. single type of cells was utilized for solvent molecule and polymers segments, which may not be very applicable for polymer segments. Another flaw or assumption was made that when we introduce 1 fragment of polymer in this 3D lattice, it will assume that all other polymer chains which were already present in the 3D lattice are distributed uniformly. Now, that is not true especially in dilute solutions, because polymer fragments are or polymers segments are indeed connected to each other. Hence, it is not true that the polymer segments which were already present in the 3D cells were distributed uniformly and that was mentioned as mean field approximation. So, this is not valid for dilute solutions, it may be valid at high concentration of polymers in solution. Total number of possible arrangements does not exclude the self intersections of polymer chains. Now, polymer chains can actually, there is a possibility that they can overlap with each other and some of the vacant cells around a particular segment may not be available due to self-intersection that was not considered during derivation of Flory Huggins theory. Also the addition of these segments in these 3D sets was purely statistical which may not be true if there is a non-zero contact energy between solvent molecules and polymer molecules for example, any specific solvent polymer interactions may lead to orientation of solvent molecules around the polymers segments, which was not considered during the derivation of Flory Huggins theory. It was also considered that the polymer solvent interaction parameter χ is not concentration dependent, which may not be true. It may be also be concentration dependent. So, these assumptions which were made during derivation of Flory Huggins theory are not perfectly applicable, that is the reason we do not get precise agreement with the experimental data when we predict a thermal chemical property using Flory Huggins theory.

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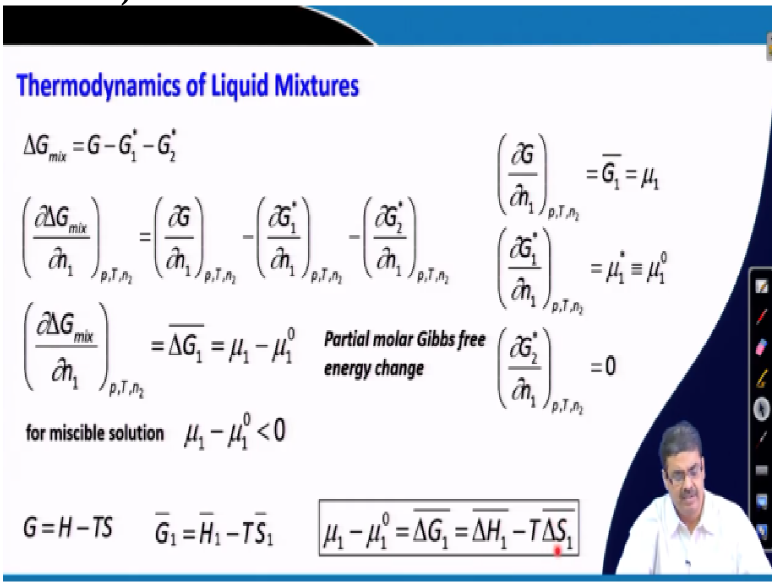

Thermodynamics of Liquid Mixtures

$$\Delta G_{mix} = G - G_1^* - G_2^*$$

$$\left(\frac{\partial \Delta G_{mix}}{\partial n_1}\right)_{p,T,n_2} = \left(\frac{\partial G}{\partial n_1}\right)_{p,T,n_2} - \left(\frac{\partial G_1^*}{\partial n_1}\right)_{p,T,n_2} - \left(\frac{\partial G_2^*}{\partial n_1}\right)_{p,T,n_2}$$

$$\left(\frac{\partial \Delta G_{mix}}{\partial n_1}\right)_{p,T,n_2} = \overline{\Delta G_1} = \mu_1 - \mu_1^0$$

Partial molar Gibbs free energy change

$$\left(\frac{\partial G}{\partial n_1}\right)_{p,T,n_2} = \overline{G}_1 = \mu_1$$

$$\left(\frac{\partial G_1^*}{\partial n_1}\right)_{p,T,n_2} = \mu_1^* \equiv \mu_1^0$$

$$\left(\frac{\partial G_2^*}{\partial n_1}\right)_{p,T,n_2} = 0$$

for miscible solution $\mu_1 - \mu_1^0 < 0$

$G = H - TS$ $\quad \overline{G}_1 = \overline{H}_1 - T\overline{S}_1$

$$\boxed{\mu_1 - \mu_1^0 = \overline{\Delta G_1} = \overline{\Delta H_1} - T\overline{\Delta S_1}}$$

Now, we will discuss how this Flory Hugging theory can be utilized to derive some of the thermodynamic parameters. Before that let me revise the thermodynamics of liquid mixtures quickly.

$$\Delta G_{mix} = G - G_1^* - G_2^*$$

Now, ΔG of mixing is given by this expression, G is the Gibbs free energy of the mixture and this is for the pure solvent and this is for pure solute, 2 is generally expressed as solute and 1 is generally utilized for solvent and this star means, we are talking about pure component.

$$\left(\frac{\partial \Delta G_{mix}}{\partial n_1}\right)_{p,T,n_2} = \left(\frac{\partial G}{\partial n_1}\right)_{p,T,n_2} - \left(\frac{\partial G_1^*}{\partial n_1}\right)_{p,T,n_2} - \left(\frac{\partial G_2^*}{\partial n_1}\right)_{p,T,n_2}$$

$$\left(\frac{\partial \Delta G_{mix}}{\partial n_1}\right)_{p,T,n_2} = \overline{\Delta G_1} = \mu_1 - \mu_1^0$$

$$\left(\frac{\partial G}{\partial n_1}\right)_{p,T,n_2} = \overline{G_1} = \mu_1; \quad \left(\frac{\partial G_1^*}{\partial n_1}\right)_{p,T,n_2} = \mu_1^* = \mu_1^0; \quad \left(\frac{\partial G_2^*}{\partial n_1}\right)_{p,T,n_2} = 0$$

So, we can differentiate this with number of moles of solvent and we get this expression. $\left(\frac{\partial G}{\partial n_1}\right)_{p,T,n_2}$ is for partial molar Gibbs free energy, which is also called chemical potential of solvent. In this case, we are using 1 for the chemical potential of pure component and if we use 1 bar pressure, then this is the standard chemical potential for solvent molecule. And obviously, $\left(\frac{\partial G_2^*}{\partial n_1}\right)_{p,T,n_2}$ is 0.

So, if we plug in these numbers into this expression, we get this right hand side is equal to μ_1 - μ_1^0 and this is we represent as partial molar Gibbs free energy change. Now, negative value of Gibbs free energy change at constant temperature and pressure indicates that the solution process is spontaneous. So, for a miscible solution, we must have this quantity less than 0.

$$G = H - TS \qquad \overline{G_1} = \overline{H_1} - T\overline{S_1}$$
$$\mu_1 - \mu_1^0 = \overline{\Delta G_1} = \overline{\Delta H_1} - T\overline{\Delta S_1}$$

We also know that G is given by H - TS, H is enthalpy and S is entropy. So, the partial quantities can be also expressed at constant temperature. So, this term can be expressed in terms of partial Gibbs free energy change and further in terms of partial molar enthalpy change, and partial molar entropy change of the of solvent.

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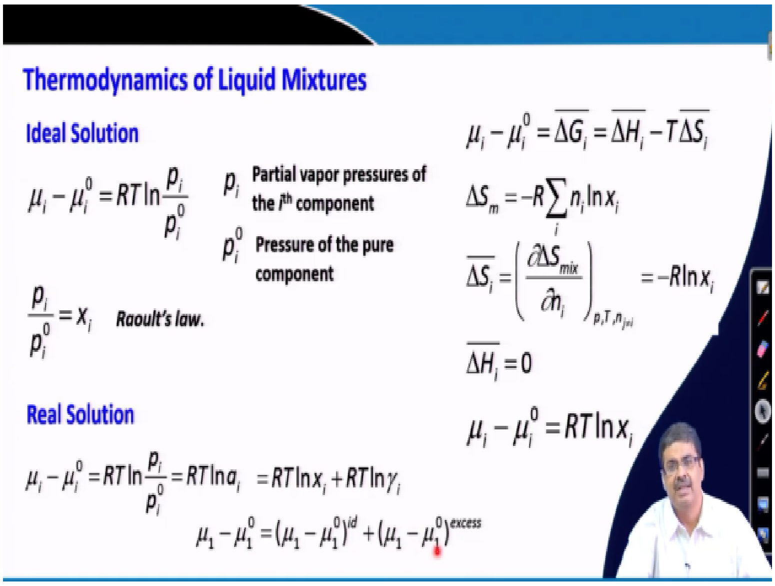

Thermodynamics of Liquid Mixtures

Ideal Solution

$\mu_i - \mu_i^0 = RT\ln\frac{p_i}{p_i^0}$

p_i Partial vapor pressures of the i^{th} component

p_i^0 Pressure of the pure component

$\frac{p_i}{p_i^0} = x_i$ Raoult's law.

Real Solution

$\mu_i - \mu_i^0 = RT\ln\frac{p_i}{p_i^0} = RT\ln a_i \quad = RT\ln x_i + RT\ln\gamma_i$

$\mu_1 - \mu_1^0 = (\mu_1 - \mu_1^0)^{id} + (\mu_1 - \mu_1^0)^{excess}$

$\mu_i - \mu_i^0 = \overline{\Delta G_i} = \overline{\Delta H_i} - T\overline{\Delta S_i}$

$\Delta S_m = -R\sum_i n_i \ln x_i$

$\overline{\Delta S_i} = \left(\frac{\partial \Delta S_{mix}}{\partial n_i}\right)_{p,T,n_{j\neq i}} = -R\ln x_i$

$\overline{\Delta H_i} = 0$

$\mu_i - \mu_i^0 = RT\ln x_i$

In case of ideal solution, we express p_i as the partial vapor pressure of i th component, p_i^0 is the pressure of the pure component. So, we have seen these in the last slide and we know that for ideal solution, the entropy of mixing is given by the following expression where n_i is the number of moles and x_i is the mole fraction of i th component. Obviously, we are talking about ideal solutions.

$$\mu_i - \mu_i^0 = \overline{\Delta G_\iota} = \overline{\Delta H_\iota} - T\overline{\Delta S_\iota}$$

$$\Delta S_m = -R\sum_i n_i \ln x_i$$

$$\overline{\Delta S_\iota} = \left(\frac{\partial \Delta S_{mix}}{\partial n_i}\right)_{p,T,n_{j,i}} = -R\ln x_i$$

$$\overline{\Delta H_\iota} = 0$$

$$\mu_i - \mu_i^0 = RT\ln x_i$$

$$\frac{p_i}{p_i^0} = x_i$$

$$\mu_i - \mu_i^0 = RT\ln\frac{p_i}{p_i^0}$$

So, this partial enthalpy change will be 0. So, if we place these two values in this expression, we get μ_i - μ_i^0 is RTln x_i. Now, if you compare the value for μ_i - μ_i^0, between the two expressions, we can write p_i/p_i^0 is equal to mole fraction of i th component and which is nothing but Roault's law. Now, for the real solution, this mole fraction is replaced by activity where this mole fraction corresponds to the ideal component and the activity coefficient gives us the deviation from ideality. So, we can express this term as ideal component plus an excess component which basically determines the deviation from ideality.

For real solution,

$$\mu_i - \mu_i^0 = RT\ln\frac{p_i}{p_i^0} = RT\ln a_i = RT\ln x_i + RT\ln\gamma_i$$

$$\mu_1 - \mu_1^0 = (\mu_1 - \mu_1^0)^{id} + (\mu_1 - \mu_1^0)^{excess}$$

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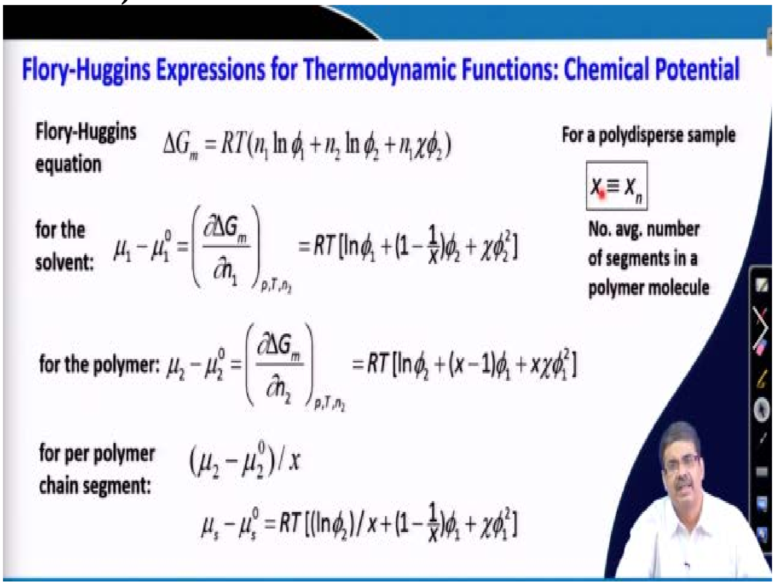

Flory-Huggins Expressions for Thermodynamic Functions: Chemical Potential

Flory-Huggins equation $\Delta G_m = RT(n_1\ln\phi_1 + n_2\ln\phi_2 + n_1\chi\phi_2)$

For a polydisperse sample

$\boxed{x \equiv x_n}$

No. avg. number of segments in a polymer molecule

for the solvent: $\mu_1 - \mu_1^0 = \left(\frac{\partial\Delta G_m}{\partial n_1}\right)_{p,T,n_2} = RT[\ln\phi_1 + (1-\frac{1}{x})\phi_2 + \chi\phi_2^2]$

for the polymer: $\mu_2 - \mu_2^0 = \left(\frac{\partial\Delta G_m}{\partial n_2}\right)_{p,T,n_1} = RT[\ln\phi_2 + (x-1)\phi_1 + x\chi\phi_1^2]$

for per polymer chain segment: $(\mu_2 - \mu_2^0)/x$

$\mu_s - \mu_s^0 = RT[(\ln\phi_2)/x + (1-\frac{1}{x})\phi_1 + \chi\phi_1^2]$

Flory-Huggins equation, $\Delta G_m = RT(n_1\ln\phi_1 + n_2\ln\phi_2 + n_1\chi\phi_2)$

For the solvent, $\mu_1 - \mu_1^0 = \left(\frac{\partial\Delta G_m}{\partial n_1}\right)_{p,T,n_2} = RT\left[\ln\phi_1 + \left(1-\frac{1}{x}\right)\phi_2 + \chi\phi_2^2\right]$

For the polymer, $\mu_2 - \mu_2^0 = \left(\frac{\partial\Delta G_m}{\partial n_2}\right)_{p,T,n_1} = RT[\ln\phi_2 + (x-1)\phi_1 + x\chi\phi_1^2]$

For per polymer chain segment, $(\mu_2 - \mu_2^0)/x$

$$\mu_s - \mu_s^0 = RT\left[{(\ln\phi_2)}/{x} + \left(1-\frac{1}{x}\right)\phi_1 + \chi\phi_1^2\right]$$

Now, we go back to the Flory Huggins equation. For solvent we can use partial Gibbs free energy or molar Gibbs free energy change with respect to solvent. If we differentiate with respect to n_1, we get the expression as shown above and for polymers we differentiate with respect to n_2 which is the number of moles of polymer molecule, we get this expression and we generally express polymer in terms of number of segments. because, while deriving the Flory Huggins expression we consider that polymers consist of several segments and each segment has same molar volume as the solvent molecule. We generally expressed this term in terms of per polymers segment. So, we divided this by x which is the number of polymer segment and if we consider that polymers have different chain length, they will have different number of segments as well. If we consider that, then instead of just writing number of segments, we can write number average number of segments in the polymer sample, but, for time being, we will not consider the average quantity, will consider as polymer chains having similar molecular weights. So, we will consider x.

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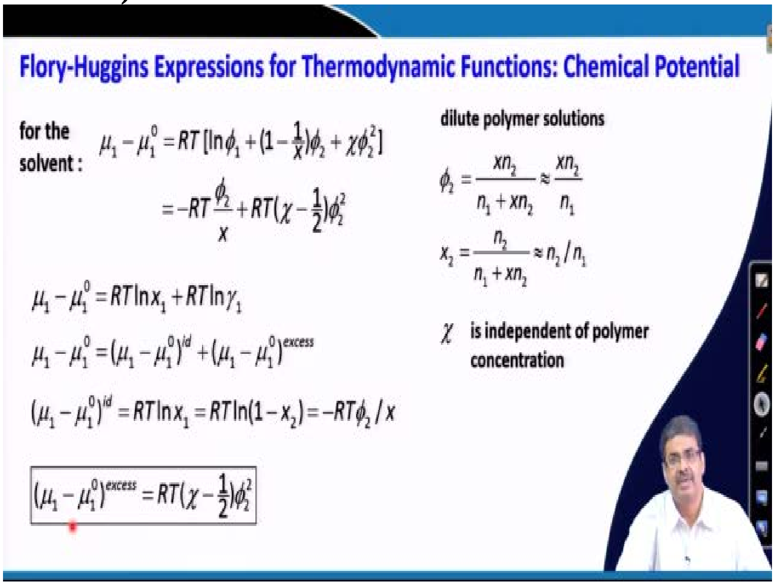

Flory-Huggins Expressions for Thermodynamic Functions: Chemical Potential

for the solvent: $\mu_1 - \mu_1^0 = RT\,[\ln\phi_1 + (1-\frac{1}{x})\phi_2 + \chi\phi_2^2]$

$= -RT\frac{\phi_2}{x} + RT(\chi - \frac{1}{2})\phi_2^2$

$\mu_1 - \mu_1^0 = RT\ln x_1 + RT\ln\gamma_1$

$\mu_1 - \mu_1^0 = (\mu_1 - \mu_1^0)^{id} + (\mu_1 - \mu_1^0)^{excess}$

$(\mu_1 - \mu_1^0)^{id} = RT\ln x_1 = RT\ln(1-x_2) = -RT\phi_2/x$

$\boxed{(\mu_1 - \mu_1^0)^{excess} = RT(\chi - \frac{1}{2})\phi_2^2}$

dilute polymer solutions

$\phi_2 = \frac{xn_2}{n_1 + xn_2} \approx \frac{xn_2}{n_1}$

$x_2 = \frac{n_2}{n_1 + xn_2} \approx n_2/n_1$

χ is independent of polymer concentration

For the solvent, $\mu_1 - \mu_1^0 = RT\left[\ln\phi_1 + \left(1 - \frac{1}{x}\right)\phi_2 + \chi\phi_2^2\right] = -RT\frac{\phi_2}{x} + RT\left(\chi - \frac{1}{2}\right)\phi_2^2$

For dilute polymer solution,

$$\phi_2 = \frac{xn_2}{n_1 + xn_2} \approx \frac{xn_2}{n_1}$$

$$x_2 = \frac{n_2}{n_1 + xn_2} \approx n_2/n_1$$

Now, for the solvent, we have seen this expression in last slide. Now, if we assume a dilute polymer solution, then we can express the volume fraction of the polymer with total number of polymer segment, this is number of polymer segment in 1 polymer chain, this is number of polymer chain could give the total volume of the polymers and this is total volume from polymer plus solvent. So, this gives the volume fraction. So, because this n_1 is much higher compared to this term, we can write approximately this equals to this. Similarly, the mole fraction of the polymer we can write or approximately like this and if we also assume that this is independent of polymer concentration, then simply by mathematical expression we can write this expression from the original gives Flory Huggins expression. We know that this can be expressed for a real solution as sum of 2 parts, one ideal part and another is excess part which quantifies the deviation from ideality. Now, this can be expressed, x_1 can be expressed as (1 - x_2).

So, if you compare these two following expressions, the first term is the ideal quantity. Hence, this second term must be equal to the excess quantity of partial molar Gibbs free energy change for a real solution. Hence, we can write this excess quantity, which is the measure of deviation from ideality as given below, where chi is the polymer solvent interaction parameter.

$$\mu_1 - \mu_1^0 = RT \ln x_1 + RT \ln \gamma_1$$

$$\mu_1 - \mu_1^0 = (\mu_1 - \mu_1^0)^{id} + (\mu_1 - \mu_1^0)^{excess}$$

$$(\mu_1 - \mu_1^0)^{id} = RT \ln x_1 = RT \ln(1 - x_2) = -RT\, \phi_2/x$$

$$(\mu_1 - \mu_1^0)^{excess} = RT\left(\chi - \frac{1}{2}\right)\phi_2^2$$

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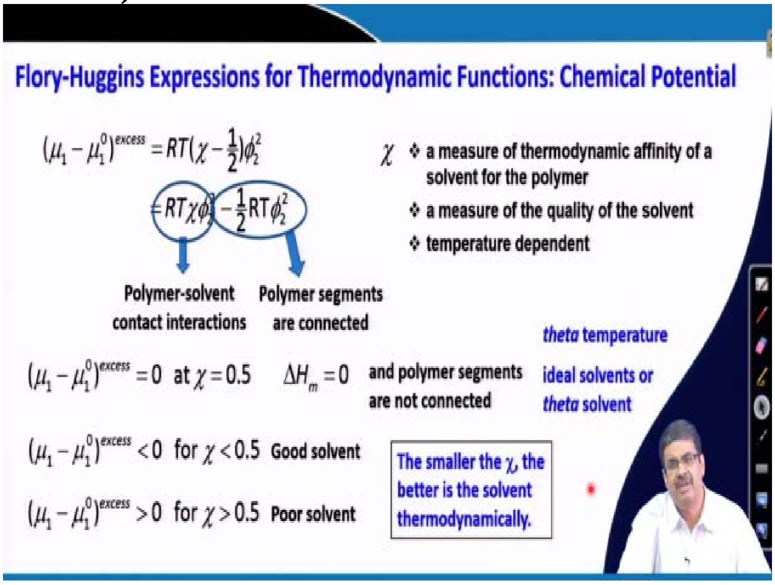

Flory-Huggins Expressions for Thermodynamic Functions: Chemical Potential

$$(\mu_1 - \mu_1^0)^{excess} = RT(\chi - \tfrac{1}{2})\phi_2^2$$

$$= \underbrace{RT\chi\phi_2^2}_{\text{Polymer-solvent contact interactions}} \underbrace{- \tfrac{1}{2}RT\phi_2^2}_{\text{Polymer segments are connected}}$$

χ
- a measure of thermodynamic affinity of a solvent for the polymer
- a measure of the quality of the solvent
- temperature dependent

$(\mu_1 - \mu_1^0)^{excess} = 0$ at $\chi = 0.5$ $\Delta H_m = 0$ and polymer segments are not connected

theta temperature

ideal solvents or theta solvent

$(\mu_1 - \mu_1^0)^{excess} < 0$ for $\chi < 0.5$ Good solvent

$(\mu_1 - \mu_1^0)^{excess} > 0$ for $\chi > 0.5$ Poor solvent

The smaller the χ, the better is the solvent thermodynamically.

As shown in the slide, this first term is because of polymer solvent contact interactions. In ideal solution, there is no contact interaction, ΔH or the enthalpy change of interaction between polymers and solvent is 0, but in this case this is not 0. In case of real solution, as enthalpy change is not 0, it also influences the polymer conformation. So, there could be the entropy change as well, due to polymers solvent interactions, and the second term is because the polymers segments are connected. The molar volume of polymers and the solvents are not same. So, this term arises because of the fact that polymers segments are connected. Once again if we look at the polymer solvent interaction parameter; it is a measure of thermodynamic affinity of the solvent for the polymer and it is a measure of quality of the solvent and it is temperature dependent.

Now, if the excess term is negative then the partial molar Gibbs change will be lower than the ideal value, which means, the polymer will dissolve in the solvent even better way than in case of ideal solution. If this is positive, then obviously, the solvent quality is not as good as ideal solution and the solubility of the polymer will lower than ideal case. Now, this is a negative term, contribute negative way to this excess term. Hence, this is the term which basically determines whether the solvent is good or solvent is not good and which indirectly is determined by this polymer solvent interaction parameter χ. Now, this is temperature dependent, and hence with change in temperature this value also will change. Hence, the miscibility of polymer and the solvent will be also dependent on the temperature at which the solution is being made.

For example, if χ is 0.5 or 1/2, then this excess term becomes 0 which means, the solvent is behaving like an ideal solvent and the polymer solvent mixture is behaving like an ideal mixture, which means that enthalpy of mixture is 0 and polymer segments are as if they are not connected. We call this solvent as ideal solvent or theta solvent and the temperature at which these polymers solvent interaction become equals to 1/2, we call that temperature as theta temperature.

This is the temperature where the solvent becomes ideal solvent for the polymer in consideration. If χ is less than 1/2, then this term become negative which means the solvent is good solvent, it is better than the ideal solvent and if it is greater than 0.5, then this term becomes positive. So, the solvent is poor solvent that means, the solvent is not as good as the ideal solvent, the solubility of the polymer decreases compared to the ideal case. Hence, the smaller is the value of this polymer solvent interaction parameter, the better is the solvent thermodynamically. So, if we manage to decrease the value of chi then the solvent will be better solvent for the polymer to dissolve and in generally, in most of the cases as we increase the temperature, the value of χ reduces or decreases. This means, if we increase the temperature, generally the solubility of the polymer in a solvent increases because the value of polymer solvent interaction parameter decreases.

We will discuss this in little more detail, when we talk about phase behavior of polymer in solution in coming lectures.

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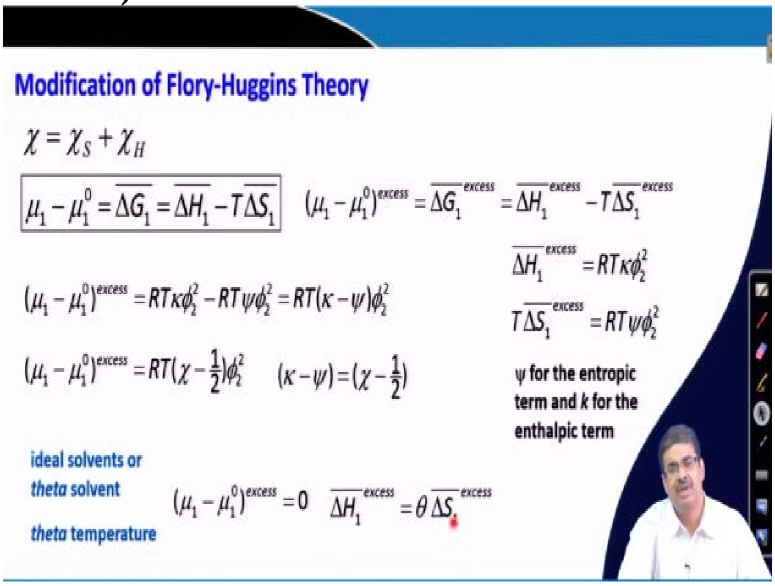

Modification of Flory-Huggins Theory

$$\chi = \chi_S + \chi_H$$

$$\boxed{\mu_1 - \mu_1^0 = \overline{\Delta G_1} = \overline{\Delta H_1} - T\overline{\Delta S_1}} \qquad (\mu_1 - \mu_1^0)^{excess} = \overline{\Delta G_1}^{excess} = \overline{\Delta H_1}^{excess} - T\overline{\Delta S_1}^{excess}$$

$$\overline{\Delta H_1}^{excess} = RT\kappa\phi_2^2$$

$$(\mu_1 - \mu_1^0)^{excess} = RT\kappa\phi_2^2 - RT\psi\phi_2^2 = RT(\kappa - \psi)\phi_2^2 \qquad T\overline{\Delta S_1}^{excess} = RT\psi\phi_2^2$$

$$(\mu_1 - \mu_1^0)^{excess} = RT(\chi - \frac{1}{2})\phi_2^2 \qquad (\kappa - \psi) = (\chi - \frac{1}{2})$$

ψ for the entropic term and k for the enthalpic term

ideal solvents or *theta* solvent

theta temperature

$$(\mu_1 - \mu_1^0)^{excess} = 0 \qquad \overline{\Delta H_1}^{excess} = \theta\overline{\Delta S_1}^{excess}$$

We will come to the modification of Flory Huggins theory. Now, this polymer solvent interaction parameter consists of entropy component and enthalpy component and we have seen this expression before. So, we can express this excess term as partial molar Gibbs free energy excess term which can be expressed in terms of enthalpy and entropy. Flory further modified this expression.

$$\chi = \chi_S + \chi_H$$

$$\mu_1 - \mu_1^0 = \overline{\Delta G_1} = \overline{\Delta H_1} - T\overline{\Delta S_1}$$

$$(\mu_1 - \mu_1^0)^{excess} = \overline{\Delta G_1}^{excess} = \overline{\Delta H_1}^{excess} - T\overline{\Delta S_1}^{excess}$$

$$\overline{\Delta H_1}^{excess} = RT\kappa\phi_2^2 \qquad T\overline{\Delta S_1}^{excess} = RT\psi\phi_2^2$$

$$(\mu_1 - \mu_1^0)^{excess} = RT\kappa\phi_2^2 - RT\psi\phi_2^2 = RT(\kappa - \psi)\phi_2^2$$

$$(\mu_1 - \mu_1^0)^{excess} = RT\left(\chi - \frac{1}{2}\right)\phi_2^2 \qquad (\kappa - \psi) = \left(\chi - \frac{1}{2}\right)$$

$$(\mu_1 - \mu_1^0)^{excess} = 0 \qquad \overline{\Delta H_1}^{excess} = \theta\overline{\Delta S_1}^{excess}$$

Now, if we replace this term with these new terms we can get an expression where ψ is the entropic term and κ is the enthalpy term. If we compare with our original Flory Huggins equation, we can equate (κ- ψ) = (χ- ½). In case of ideal solvent because the excess term becomes 0, this excess partial molar enthalpy becomes equals to θ. This is the θ temperature and multiplied by the partial molar entropy change. Now, this θ is a temperature, this is a positive term. Hence, the sign of these 2 excess terms must be same, which means if the partial molar enthalpy change increases, the corresponding entropy also will increase and θ sometimes can be said as the ratio of the partial molar excess enthalpy divided by partial molar excess entropy.

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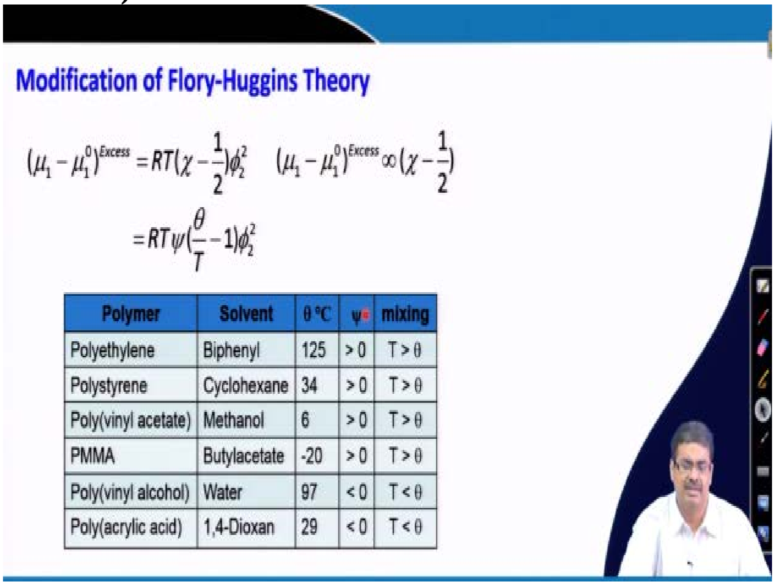

Modification of Flory-Huggins Theory

$$(\mu_1-\mu_1^0)^{Excess}=RT(\chi-\frac{1}{2})\phi_2^2 \qquad (\mu_1-\mu_1^0)^{Excess}\propto(\chi-\frac{1}{2})$$

$$=RT\psi(\frac{\theta}{T}-1)\phi_2^2$$

Polymer	Solvent	θ °C	ψ	mixing
Polyethylene	Biphenyl	125	> 0	T > θ
Polystyrene	Cyclohexane	34	> 0	T > θ
Poly(vinyl acetate)	Methanol	6	> 0	T > θ
PMMA	Butylacetate	-20	> 0	T > θ
Poly(vinyl alcohol)	Water	97	< 0	T < θ
Poly(acrylic acid)	1,4-Dioxan	29	< 0	T < θ

$$(\mu_1-\mu_1^0)^{excess}=RT\left(\chi-\frac{1}{2}\right)\phi_2^2=RT\psi\left(\frac{\theta}{T}-1\right)\phi_2^2$$
$$(\mu_1-\mu_1^0)^{excess}\propto\left(\chi-\frac{1}{2}\right)$$

So, this is the Flory Huggins theory. Now, as we explained that this may not accurately predict the solubility behavior, but this actually is proportional to this term. For many polymers solvent systems, if we decrease the value of χ, polymer solvent interaction parameter, this terms comes down which means the solubility of the polymer in that particular solvent increases.

We can equate this term as well using the modified Flory Huggins theory and in this particular, this is entropic term. Now, for some solvents, most of the solvents, this entropic term is positive, which means that on dissolution, due to contact interactions between the solvent and solute molecules, the entropy change become positive and in this case, the mixing will happen only when temperature is greater than the θ temperature, in that case this term becomes negative.

Now, in some solvent polymer system, if there is strong hydrogen bonding or some strong electrostatic interaction, in that case, entropy terms can be negative. Due to the strong hydrogen bond formation or hydrophobic interaction, there is actually decrease in entropy due to contact between polymer and solvent molecules. In that case, θ must be greater than the temperature or temperature must be lower than the θ temperature to effect the mixing between polymer solvent system. So, to basically to predict or to identify a solvent for a particular polymer, polymer sample, we need to have idea about their θ temperature as well as the sign of this entropy factor which basically depends on the interaction between interaction behavior between polymer and the solvent system.

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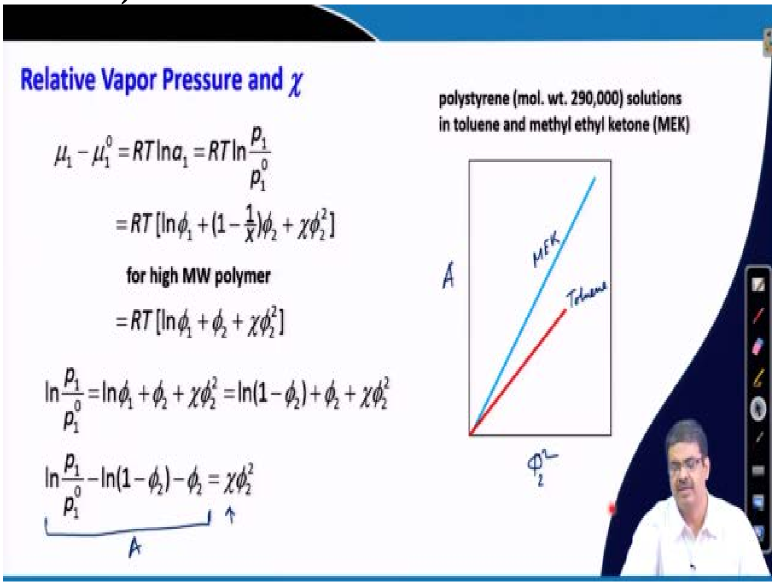

Relative Vapor Pressure and χ

$$\mu_1-\mu_1^0=RT\ln a_1=RT\ln\frac{p_1}{p_1^0}$$

$$=RT[\ln\phi_1+(1-\frac{1}{x})\phi_2+\chi\phi_2^2]$$

for high MW polymer

$$=RT[\ln\phi_1+\phi_2+\chi\phi_2^2]$$

$$\ln\frac{p_1}{p_1^0}=\ln\phi_1+\phi_2+\chi\phi_2^2=\ln(1-\phi_2)+\phi_2+\chi\phi_2^2$$

$$\underbrace{\ln\frac{p_1}{p_1^0}-\ln(1-\phi_2)-\phi_2}_{A}=\chi\phi_2^2 \uparrow$$

polystyrene (mol. wt. 290,000) solutions in toluene and methyl ethyl ketone (MEK)

$$\mu_1-\mu_1^0=RT\ln a_1=RT\ln\frac{p_1}{p_1^0}$$

$$=RT\left[\ln\phi_1+\left(1-\frac{1}{x}\right)\phi_2+\chi\phi_2^2\right]$$

For high MW polymer, $\mu_1-\mu_1^0=RT[\ln\phi_1+\phi_2+\chi\phi_2^2]$

We will now talk about relative vapor pressure and χ. This helps us to determine the value of χ. We go back to the original equation of μ_1 - μ_1^0 and we can write this expression from Flory Huggins theory. If the polymer molecular weight is large, then x will be also large, in that case, we can ignore 1/x compared to 1. So, we can just write this term and we can basically rearrange the term to get the final expression.

Now, what is p_i ? p_i is the partial vapor pressure of the solvent in the solution and p_i^0 is the vapor pressure of the pure solvent at that particular temperature. This is one example of polystyrene molecular weight of 2,90,000 in toluene and methyl ethyl ketone. So, if we plot $\ln\frac{p_1}{p_1^0} - \ln(1-\phi_2) - \phi_2$ in Y axis, and ϕ_2^2 in the X axis then the slope will be given by the polymer solvent action parameter. This is for methyl ethyl ketone and this is for toluene for this particular example. So, from just by measuring the vapor pressure of the solution and with the knowledge of the vapor pressure of pure solvent, we can actually find out the value of polymer solvent interaction parameter using this equation.

$$\ln\frac{p_1}{p_1^0} = \ln\phi_1 + \phi_2 + \chi\phi_2^2 = \ln(1-\phi_2) + \phi_2 + \chi\phi_2^2$$

$$\ln\frac{p_1}{p_1^0} - \ln(1-\phi_2) - \phi_2 = \chi\phi_2^2$$

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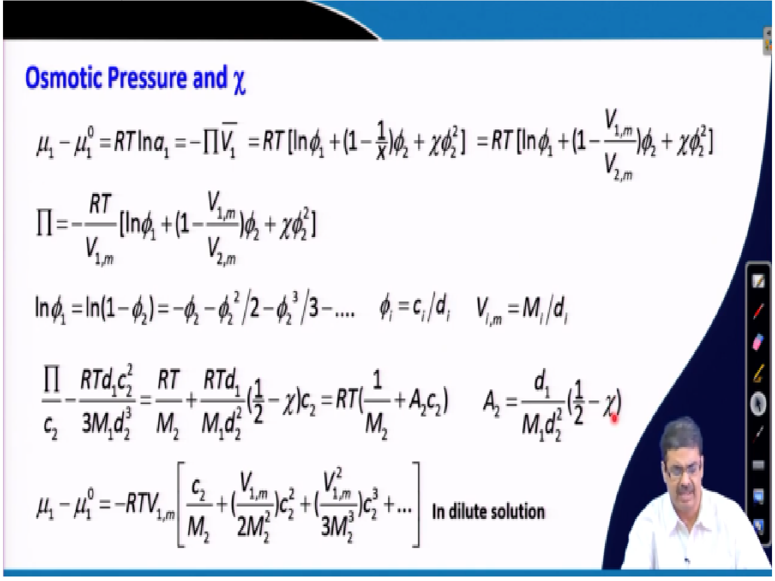

Osmotic Pressure and χ

$$\mu_1 - \mu_1^0 = RT\ln a_1 = -\Pi\overline{V_1} = RT[\ln\phi_1 + (1-\frac{1}{x})\phi_2 + \chi\phi_2^2] = RT[\ln\phi_1 + (1-\frac{V_{1,m}}{V_{2,m}})\phi_2 + \chi\phi_2^2]$$

$$\Pi = -\frac{RT}{V_{1,m}}[\ln\phi_1 + (1-\frac{V_{1,m}}{V_{2,m}})\phi_2 + \chi\phi_2^2]$$

$$\ln\phi_1 = \ln(1-\phi_2) = -\phi_2 - \phi_2^2/2 - \phi_2^3/3 - .... \quad \phi_i = c_i/d_i \quad V_{i,m} = M_i/d_i$$

$$\frac{\Pi}{c_2} - \frac{RTd_1c_2^2}{3M_1d_2^3} = \frac{RT}{M_2} + \frac{RTd_1}{M_1d_2^2}(\frac{1}{2}-\chi)c_2 = RT(\frac{1}{M_2} + A_2c_2) \quad A_2 = \frac{d_1}{M_1d_2^2}(\frac{1}{2}-\chi)$$

$$\mu_1 - \mu_1^0 = -RTV_{1,m}\left[\frac{c_2}{M_2} + (\frac{V_{1,m}}{2M_2^2})c_2^2 + (\frac{V_{1,m}^2}{3M_2^3})c_2^3 + ...\right]$$ In dilute solution

$$\mu_1 - \mu_1^0 = RT\ln a_1 = -\Pi\overline{V_1} = RT\left[\ln\phi_1 + \left(1-\frac{1}{x}\right)\phi_2 + \chi\phi_2^2\right]$$

$$= RT\left[\ln\phi_1 + \left(1-\frac{V_{1,m}}{V_{2,m}}\right)\phi_2 + \chi\phi_2^2\right]$$

$$\Pi = -\frac{RT}{V_{1,m}}\left[\ln\phi_1 + \left(1-\frac{V_{1,m}}{V_{2,m}}\right)\phi_2 + \chi\phi_2^2\right]$$

$$\ln \phi_1 = \ln(1-\phi_2) = -\phi_2 - \phi_2^2/2 - \phi_2^3/3 - \cdots \qquad \phi_i = c_i/d_i \quad V_{i,m} = M_i/d_i$$

$$\frac{\Pi}{c_2} - \frac{RTd_1c_2^2}{3M_1d_2^3} = \frac{RT}{M_2} + \frac{RTd_1}{M_1d_2^2}\left(\frac{1}{2}-\chi\right)c_2 = RT\left(\frac{1}{M_2} + A_2c_2\right) \qquad A_2 = \frac{d_1}{M_1d_2^2}\left(\frac{1}{2}-\chi\right)$$

$$\mu_1 - \mu_1^0 = -RTV_{1,m}\left[\frac{c_2}{M_2} + \left(\frac{V_{1,m}}{2M_2^2}\right)c_2^2 + \left(\frac{V_{1,m}^2}{3M_2^3}\right)c_2^3 + \cdots\right] \quad \textit{in dilute solution}$$

We can also use osmotic pressure and determine polymer solvent interaction parameter. Now, here Π is the osmotic pressure, and $\overline{V_1}$ is partial molar volume of the solvent. We can again write the Flory Huggins theory and rearrange. In this case x is the ratio of molar volume of the polymer divided by molar volume of the solvent. So, we can just rearrange, this is the molar volume of the solvent molecule and this is the molar volume of polymer molecule. So, you can rearrange and get the osmotic pressure in this way and with the knowledge that we can express the mole volume fraction of solvent as volume fraction of polymer using this approximation. Also we can express this volume fraction of either solvent or the polymer as concentration of that solvent or polymer divided by the density, and molar volume as molecular weight divided by density. So, if you utilize all these mathematical formulas, then we can express the osmotic pressure divided by the concentration of the solute and we can have this expression and in case of dilute solution, we can write this as a virial expression. Now, this is just a mathematical derivation so there is nothing to be discussed too much. This term A_2 is given by this expression is also known as polymer solvent interaction term, which is related to the volume of solvent interaction parameter.

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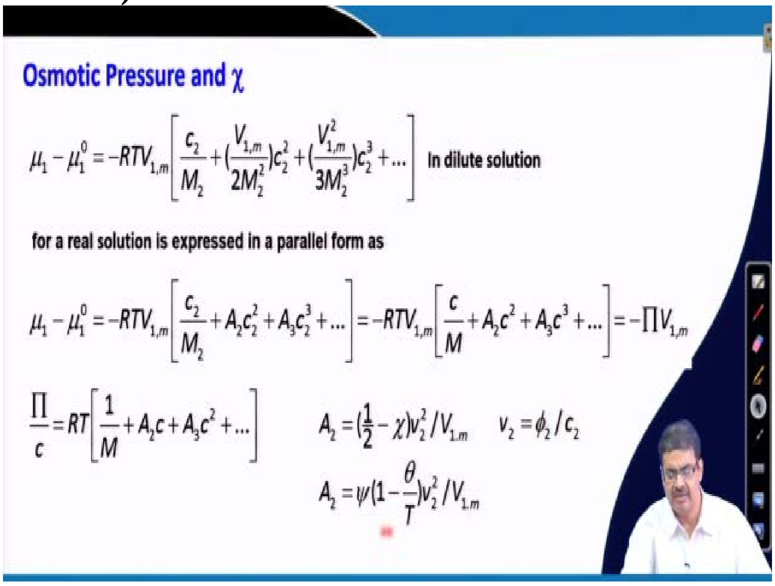

Osmotic Pressure and χ

$$\mu_1 - \mu_1^0 = -RTV_{1,m}\left[\frac{c_2}{M_2} + (\frac{V_{1,m}}{2M_2^2})c_2^2 + (\frac{V_{1,m}^2}{3M_2^3})c_2^3 + \ldots\right] \text{ In dilute solution}$$

for a real solution is expressed in a parallel form as

$$\mu_1 - \mu_1^0 = -RTV_{1,m}\left[\frac{c_2}{M_2} + A_2c_2^2 + A_3c_2^3 + \ldots\right] = -RTV_{1,m}\left[\frac{c}{M} + A_2c^2 + A_3c^3 + \ldots\right] = -\Pi V_{1,m}$$

$$\frac{\Pi}{c} = RT\left[\frac{1}{M} + A_2c + A_3c^2 + \ldots\right] \qquad A_2 = (\frac{1}{2} - \chi)v_2^2/V_{1.m} \qquad v_2 = \phi_2/c_2$$

$$A_2 = \psi(1 - \frac{\theta}{T})v_2^2/V_{1.m}$$

$$\mu_1 - \mu_1^0 = -RTV_{1,m}\left[\frac{c_2}{M_2} + \left(\frac{V_{1,m}}{2M_2^2}\right)c_2^2 + \left(\frac{V_{1,m}^2}{3M_2^3}\right)c_2^3 + \cdots\right] \quad in\ dilute\ solution$$

For a real solution is expressed in a parallel form as

$$\mu_1 - \mu_1^0 = -RTV_{1,m}\left[\frac{c_2}{M_2} + A_2c_2^2 + A_3c_2^3 + \cdots\right] = -RTV_{1,m}\left[\frac{C}{M} + A_2c^2 + A_3c^3 + \cdots\right] = -\Pi V_{1,m}$$

$$\frac{\Pi}{c} = RT\left[\frac{1}{M} + A_2c + A_3c^2 + \cdots\right]$$

$$A_2 = \left(\frac{1}{2} - \chi\right)v_2^2/V_{1,m} \qquad v_2 = \phi_2/c_2$$

$$A_2 = \psi\left(1 - \frac{\theta}{T}\right)v_2^2/V_{1,m}$$

So, in dilute solution, we can express this quantity as this, and for real solution, we can express this term as a virial expression. We can express this term in terms of osmotic pressure and molar volume of the solvent. So, finally, we can express the osmotic pressure in terms of concentration, c is the concentration of the polymer and we can get this expression where M is the molecular weight of the polymer and c is the concentration of the polymer in solution and these are the virial coefficients.

If we plot now, we can measure the osmotic pressure at different concentration and then plot Π/c with respect to concentration and from the intercept we can get the molecular weight and from the slope initial slope, we can get this A_2 term which is this. So, from there we can get the polymer solving interaction parameter as well. Now, this expression also can be used to determine the polymer molecular weight.

When we discuss determination of polymer molecular weight after 2 lectures, we will recall the equation and just show how the static pressure measurement can be used to determine the molecular weight of a polymer sample. v_2 is the volume of the polymer which can be expressed as volume fraction by concentration. In next lecture we will discuss about solubility parameters and how to use solubility parameters to determine and predict the solubility behavior of polymer in a particular sample.