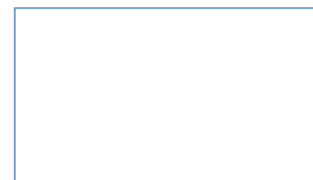


Polymer Process Engineering
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Lecture – 07
Thermodynamics of polymer systems-II

Hello friends, welcome to the next section of the thermodynamics of polymers. of polymeric systems under the edges of polymer process engineering. Now in previously, we covered what is thermodynamics how these thermodynamics is applicable to the polymeric system. We discussed about the polymer PVT data, we discussed about the equations of state for the polymeric system and calorimetric data. Now, in this particular segment, we are going to discuss the enthalpy and entropy calculation for polymers. Then we will discuss about the phase behaviour of a polymeric system, we will discuss the fugacity and activity, we will have a brief outlook on the equilibrium conditions because it plays a very vital role during the polymerization process.

Topics to be covered

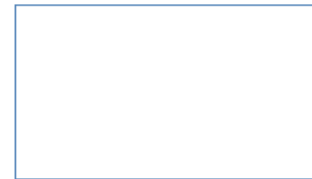
- **Enthalpy and Entropy Calculations for Polymers**
- **Phase Behaviour of Polymer System**
- **Fugacity and Activity**
- **Equilibrium conditions**
- **Theories in thermodynamics**



And then I will discuss couple of theories which are applicable in the polymeric thermodynamic studies. So, let us start with the thermodynamic properties for polymers. The principal thermodynamic properties used in processing they are enthalpy and entropy as per the previous discussion when we are having the granules and we need to develop any kind of a useful product and ultimately we need to melt or we need to subject in those melt in either in the different type of a moulding operation where we need to apply the heat and this heat plays a very vital role in shaping all those polymers that becomes the useful product over the period of time. Now, the knowledge about those thermodynamic behaviour is quite essential and these are usually represented in the form of enthalpy and entropy.

Thermodynamic properties for polymer systems

- The principal thermodynamic properties used in processing are enthalpy and entropy.
- Basically, these are functions of pressure and temperature that can be calculated from appropriate calorimetric and P-V-T data.
- Another factor that must be considered is the state of the polymer (i.e., solid or molten).



But you cannot measure these enthalpy and entropy directly therefore, you require certain correlations and as discussed in the previous lecture that these correlations can be developed with the help of a pressure volume temperature data. So, therefore, the importance of these pressure volume temperature data cannot be overlooked. So, these enthalpies as evident when we are saying that enthalpy and entropy they are dependent on the pressure volume temperature data this can be calculated from the appropriate calorimetric data and p-v-t data. Another factor this must be considered in is the state of polymer that is solid or molten if it is molten then again you need to have such kind of a data for your ready reference. Now, for solid polymers the enthalpy can be written as the temperature and pressure constant minus that is T^* to T C_p solid dT this is a use of thermodynamic equation and for Entropy it can be represented as $S(T, P)$ minus $S(T^*, P)$, which is the base temperature over T dT .

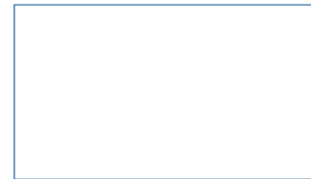
Thermodynamic properties for polymer systems

- For a solid polymer;
- Enthalpy can be written as;

$$H_{T,P} - H_{T^*,P} = \int_{T^*}^T (C_p)_{\text{solid}} dT$$

- Entropy can be written as;

$$S_{T,P} - S_{T^*,P} = \int_{T^*}^T \frac{(C_p)_{\text{solid}}}{T} dT$$



$$H_{T,P} - H_{T^*,P} = \int_{T^*}^T (C_p)_{\text{solid}} dT$$

$$S_{T,P} - S_{T^*,P} = \int_{T^*}^T \frac{(C_p)_{\text{solid}}}{T} dT$$

Here H is the enthalpy, S is the entropy, T is the temperature we can say in the absolute, and P is a pressure, either you may represent in psi or atom atmospheric; then Cp is the specific heat at constant pressure usually represented by the calorie per gram Kelvin or BTU per pound very rankine. T star is the base temperature this equation represents the change in the enthalpy and entropy at constant pressure because you see here we have kept the temperature sorry pressure constant from the base temperature at any particular temperature. Now, in the calculation of these properties the constant pressure is taken as atmospheric since you see that Cp data these are available at that pressure and the base temperature that is T star can be any number of different points like 0 degree Celsius Kelvin or 100 degree Celsius as per that is sometimes it is referred as the reference data. Now, it is set to some extent by the availability of Cp data. So, the benchmarking is either this reference temperature or T star or the Cp data.

Now, for example, like base temperature T star lower than degree Celsius should not be chosen if specific heat data are not available below that particular temperature. The end result of computing enthalpies and entropies in to yield data dependent on base temperature selected, whatever base temperature you have selected, that depends on over it. Now, however, it is quite important to notice that most computations involving the enthalpy and entropy actually involve change in these quantities. Like suppose we want to determine the enthalpy change from a temperature T1 and to another high temperature T2. Then delta H if we move from T1 to T2 this can be given as H T2 pressure

we are keeping constant, then this is the base temperature or reference temperature minus H_{T1} . Here we use T_2 at constant pressure $H_{T2,P}$ minus $H_{T1,P}$ at constant pressure.

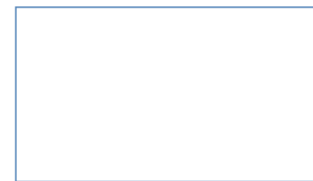
Thermodynamic properties for polymer systems

- The end result of computing enthalpies and entropies seem to yield data dependent on the T^* selected.
- However, it is important to notice that most computations involving enthalpy and entropy actually involve changes in these quantities.
- e.g., suppose we want to determine the enthalpy change from a temperature T_1 to another higher temperature, T_2 .

Then,

$$\Delta H \text{ from } T_1 \text{ to } T_2 = (H_{T_2,P} - H_{T^*,P}) - (H_{T_1,P} - H_{T^*,P})$$

$$\Delta H \text{ from } T_1 \text{ to } T_2 = H_{T_2,P} - H_{T_1,P}$$



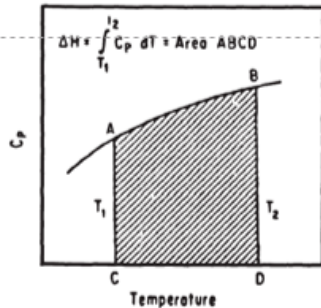
$$\Delta H \text{ from } T_1 \text{ to } T_2 = (H_{T_2,P} - H_{T^*,P}) - (H_{T_1,P} - H_{T^*,P})$$

$$\Delta H \text{ from } T_1 \text{ to } T_2 = H_{T_2,P} - H_{T_1,P}$$

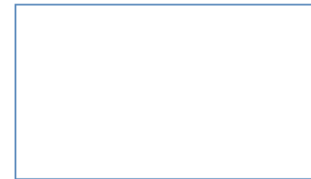
Hence, the change in the enthalpy or entropy at constant pressure with temperature is independent of the selected base temperature that is T^* . So, the method frequently used to compute an enthalpy change is to solve the $C_p dT$ integral graphically and this is schematically shown in this particular figure. This is this figure shows the change of enthalpy with temperature. So, x axis temperature and y axis the enthalpy. Now, this particular area ABCD this represents the enthalpy change.

Thermodynamic properties for polymer systems

- Hence, the change in enthalpy or entropy, at constant pressure, with temperature is independent of the selected base temperature T^* .
- A method frequently used to compute an enthalpy change is to solve the
- $C_p dT$ integral graphically. This is shown schematically in Figure.



Figure; Showing change of enthalpy with temperature



So, the same approach can be used for entropy by plotting C_p over T versus T and then evaluating the area under curve. Now, semi crystalline and amorphous polymer undergo somewhat different experiences as the temperature increases. So, the semi crystalline polymers ultimately exhibit a melting point and form a true melt whereas the amorphous usually soften, but do not melt. Hence the solid polymer equation for enthalpy and entropy they are valid for high temperature. On the other hand, the discontinuity that is the melting for the semi crystalline polymer makes it necessary to change the form of the equation for these materials.

So, the altered form of semi crystalline polymer this can be given as H at constant temperature and pressure that is for the melt minus H at the base temperature and pressure. This can be represented as from base temperature to the temperature of fusion C_p we need to have for the solid dT plus ΔH fusion plus from T fusion to T C_p melt dT . for the entropy this can be given as S at constant temperature for the melt minus S for the base temperature and constant pressure from base temperature to fusion then C_p for solid over T dT plus ΔH for the fusion over T fusion plus integration from T fusion to T C_p melt over T dT . Now the specific heats for the molten and solid cases they are different in both the equation the heat of fusion of the material must be included in that particular aspect. Basically, these equations involve at constant pressure taking material up to the melting point that is the temperature of fusion and melting it that is called the heat of fusion and then moving from melting point up to the final temperature.

Thermodynamic properties for polymer systems

- Hence, the solid polymer equations for enthalpy and entropy are valid for high temperatures.
- On the other hand, the discontinuity (melting) for the semicrystalline polymer makes it necessary to change the form of the equations for these materials.
- The altered form for semicrystalline polymers is

$$(H_{T,P})_{\text{melt}} - H_{T^*,P} = \int_{T^*}^{T_{\text{fusion}}} (C_p)_{\text{solid}} dT + \Delta H_{\text{fusion}} + \int_{T_{\text{fusion}}}^T (C_p)_{\text{melt}} dT$$

$$(H_{T,P})_{\text{melt}} - H_{T^*,P} = \int_{T^*}^{T_{\text{fusion}}} (C_p)_{\text{solid}} dT + \Delta H_{\text{fusion}} + \int_{T_{\text{fusion}}}^T (C_p)_{\text{melt}} dT$$

$$(S_{T,P})_{\text{melt}} - S_{T^*,P} = \int_{T^*}^{T_{\text{fusion}}} \frac{(C_p)_{\text{solid}}}{T} dT + \frac{\Delta H_{\text{fusion}}}{T_{\text{fusion}}} + \int_{T_{\text{fusion}}}^T \frac{(C_p)_{\text{melt}}}{T} dT$$

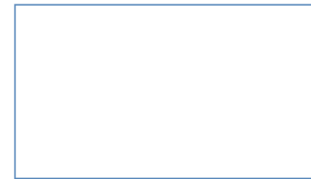
Now once again as with the solid material the choice of base temperature becomes unimportant since the usual case involve determining the change in the enthalpy or entropy and that is a change in enthalpy of a melt from at one temperature to another this can be given as ΔH_{melt} and let us take from T_1 to T_2 for both the cases then it can be given as $H_{T_2,P}$ for the melt minus H at constant base temperature and pressure minus H at constant T_1 and constant temperature constant pressure then $H_{T_2,P}$ minus $H_{T_1,P}$ and ΔH_{melt} from T_1 to T_2 this can be given as $H_{T_2,P}$ minus $H_{T_1,P}$. Now there can also be a pressure effect on either enthalpy or entropy such effect can be given as $H_{T,P}$ minus $H_{T,P_{\text{base}}}$ from base pressure to P minus $T \left(\frac{\partial V}{\partial T} \right)_P dP$ and $S_{T,P}$ minus $S_{T,P_{\text{base}}}$ is equal to minus base pressure to P $\left(\frac{\partial V}{\partial T} \right)_P dP$. Now these equations are constant temperature and this base pressure represents the standard pressure usually the atmospheric pressure. So, one atmosphere is chosen for this kind of a thing and generic equation. The base is usually taken for pressure and temperature that are the atmospheric pressure and either 0 or 25 degree Celsius or 1273 Kelvin or 298 Kelvin.

Thermodynamic properties for polymer systems

- Once again, as with the solid material, the choice of T^* becomes unimportant since the usual case involves determining changes in enthalpy or entropy.
- e.g., a change in enthalpy of a melt from one temperature to another would be given by

$$\Delta H_{\text{melt}} \text{ from } T_1 \text{ to } T_2 = \left[\left(H_{T_2, P} \right)_{\text{melt}} - \left(H_{T^*, P} \right) \right] - \left[\left(H_{T_1, P} \right)_{\text{melt}} - \left(H_{T^*, P} \right) \right]$$

$$\Delta H_{\text{melt}} \text{ from } T_1 \text{ to } T_2 = \left(H_{T_2, P} \right)_{\text{melt}} - \left(H_{T_1, P} \right)_{\text{melt}}$$



$$\Delta H_{\text{melt}} \text{ from } T_1 \text{ to } T_2 = \left[\left(H_{T_2, P} \right)_{\text{melt}} - \left(H_{T^*, P} \right) \right] - \left[\left(H_{T_1, P} \right)_{\text{melt}} - \left(H_{T^*, P} \right) \right]$$

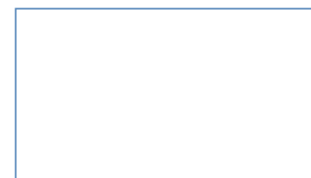
$$\Delta H_{\text{melt}} \text{ from } T_1 \text{ to } T_2 = \left(H_{T_2, P} \right)_{\text{melt}} - \left(H_{T_1, P} \right)_{\text{melt}}$$

Thermodynamic properties for polymer systems

- There can also be a pressure effect on either enthalpy or entropy. Such effects are given by;

$$H_{T, P} - H_{T, P^*} = \int_{P^*}^P \left[V - T \left\{ \frac{\partial V}{\partial T} \right\}_P \right] dP$$

$$S_{T, P} - S_{T, P^*} = - \int_{P^*}^P \left(\frac{\partial V}{\partial T} \right)_P dP$$



$$H_{T,P} - H_{T,P^*} = \int_{P^*}^P \left[V - T \left\{ \frac{\partial V}{\partial T} \right\}_P \right] dP$$

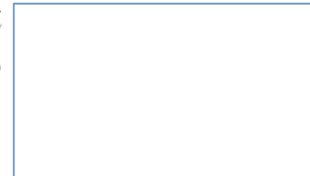
$$S_{T,P} - S_{T,P^*} = - \int_{P^*}^P \left(\frac{\partial V}{\partial T} \right)_P dP$$

The pressure corrections can be applied for either a solid or molten polymer. This is the only stipulation that the function ∂V over ∂T at constant pressure be determined in the appropriate state and that is the solid or melt. Now let us talk about the phase behaviour of polymeric solution. Now formation of solution is quite important sometimes with the help of a solvent and sometimes with the help of a CO motor things. The equilibrium condition for phase equilibrium can be derived in the simplest way using the Gibbs energy.

Thermodynamic properties for polymer systems

❖ Phase Behavior of Polymer Solutions

- The equilibrium conditions for phase equilibria can be derived in the simplest way using the Gibbs energy (G).
- According to the second law of thermodynamics, the total Gibbs energy of a closed system at constant temperature and pressure is a minimum at equilibrium.
- If this condition is combined with the condition that the total number of moles of component 'i' is constant in a closed system.



We have talked about this Gibbs energy in the previous segment. Now according to the second law of thermodynamics the total Gibbs energy of the closed system at constant temperature and pressure is the minimum of equilibrium. Now if this condition is combined with the condition that the total number of moles of component i is constant in a closed system where you see that can be mathematically you can represent like this which is constant. Now $\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma$. Now i is 1, 2 up to n.

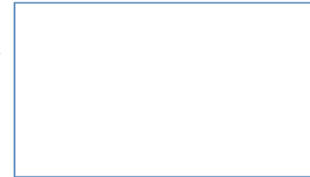
Thermodynamic properties for polymer systems

$$\sum_{\alpha} n_i^{\alpha} = \text{constant}$$

$$\mu_i^{\alpha} = \mu_i^{\beta} = \dots = \mu_i^{\pi} \quad \text{for } i = 1, 2, \dots, N$$

Where,

- n_i^{α} is number of moles of component 'i' in phase a,
- The equilibrium conditions given by second equation can easily be derived for a system of π phases and N components.



$$\sum_{\alpha} n_i^{\alpha} = \text{constant}$$

$$\mu_i^{\alpha} = \mu_i^{\beta} = \dots = \mu_i^{\pi} \quad \text{for } i = 1, 2, \dots, N$$

Now this particular n_i^{α} is a number of moles of component in i th phase α and the equilibrium condition given by the second this equation can easily be derived with the system for π phases these are the phases. Now let us talk about the chemical potential in brief. The chemical potential of component i in the phase α is defined by the equation which we are going to write that is μ_i^{α} is equal to $\left(\frac{\partial n_i}{\partial n_i} \right)_{P, T, n_j \neq i}$. Now let us talk about the fugacity and activity. Now in thermodynamic treatment of phase equilibria auxiliary thermodynamic functions such as fugacity coefficient and activity coefficients they are often used.

$$\mu_i^{\alpha} = \left(\frac{\partial \left(\sum_i n_i^{\alpha} g^{\alpha} \right)}{\partial n_i^{\alpha}} \right)_{P, T, n_j \neq i}$$

Thermodynamic properties for polymer systems

❖ Chemical potential

The chemical potential of component 'i' in phase α is defined by equation given below, where 'g' is the molar Gibbs energy.

$$\mu_i^\alpha = \left(\frac{\partial \left(\sum_i n_i^\alpha g^\alpha \right)}{\partial n_i^\alpha} \right)_{P, T, n_{j \neq i}}$$



These functions are closely related to the Gibbs free energy. Now the fugacity of a component i in a mixture if we are representing by f_i is defined as $\phi_i p_i$ this is the fugacity coefficient is equal to fugacity of ith component and this is the p_i . Now according to this definition f_i is equal to the partial pressure of p_i in the case of ideal gas. So, the units of fugacity is same as a pressure. Now it is the measure of the deviation from ideal gas behaviour or ideal behaviour.

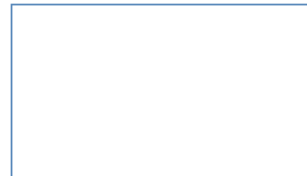
Thermodynamic properties for polymer systems

❖ Fugacity and Activity

- In the thermodynamic treatment of phase equilibria, auxiliary thermodynamic functions such as the fugacity coefficient and the activity coefficient are often used.
- These functions are closely related to the Gibbs energy.
- The fugacity of component 'i' in a mixture, represented by f_i , is defined by as;

$$d\mu_i \equiv RT \ln \hat{f}_i \quad \text{at constant } T$$

$$\lim_{P \rightarrow 0} \frac{\hat{f}_i}{P_i} = 1$$



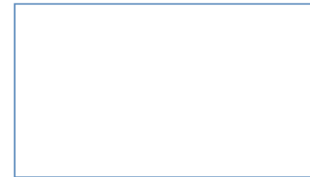
$$d\mu_i \equiv RT \ln \hat{f}_i \quad \text{at constant } T$$

$$\lim_{P \rightarrow 0} \frac{\hat{f}_i}{P_i} = 1$$

Thermodynamic properties for polymer systems

- According to this definition, f_i is equal to the partial pressure P_i in the case of an ideal gas.
- It is a measure of the deviation from ideal gas behavior.
- The fugacity coefficient is defined as;

$$\hat{\phi}_i = \frac{\hat{f}_i}{P_i}$$



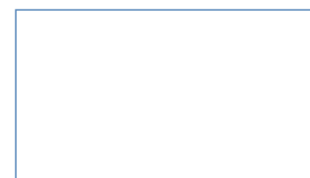
So, we have already defined the fugacity coefficient in the previous slide. Now the fugacity coefficient can be calculated from any equation of state. Let us talk about this: $RT \ln \hat{\phi}_i$ is equal to $\int_0^P (\bar{v}_i - \frac{RT}{P}) dP$. All these terms are in their usual denoting and $RT \ln \hat{\phi}_i$ is equal to $-\int_{\infty}^V \left[\left(\frac{\partial P}{\partial n_i} \right)_{V, T, n_{j \neq i}} - \frac{RT}{V} \right] + RT \ln \left(\frac{\sum_i n_i RT}{PV} \right)$. Now, sometimes activity plays a very vital role this is defined as the ratio of f_i and to the fugacity of component i in the standard state that is denoted as f_i° under the same pressure and temperature conditions. So, A_i that is the activity is defined as f_i / f_i° at same temperature pressure and x_i over f_i° under the same temperature pressure conditions under the standard condition.

Thermodynamic properties for polymer systems

- The fugacity coefficient can be calculated from an equation of state

$$RT \ln \hat{\phi}_i = \int_0^P \left(\bar{v}_i - \frac{RT}{P} \right) dP$$

$$RT \ln \hat{\phi}_i = - \int_{\infty}^V \left[\left(\frac{\partial P}{\partial n_i} \right)_{V, T, n_{j \neq i}} - \frac{RT}{V} \right] + RT \ln \left(\frac{\sum_i n_i RT}{PV} \right)$$



$$RT \ln \hat{\phi}_i = \int_0^P \left(\bar{v}_i - \frac{RT}{P} \right) dP$$

$$RT \ln \hat{\phi}_i = - \int_{\infty}^V \left[\left(\frac{\partial P}{\partial n_i} \right)_{V, T, n_{j \neq i}} - \frac{RT}{V} \right] + RT \ln \left(\frac{\sum_i n_i RT}{PV} \right)$$

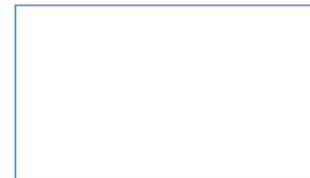
Thermodynamic properties for polymer systems

- The activity (a_i) is defined as the ratio of f_i and the fugacity of component 'i' in the standard state f_i^0 at the same P and T.

$$a_i \equiv \frac{\hat{f}_i(P, T, x)}{f_i^0(P, T, x^0)}$$

- An ideal solution is defined by Eq.

$$a_i^{id} \equiv x_i$$



$$a_i \equiv \frac{\hat{f}_i(P, T, x)}{f_i^0(P, T, x^0)} \quad a_i^{id} \equiv x_i$$

So, the ideal solution is defined as A_i this is i^d represents the ideal is equal to x_i . Now the activity coefficient of component i is a measure of deviation from the ideal solution behaviour so that the fugacity of non-ideal liquid solution this can be written as γ_i is equal to A_i over A_i^{id} and the fugacity of i th component can be represented as $x_i \gamma_i$ these are the mole fractions i f naught. Now the activity coefficient can be calculated from a model for molar excess Gibbs energy, sometimes referred as g^E . Now this can be mathematically represented as $RT \ln \gamma_i$ is equal to $\Delta \sum n_i g^E$ over i and $\Delta \ln i$ at constant pressure temperature, and n_j is not equal to i . Now in this approach the standard state fugacity f_i^0 of a liquid component is usually the fugacity of the pure liquid component and is closely related to the vapour pressure of i^{th} component under the saturation condition for that particular segment.

$$\gamma_i \equiv \frac{a_i}{a_i^{id}}$$

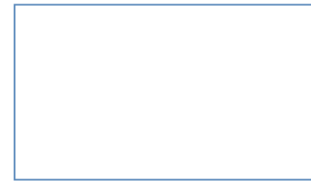
$$\hat{f}_i = x_i \gamma_i f_i^0$$

Thermodynamic properties for polymer systems

- The activity coefficient of component 'i', is a measure of the deviation from ideal solution behavior, so the fugacity of a non-ideal liquid solution can be written as;

$$\gamma_i \equiv \frac{a_i}{a_i^{id}}$$

$$\hat{f}_i = x_i \gamma_i f_i^0$$

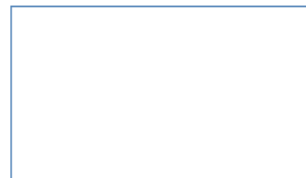


Thermodynamic properties for polymer systems

- The activity coefficient can be calculated from a model for the molar excess Gibbs energy (g^E)

$$RT \ln \gamma_i = \left(\frac{\partial \left(\sum_i n_i g^E \right)}{\partial n_i} \right)_{P, T, n_j \neq i}$$

- In this approach the standard state fugacity f_i^0 of a liquid component is usually the fugacity of the pure liquid component, and is closely related to the vapor pressure P_i^{sat} of that component.



$$RT \ln \gamma_i = \left(\frac{\partial \left(\sum_i n_i g^E \right)}{\partial n_i} \right)_{P, T, n_j \neq i}$$

Now on the vapour pressure curve of a pure component we can have this like f_i^0 with component in the liquid phase p saturation t these are the constant then f_i^0 is the p_i saturation t that is equal to this is for the vapour ϕ_i in p_i saturation. Now another this f_i^0 for the liquid given at the desired pressure and temperature this can be represented like this p_i saturation then e to the power p_i saturation to p μ_i over Rt which is equal to f_i^0 p_i saturation t that is the constant to exponential then integration of p_i saturation to p μ_i over Rt dp . So if we combine these 2 equations we can have

this f_i for the liquid phase under the given pressure and temperature this is equal to $\phi_i^V p_i^{sat}$ to the power integration p_i^{sat} to p v_i^L over RT dP . Now this v_i^L of i^{th} component is the molar volume of a pure liquid i and at low pressure the fugacity coefficient and the exponential term they are close to 1. So we can represent close to 1 sorry then we can represent f_i this is equal to p_i^{sat} .

Thermodynamic properties for polymer systems

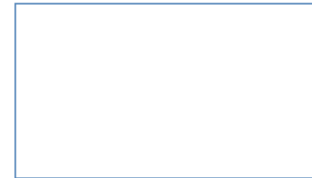
- On the vapor-pressure curve of a pure component, we have;

$$f_i^L(P_i^{sat}, T) = f_i^V(P_i^{sat}, T) = \phi_i^V(P_i^{sat}, T)P_i^{sat}$$

$$f_i^L(P, T) = f_i^L(P_i^{sat}, T) \exp\left(\int_{P_i^{sat}}^P \frac{d\mu_i^L}{RT}\right) = f_i^L(P_i^{sat}, T) \exp\left(\int_{P_i^{sat}}^P \frac{v_i^L}{RT} dP\right)$$

- On combining above two equations, we have;

$$f_i^L(P, T) = \phi_i^V(P_i^{sat}, T)P_i^{sat} \exp\left(\int_{P_i^{sat}}^P \frac{v_i^L}{RT} dP\right)$$



$$f_i^L(P_i^{sat}, T) = f_i^V(P_i^{sat}, T) = \phi_i^V(P_i^{sat}, T)P_i^{sat}$$

$$f_i^L(P, T) = f_i^L(P_i^{sat}, T) \exp\left(\int_{P_i^{sat}}^P \frac{d\mu_i^L}{RT}\right) = f_i^L(P_i^{sat}, T) \exp\left(\int_{P_i^{sat}}^P \frac{v_i^L}{RT} dP\right)$$

$$f_i^L(P, T) = \phi_i^V(P_i^{sat}, T)P_i^{sat} \exp\left(\int_{P_i^{sat}}^P \frac{v_i^L}{RT} dP\right)$$

So, by this way because this is purely you can say sometimes referred as an ideal condition so this is a very generic term. Now equilibrium conditions the equilibrium conditions for low pressure vapour liquid equilibrium VLE the equilibrium conditions can be written as f_i for the liquid phase to the fugacity at vapour phase and this can be written as $x_i \gamma_i f_i^{\text{naught}}$ is equal to $\gamma_i^V p_i^{\text{sat}}$ where x_i and γ_i they are the liquid phase and vapour phase mole fraction of component i . Now the truncated virial equation because virial equation of state is again very useful equation for determining the thermodynamic behaviour of any component or any chemical component. So the truncated virial equation or ideal gas equation is often used as the equation of state. Now the later case all fugacity coefficients are 1 so the simplest form can be written as $x_i \gamma_i p_i^{sat}$ is equal to $\gamma_i^V p_i^{\text{sat}}$.

$$f_i^L \approx P_i^{sat}$$

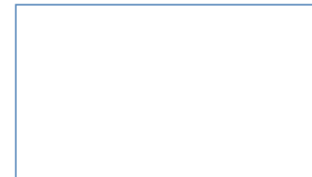
Thermodynamic properties for polymer systems

Where,

v_i^L is the molar volume of pure liquid 'i'.

- At low pressure the fugacity coefficient and the exponential term are close to 1, so

$$f_i^L \approx P_i^{sat}$$



Now in the case of low-pressure liquid liquid equilibrium LLE the equilibrium condition is given by $f_i^L = f_i^V$ or $x_i \gamma_i \phi_i^L = x_i \gamma_i \phi_i^V$ that is the standard condition. Now the two liquid phases are indicated by a prime that is this one and double prime for both liquid phases the standard fugacity is chosen as the pure liquid component in that case it can be represented as $x_i \gamma_i^L = \psi_i \gamma_i^V$. Now for calculation of high-pressure vapour liquid equilibrium or liquid liquid equilibrium an equation of state is always used for both phases. The equilibrium condition is used which is usually given by $f_i^\alpha = f_i^\beta$ or if we expand this thing to $x_i \psi_i^\alpha P^\alpha = x_i \psi_i^\beta P^\beta$ or $x_i \psi_i^\alpha = x_i \psi_i^\beta \frac{P^\beta}{P^\alpha}$. Now low-pressure vapour liquid equilibrium since the polymer have no vapour pressure and as a consequence the vapour phase does not contain any kind of polymer.

$$\hat{f}_i^L = \hat{f}_i^V$$

$$x_i \gamma_i f_i^0 = \gamma_i \hat{\phi}_i P$$

Thermodynamic properties for polymer systems

❖ Equilibrium Conditions

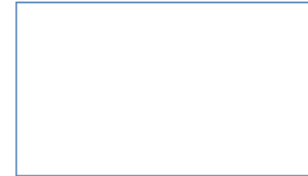
- Equilibrium Conditions For low-pressure vapor-liquid equilibria (VLE) the equilibrium condition can be written as;

$$\hat{f}_i^L = \hat{f}_i^V$$

$$x_i \gamma_i f_i^0 = \gamma_i \hat{\phi}_i P$$

Where,

x_i and y_i are the liquid-phase and vapor-phase mole fraction of component 'i'.



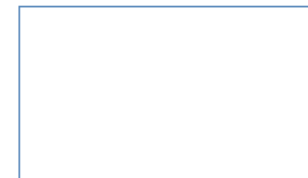
Thermodynamic properties for polymer systems

- The truncated virial equation or the ideal gas equation is often used as the equation of state.
- In the latter case all fugacity coefficients are 1, so the simplest form can be written as;

$$x_i \gamma_i P_i^{sat} = \gamma_i P$$

- In the case of low-pressure liquid-liquid equilibria (LLE) the equilibrium condition is given by Eq.

$$\hat{f}_i' = \hat{f}_i'' \quad \text{or} \quad (x_i \gamma_i f_i^0)' = (x_i \gamma_i f_i^0)''$$



$$x_i \gamma_i P_i^{sat} = \gamma_i P \quad \hat{f}_i' = \hat{f}_i'' \quad \text{or} \quad (x_i \gamma_i f_i^0)' = (x_i \gamma_i f_i^0)''$$

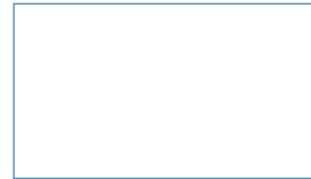
Thermodynamic properties for polymer systems

- The two liquid phases are indicated by prime (0) and double prime (00).
- If for both liquid phases the standard fugacity is chosen as the pure liquid component, then;

$$(x_i \gamma_i)' = (x_i \gamma_i)''$$

- For the calculation of high-pressure vapor-liquid equilibria or liquid-liquid equilibria an equation of state is always used for both phases.
- The equilibrium condition is used, which is given by Eq

$$\hat{f}_i^\alpha = \hat{f}_i^\beta \quad \text{or} \quad (x_i \hat{\phi}_i P)^\alpha = (x_i \hat{\phi}_i P)^\beta \quad \text{or} \quad (x_i \hat{\phi}_i)^\alpha = (x_i \hat{\phi}_i)^\beta$$



$$(x_i \gamma_i)' = (x_i \gamma_i)''$$

$$\hat{f}_i^\alpha = \hat{f}_i^\beta \quad \text{or} \quad (x_i \hat{\phi}_i P)^\alpha = (x_i \hat{\phi}_i P)^\beta \quad \text{or} \quad (x_i \hat{\phi}_i)^\alpha = (x_i \hat{\phi}_i)^\beta$$

So, the equilibrium conditions for low pressure vapour liquid equilibrium of polymer situation are only applicable to the solvent because sometimes solvents are being added to the polymeric system to make more flexible or the case where the weight fraction of polymer w_p is used as a composition variable. So, in that case p is equal to $x_s \gamma_s p$ saturation and that is p is equal to $1 - w_p \Omega_s p$ saturation where this Ω_s is the weight fraction based on the activity coefficient of the solvent. Now the relation between a mole fraction-based activity coefficient and a weight fraction-based activity coefficient Ω_s of a component i is given by this particular equation that is $\gamma_i / \Omega_i w_i$ over x_i that is $m_i j$ is equal from 1 to summation n w_j over m_j where w_j is the weight fraction and m_i is the molecular weight of component i . Now P-J Flory along with this co-worker they have described this thermodynamic behaviour in a more elaborative way and they adopted the liquid-liquid equilibrium. So, as per this P-J Huggins theory of polymer solution which is based on a rigid lattice model in which a polymer molecule is assumed to consist of R segments of a size of a solvent molecule.

$$P = x_s \gamma_s P_s^{sat}$$

$$P = (1 - w_p) \Omega_s P_s^{sat}$$

Thermodynamic properties for polymer systems

❖ Low-pressure Vapor–Liquid Equilibria

- Since polymers have no vapor pressure and as a consequence the vapor phase does not contain polymer.
- The equilibrium conditions for low-pressure vapor–liquid equilibria of polymer solutions are only applicable to the solvents or in a case where the weight fraction of polymer w_p is used as a composition variable.

$$P = x_s \gamma_s P_s^{sat}$$

$$P = (1 - w_p) \Omega_s P_s^{sat}$$

Where, Ω_s is the weight fraction based activity coefficient of the solvent.

Thermodynamic properties for polymer systems

- The relation between a mole fraction based activity coefficient and a weight fraction based activity coefficient Ω_s of component 'i' is given by the following equation.

$$\frac{\gamma_i}{\Omega_i} = \frac{w_i}{x_i} = M_i \sum_{j=1}^N \frac{w_j}{M_j}$$

Where,

w_i is weight fraction

M_i is molecular weight of component 'i'

$$\frac{\gamma_i}{\Omega_i} = \frac{w_i}{x_i} = M_i \sum_{j=1}^N \frac{w_j}{M_j}$$

So, the Flory Huggins expression for the Gibbs energy of mixing of n_s moles of solvent and n_p moles of polymer which is given as $\Delta G_{mix} = n_s RT \ln \phi_s + n_p RT \ln \phi_p + n_s \phi_p \chi_{12}$. Now first two terms in this particular equation of this particular representation so called the combined entropy of mixing and the third term in that particular approximation is for the enthalpy of mixing. In practice χ_{12} is a Flory Huggins interaction parameter


and which is used as an adjustable temperature dependent parameter and ϕ_s and ϕ_p are the segment fractions of solvent and polymer respectively. So, we can represent these terms mathematically x_i is equal to $n_s / (n_s + r n_p)$ and this ϕ_i is equal to $r n_p / (n_s + r n_p)$. Now, according to the original Flory Huggins theory χ is given by is proportional to $\frac{2 \epsilon_{sp} - \epsilon_{ss} - \epsilon_{pp}}{T}$ where ϵ_{ss} , ϵ_{pp} and ϵ_{sp} they are the interaction energies between the two solvent molecules and two polymer segments and a solvent molecule and a polymer segment respectively.

Thermodynamic of polymer systems

❖ **Flory–Huggins Theory and Liquid–Liquid Equilibria**

- The Flory-Huggins theory of polymer solutions is based on a rigid lattice model in which a polymer molecule is assumed to consist of ‘r’ segments of the size of a solvent molecule.
- The Flory-Huggins expression for the Gibbs energy of mixing for N_s moles of solvent and N_p moles of polymer is given as;

$$\frac{\Delta_{mix}G}{RT} = N_s \ln \phi_s + N_p \ln \phi_p + \phi_s \phi_p (N_s + r N_p) \chi$$


32

$$\frac{\Delta_{mix}G}{RT} = N_s \ln \phi_s + N_p \ln \phi_p + \phi_s \phi_p (N_s + r N_p) \chi$$


Thermodynamic of polymer systems

$$\phi_s = \frac{N_s}{N_s + r N_p} \quad \text{and} \quad \phi_p = \frac{r N_p}{N_s + r N_p}$$

- According to the original Flory–Huggins theory χ is given by Eq.

$$\chi \propto \frac{(2\epsilon_{sp} - \epsilon_{ss} - \epsilon_{pp})}{T}$$

Where, ϵ_{ss} , ϵ_{pp} , and ϵ_{sp} are the interaction energies between two solvent molecules, two polymer segments, and a solvent molecule and a polymer segment, respectively.


34

$$\varphi_s = \frac{N_s}{N_s + rN_p} \quad \text{and} \quad \varphi_p = \frac{rN_p}{N_s + rN_p}$$

$$\chi \propto \frac{(2\varepsilon_{sp} - \varepsilon_{ss} - \varepsilon_{pp})}{T}$$

So, the expression for the mole fraction-based activity coefficient of solvent and polymers can be written as $\ln \gamma_s$ is equal to $\ln(1 - \varphi_p) + \frac{\varphi_p}{r} + \left(1 - \frac{1}{r}\right)\varphi_p + \varphi_p^2\chi$ or $\ln \gamma_p$ is equal to $\ln[(1 - \varphi_p)r + \varphi_p] - (r - 1)(1 - \varphi_p) + r(1 - \varphi_p)^2\chi$ where r is approximated by the ratio of the molar volumes of pure liquid polymer and pure solvent. The activity coefficient of the solvent is strongly dependent on r for low values of r but at high values of r γ_s becomes practically independent of r . This implies the equilibrium pressure of low-pressure vapor-liquid equilibrium for a polymer-solvent system which is hardly dependent on the molecular weight of the polymer. Now, in the original formulation of a Flory Huggins theory this ΔG for the mixture increases with decreasing temperature, which leads to the liquid phase split with an upper critical solution temperature. Now, per mole of lattice size, the entropy of mixing of the polymer-solvent system is much less than for the solvent system because this polymer-solvent system shows a strong tendency to demix the solvent system.

Thermodynamic of polymer systems

- The expressions for the mole fraction based activity coefficients of solvent and polymer are written as;

$$\ln \gamma_s = \ln \left[(1 - \varphi_p) + \frac{\varphi_p}{r} \right] + \left(1 - \frac{1}{r} \right) \varphi_p + \varphi_p^2 \chi$$

$$\ln \gamma_p = \ln[(1 - \varphi_p)r + \varphi_p] - (r - 1)(1 - \varphi_p) + r(1 - \varphi_p)^2 \chi$$

- Often 'r' is approximated by the ratio of the molar volumes of pure liquid polymer and pure solvent.

$$\ln \gamma_s = \ln \left[(1 - \varphi_p) + \frac{\varphi_p}{r} \right] + \left(1 - \frac{1}{r} \right) \varphi_p + \varphi_p^2 \chi$$

$$\ln \gamma_p = \ln[(1 - \varphi_p)r + \varphi_p] - (r - 1)(1 - \varphi_p) + r(1 - \varphi_p)^2 \chi$$

Now, here this particular figure shows the liquid liquid equilibrium for polymer solvent system at a different polymer chain length r and this is calculated from the Flory Huggins theory you can see the

changes. Now, this figure shows the influence of R on the location and the shape of the liquid two phase region with increase in R you see that gradually we are increasing R the two-phase region increases in size and becomes more asymmetric. The critical point the temperature maximum of two-phase region shifts with increasing R to lower values of χ higher temperature and lower values of ϕ_p . Now, this at say R infinity when we take this R infinity the critical point found at a limiting value of χ half and ϕ_p is equal to 0 and for χ_p is equal to 0. Now, this follows directly from the critical point condition where Gibbs free energy per mole G is the Gibbs free energy per mole of lattice side.

Thermodynamic of polymer systems

- **Figure shows;**
- Schematically the influence of 'r' on the location and shape of the liquid-liquid two-phase region.
- With increasing 'r', the two-phase region increases in size and becomes more asymmetric.
- The critical point, the temperature maximum of the two-phase region, shifts with increasing 'r' to lower values of χ , higher temperature, and lower values of ϕ_p .

Flory-Huggins interaction parameter χ

Segment fractions of polymer ϕ_p

Source; Richard G. Grisley, Polymer process engineering, 1st edition, published by Chapman & amp; Hall (1995).
39

Now, this Gibbs energy relations this can be written as $\frac{\partial G}{\partial \chi_p}$ at constant pressure and temperature $\frac{\partial^2 G}{\partial \chi_p^2}$ is equal to 0 which leads to this critical $\frac{1}{2} + \frac{1}{\sqrt{r}}$ and χ_{crit} at given pressure is equal to $1 + \frac{1}{\sqrt{r}}$. Now, the theta temperature is usually represented as theta is the highest possible upper critical solution temperature within the framework of a Flory Huggins theory. Many polymers solvent system the temperature above this theta temperature show a second reason with the liquid-liquid invincibility which is characterized by the occurrence of lower critical solution temperature and sometimes which is referred as LCST. Now, this particular figure shows the liquid-liquid equilibrium at low temperature two phase region with UCST and a high temperature two phase region with LCST. Now, this phenomenon cannot be explained on the basis of the original Flory Huggins theory.

$$\left(\frac{\partial \bar{G}}{\partial \phi_p} \right)_{P,T} = \left(\frac{\partial^2 \bar{G}}{\partial \phi_p^2} \right) = 0$$

$$\chi^{crit} = \frac{1}{2} \left(1 + \frac{1}{\sqrt{r}} \right)^2$$

$$\phi_p^{crit} = \frac{1}{1 + \sqrt{r}}$$

Thermodynamic of polymer systems

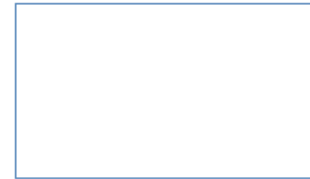
Gibbs energy relation can be written as;

$$\left(\frac{\partial \bar{G}}{\partial \phi_p}\right)_{P,T} = \left(\frac{\partial^2 \bar{G}}{\partial \phi_p^2}\right) = 0$$

Which leads to

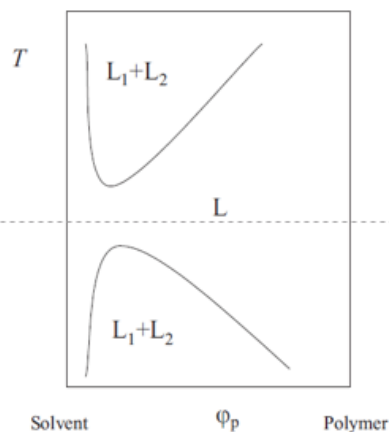
$$\chi^{crit} = \frac{1}{2} \left(1 + \frac{1}{\sqrt{r}}\right)^2$$

$$\phi_p^{crit} = \frac{1}{1 + \sqrt{r}}$$

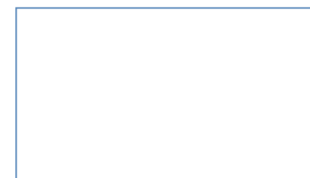


So, other co-workers Delmas and Patterson they calculated binary critical curves of polymer solvent system using the Flory equation of state. So, as per these authors the reason for the occurrence of LCST is the large difference in the thermal expansion of pure liquid polymer and pure solvent which leads to increasing difference in free volume with increasing temperature and LCST type liquid-liquid phase split at temperature below the critical point of the solvent. So, here you see this if the molecular weight of the polymer is increased then UCST and LCST approaches to each other here you can see clearly. Now, another possibility that UCST and LCST never meets and each liquid-liquid region this shows the difference of different theta temperature for R tends to infinity. Another type of LCST is connected to a specific interaction, like hydrogen bonding.

Thermodynamic of polymer systems



Figure; Showing liquid-liquid equilibria showing a low-temperature two-phase region with a UCST and a high temperature two phase region with a LCST.



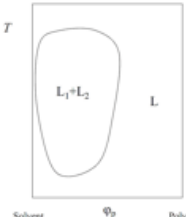
Now, this type of LCST temperature is found at temperature below the UCST here you see like this. Now, let us talk about the high-pressure liquid-liquid and vapour liquid equilibria system where the

separate low and high temperature region of demixing the system in which the low and high temperature region of demixing have merged showing as minimum cloud pressure and system in which the low- and high-pressure temperature region of demixing have merged without the minimum cloud pressure. So, this figure shows the phase behaviour of a binary polymer solution at constant composition in pressure versus temperature diagram. Now, in the case of say curve A this curve the mixture at a low temperature shows a liquid-liquid region characterised by UCST behaviour and a high temperature a liquid-liquid region characterised by LCST behaviour. Now, the curve that separates the liquid-liquid region from one phase liquid region is often called a cloud point curve.


Thermodynamic of polymer systems

- Another type of LCST is connected to specific interactions like hydrogen bonding.
- This type of LCST is found at temperatures below the UCST.

- The resulting phase diagram is presented in the figure.
- The figure shows a closed-loop region of liquid-liquid immiscibility.



Figure; Showing closed-loop liquid-liquid equilibria



Source; Richard G. Grisley, Polymer process engineering, 1st edition, published by Chapman & amp; Hali (1995).

47

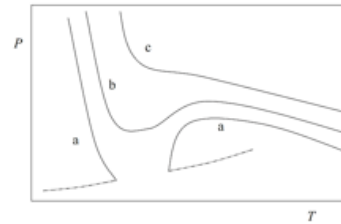
The liquid-liquid vapour curve is found in many cases very close to vapour pressure curve of the pure solvent because of polymer concentration in the vapour phase and in the solvent rich liquid phase is low. Now, in this particular case this again the p t diagram a pressure minimum. Now, pressure minima a pressure below this minimum the hour glass shape two phase region they are formed. Now, in case of curve C this curve the cloud point curve is found at much higher pressure and no longer shows a minimum. Now, in in going from a case A to case C the mutual solubility of polymer and solvent decreases.

Thermodynamic of polymer systems

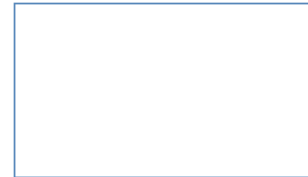
❖ High-pressure Liquid–Liquid and Vapor–Liquid Equilibria

- System with separate low and high temperature regions of de-mixing.
- System in which the low and high temperature regions of de-mixing have merged, showing a minimum cloud pressure.
- System in which the low and high temperature regions of de-mixing have merged, without a minimum cloud pressure.

Note; The full curves are cloud-point curves; the broken curves are liquid-liquid vapor curves.



Figure; Showing P, T phase diagram for a constant composition polymer-solvent system



So, dear friends in this particular segment we discussed about the different polymer solution behaviour. Apart from this we discussed different theories which are applicable for this phase behaviour and for your convenience we have enlisted couple of references which can you can be utilized as per the case needed. Thank you very much.