Polymer Process Engineering
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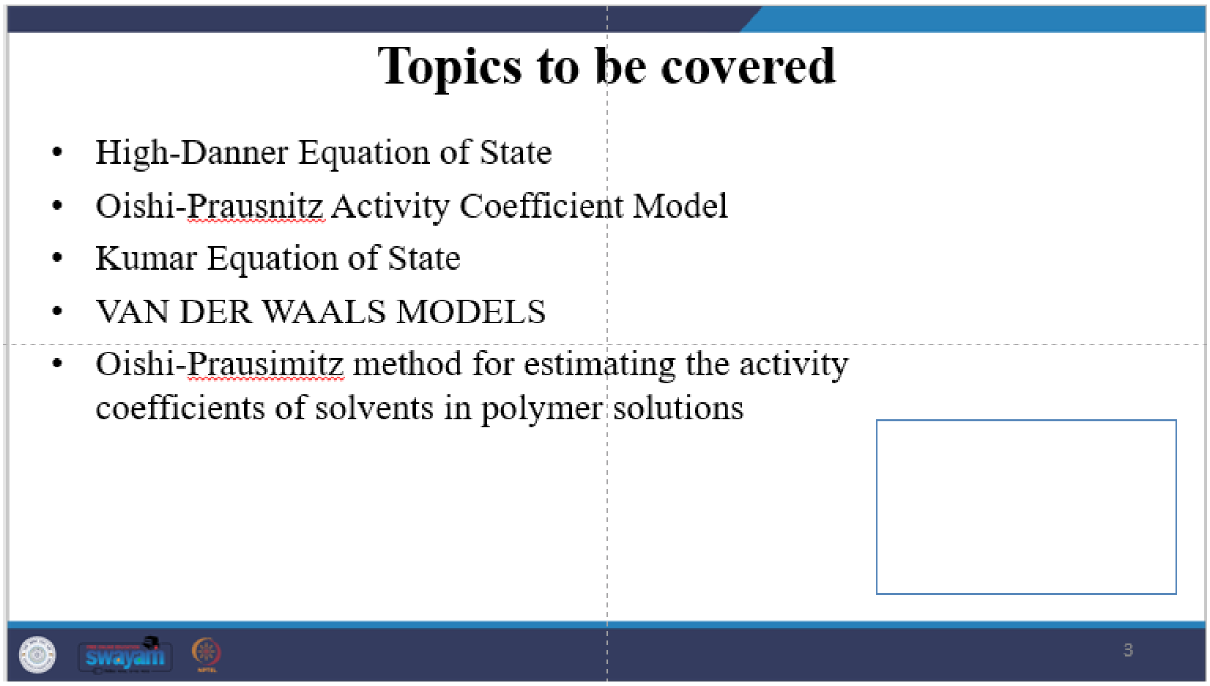
Lecture – 10
Thermodynamics of polymer systems-V

Hello friends, welcome to the fifth segment of the thermodynamics of the Photo pilot. So, today, we will discuss the statistical associating fluid theory that is called SAFT. Then we discussed the SAFT application and then we discussed the varicose equation of state. Now, in this particular segment, we are going to some more recursion of state. First is the high Diner equation of state, and then we will discuss about the OC transactivity coefficient model. We will discuss the Kumar equation of state, then the Van der Waal models and again, we will discuss the OC methods for estimating the activity coefficient of solvent in polymeric solution.

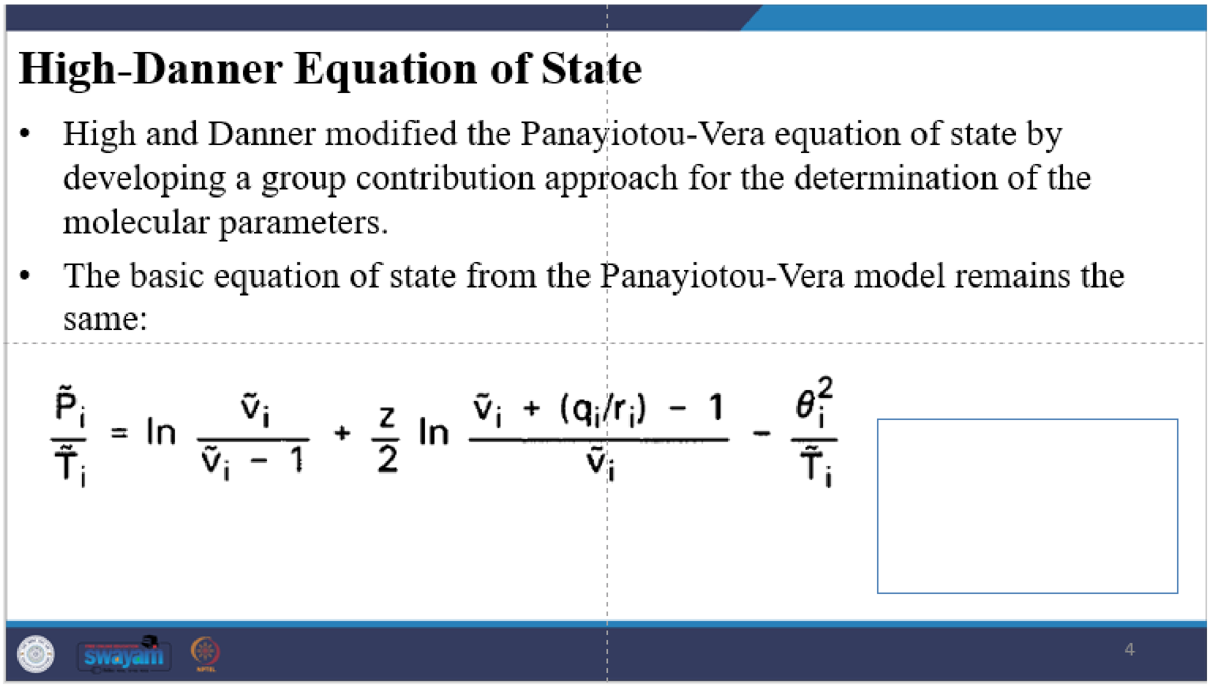


Topics to be covered

- High-Danner Equation of State
- Oishi-Prausnitz Activity Coefficient Model
- Kumar Equation of State
- VAN DER WAALS MODELS
- Oishi-Prausimitz method for estimating the activity coefficients of solvents in polymer solutions

Now, high Diner equation, this high Diner they modified the varicose equation of state by developing group contribution approach for the determination of molecular parameter. The basic equation of state from the Vera model, this remains the same and that is the reduced pressure of ith component. The reduced temperature of ith component is equal to ln reduced volume of ith component and again reduced volume minus 1 plus z over 2 ln reduced volume plus qi over ri minus 1 over reduced volume minus theta i over reduced temperature. Now, as in the very equation of state, the molecules are not assumed to randomly mix and the same non-random mixing expressions are used. Now, in addition, as in the Vera model, the volume of the lattice site is fixed and assumed to be 9.75 into 10 to the power minus 3-meter cube per kilo mole.

$$\frac{\tilde{P}_i}{\tilde{T}_i} = \ln \frac{\tilde{v}_i}{\tilde{v}_i - 1} + \frac{z}{2} \ln \frac{\tilde{v}_i + (q_i/r_i) - 1}{\tilde{v}_i} - \frac{\theta_i^2}{\tilde{T}_i}$$

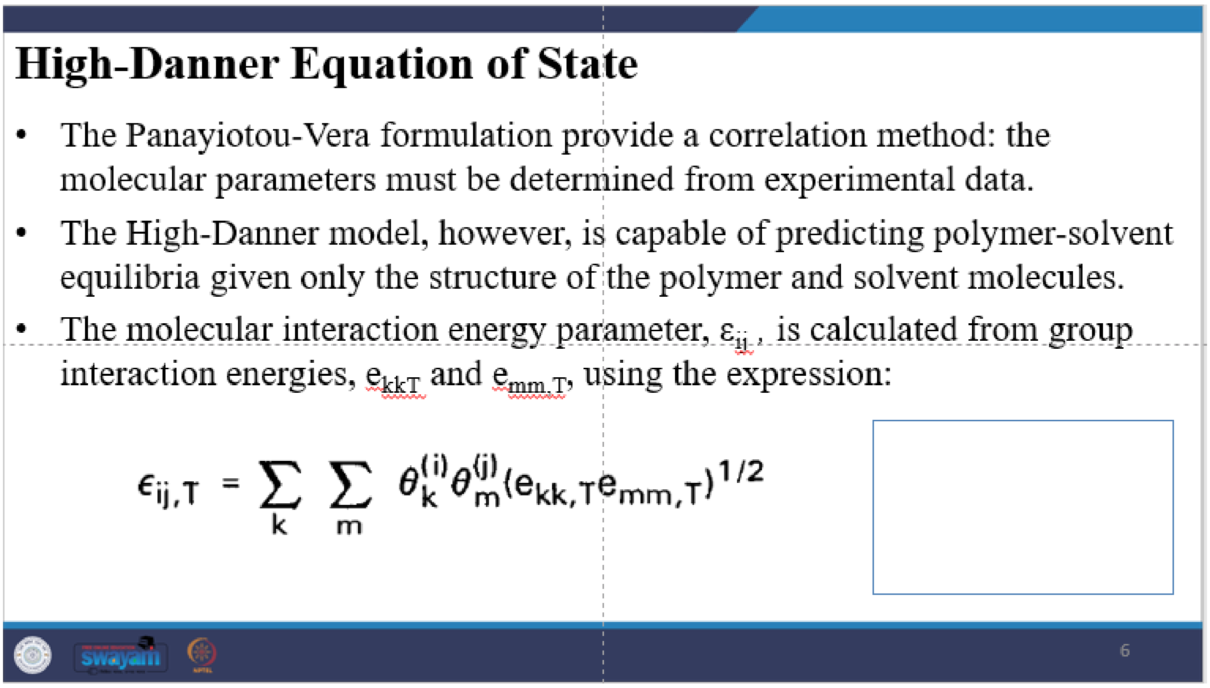


High-Danner Equation of State

- High and Danner modified the Panayiotou-Vera equation of state by developing a group contribution approach for the determination of the molecular parameters.
- The basic equation of state from the Panayiotou-Vera model remains the same:

$$\frac{\tilde{P}_i}{\tilde{T}_i} = \ln\frac{\tilde{v}_i}{\tilde{v}_i - 1} + \frac{z}{2}\ln\frac{\tilde{v}_i + (q_i/r_i) - 1}{\tilde{v}_i} - \frac{\theta_i^2}{\tilde{T}_i}$$

The major difference between the high Diner and the Vera model is that the molecular parameters, that is siren 11 and reference volume, are calculated from a group contribution in the high Diner approach. The Vera formulation provides a correlation method and the molecular parameter must be determined from experimental data. The high Diner model, however, is capable of predicting polymer solvent, calberia given only the structure of polymer and solvent molecules. So, the molecular interaction energy parameter, siren ij is calculated from group interaction energy, that is Ekk t and Emm t using the expression.



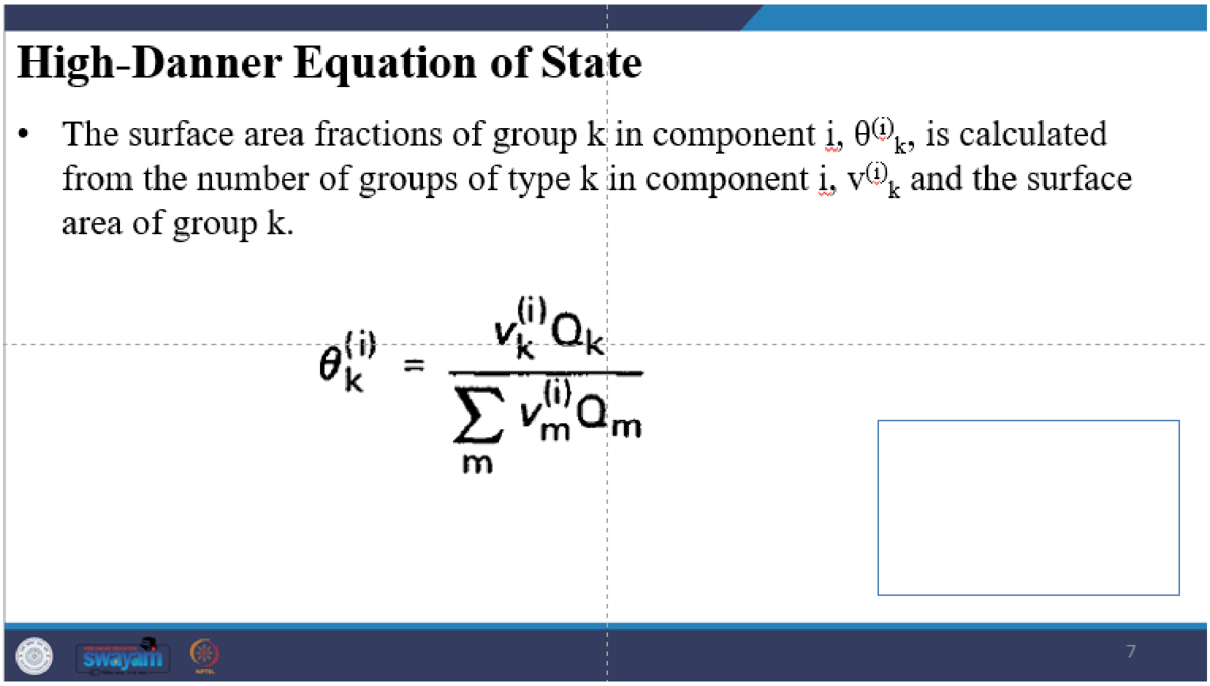
High-Danner Equation of State

- The Panayiotou-Vera formulation provide a correlation method: the molecular parameters must be determined from experimental data.
- The High-Danner model, however, is capable of predicting polymer-solvent equilibria given only the structure of the polymer and solvent molecules.
- The molecular interaction energy parameter, ε_{ij} , is calculated from group interaction energies, e_{kkT} and $e_{mm,T}$, using the expression:

$$\epsilon_{ij,T} = \sum_k \sum_m \theta_k^{(i)}\theta_m^{(j)}(e_{kk,T}e_{mm,T})^{1/2}$$

$$\epsilon_{ij,T} = \sum_{k} \sum_{m} \theta_{k}^{(i)} \theta_{m}^{(j)} (e_{kk,T} e_{mm,T})^{1/2}$$

$$\theta_{k}^{(i)} = \frac{v_{k}^{(i)} Q_{k}}{\sum_{m} v_{m}^{(i)} Q_{m}}$$



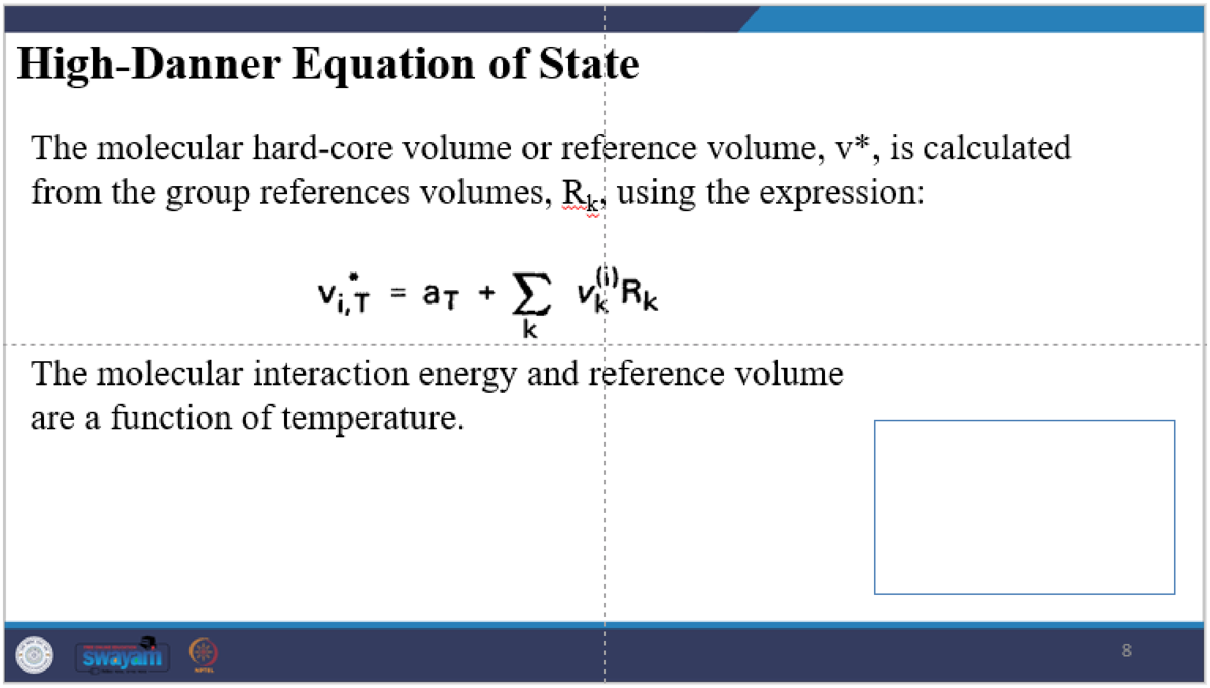
High-Danner Equation of State

- The surface area fractions of group k in component i, $\theta^{(i)}_{k}$, is calculated from the number of groups of type k in component i, $v^{(i)}_{k}$ and the surface area of group k.

$$\theta_{k}^{(i)} = \frac{v_{k}^{(i)} Q_{k}}{\sum_{m} v_{m}^{(i)} Q_{m}}$$

Now, they are going to give the expression siren ij t is equal to beta k i Emm t to the power half. Now, the surface area fraction of the group k in the component i and theta i k is calculated from the number of groups of type k in component i and the surface area of group k. So, theta k theta i is equal to vki qk over vm qm. The molecular hardcore volume or reference volume v is calculated from the group reference volume rk and you can use this particular equation that is v i a t plus summation k vki into rk. The molecular interaction energy and reference volume are function of temperature.

$$v_{i,T}^{*} = a_{T} + \sum_{k} v_{k}^{(i)} R_{k}$$



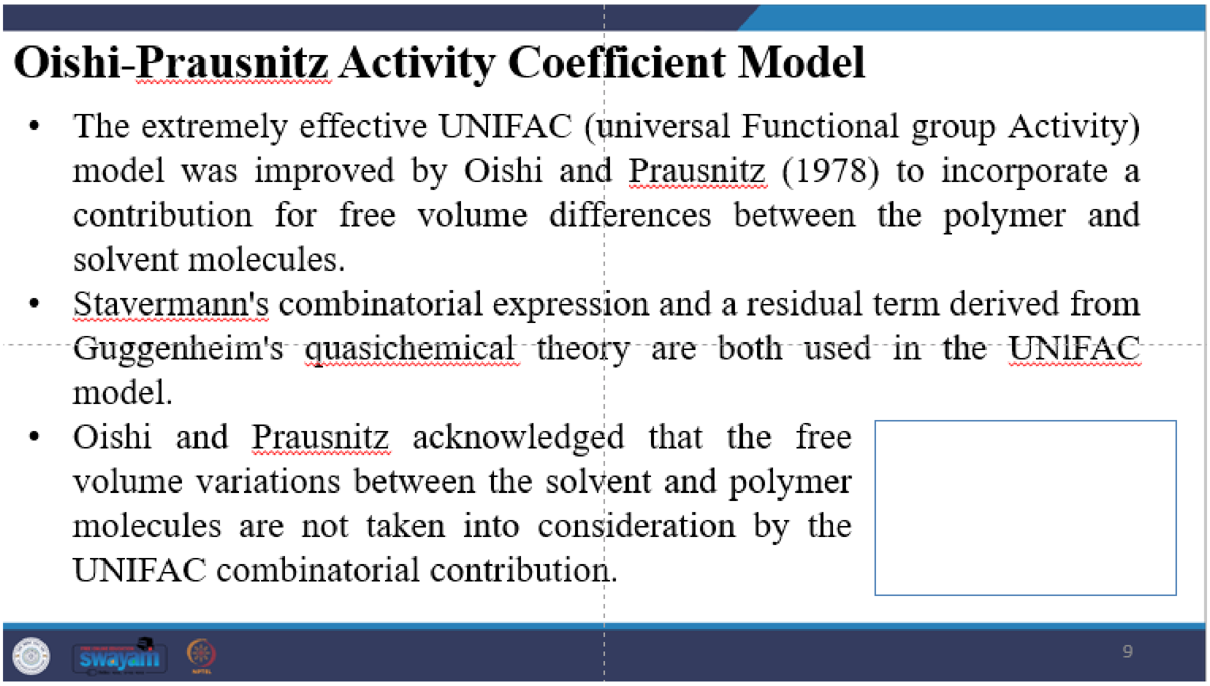
High-Danner Equation of State

The molecular hard-core volume or reference volume, v*, is calculated from the group references volumes, R_k, using the expression:

$$v^*_{i,T} = a_T + \sum_k v_k^{(i)} R_k$$

The molecular interaction energy and reference volume are a function of temperature.

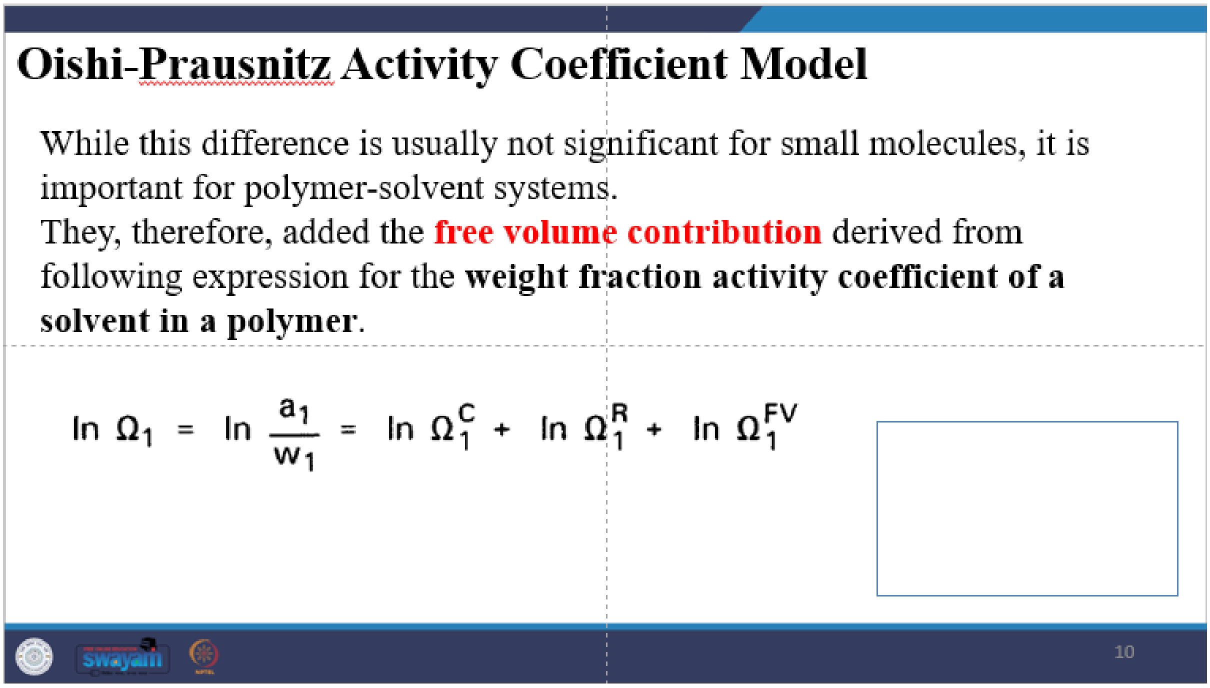
Now, the extremely effective unifac model that is a universal functional group activity model this was improved by Oshie and Pronitz in 1978 to incorporate a contribution of for free volume differences between the polymer and solvent molecule. Now Star-Weinman combinatorial expression and residual term derived from the Gagen-Himm's the quasi chemical theory they are both used in the unifac model. Now, Oshie et al they acknowledge that the free volume variation between the solvent and the polymer molecule are not taken into consideration by the unifac combinatorial contribution. Now, while this particular difference is usually not significant for small molecule it is important for polymer solvent system. Now, they therefore added a free volume contribution derived from the expression that is a weight fraction activity coefficient of a solvent in a polymer.



Oishi-Prausnitz Activity Coefficient Model

- The extremely effective UNIFAC (universal Functional group Activity) model was improved by Oishi and Prausnitz (1978) to incorporate a contribution for free volume differences between the polymer and solvent molecules.
- Stavermann's combinatorial expression and a residual term derived from Guggenheim's quasichemical theory are both used in the UNIFAC model.
- Oishi and Prausnitz acknowledged that the free volume variations between the solvent and polymer molecules are not taken into consideration by the UNIFAC combinatorial contribution.

So, ln omega 1 is equal to ln A 1 W 1 is equal to ln omega 1 C plus ln omega 1 R plus ln omega 1 F v. The free volume contribution is given by ln omega 1 F v 3 C 1 ln reduce volume 1 1 by 3 minus 1, this volume 1 by 3 minus 1 minus C 1 reduce volume 1 over reduce volume m minus 1 into reduce volume 1 over 1 by 3 v 1 1 by 3 minus 1. Now, here this C 1 is an external degree of freedom parameter for the solvent. Now, this Oishi-Prausnitz model the unifac free volume is currently the most accurate method available to predict the solvent activities in polymer. Now, this required the Oishi-Prausnitz model they are densities of a pure solvent and a pure polymer at the temperature of the mixture and the structure of the solvent and polymer.

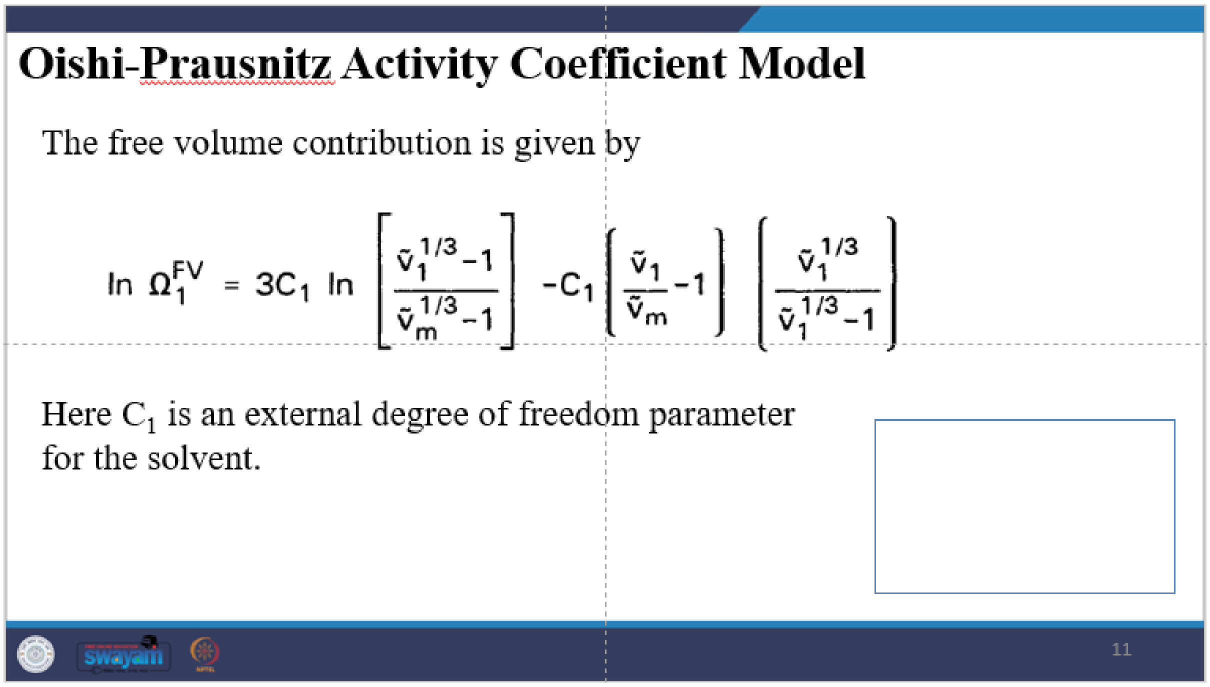


Oishi-Prausnitz Activity Coefficient Model

While this difference is usually not significant for small molecules, it is important for polymer-solvent systems.
They, therefore, added the **free volume contribution** derived from following expression for the **weight fraction activity coefficient of a solvent in a polymer**.

$$\ln \Omega_1 = \ln \frac{a_1}{w_1} = \ln \Omega_1^C + \ln \Omega_1^R + \ln \Omega_1^{FV}$$

$$\ln \Omega_1 = \ln \frac{a_1}{w_1} = \ln \Omega_1^C + \ln \Omega_1^R + \ln \Omega_1^{FV}$$



Oishi-Prausnitz Activity Coefficient Model

The free volume contribution is given by

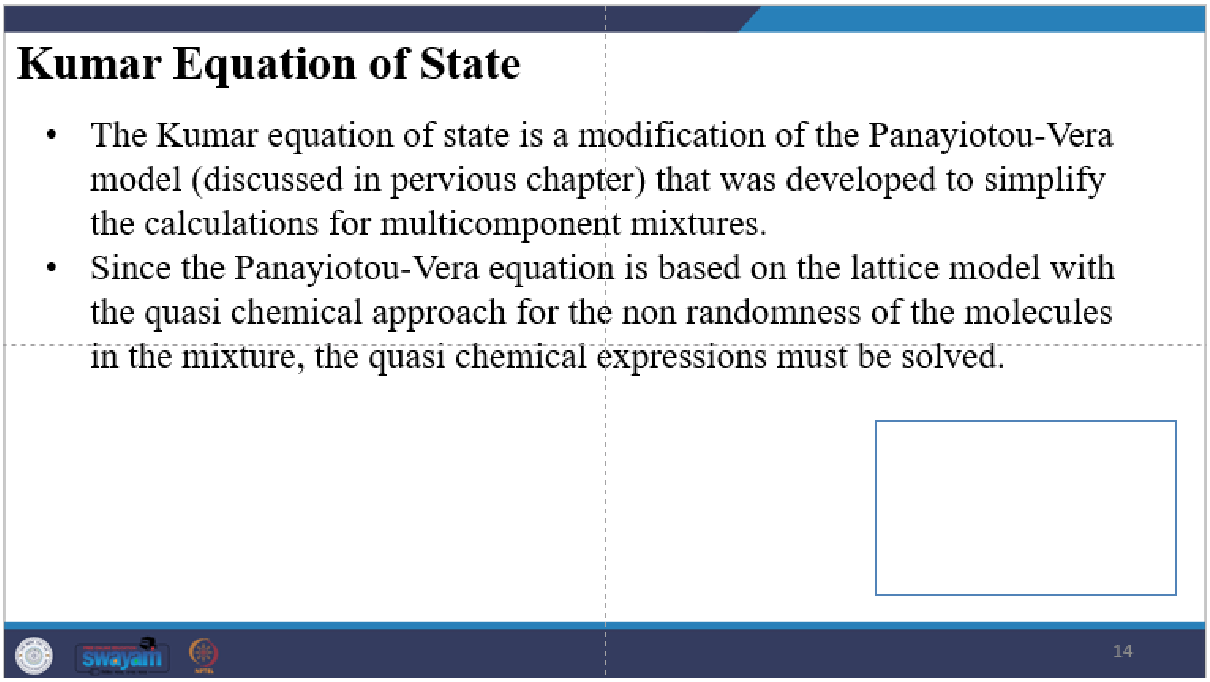
$$\ln \Omega_1^{FV} = 3C_1 \ln \left[\frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}_m^{1/3} - 1} \right] - C_1 \left\{ \frac{\tilde{v}_1}{\tilde{v}_m} - 1 \right\} \left\{ \frac{\tilde{v}_1^{1/3}}{\tilde{v}_1^{1/3} - 1} \right\}$$

Here C_1 is an external degree of freedom parameter for the solvent.

$$\ln \Omega_1^{FV} = 3C_1 \ln \left[\frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}_m^{1/3} - 1} \right] - C_1 \left(\frac{\tilde{v}_1}{\tilde{v}_m} - 1 \right) \left(\frac{\tilde{v}_1^{1/3}}{\tilde{v}_1^{1/3} - 1} \right)$$

Now, molecules that can be constructed from the groups available in the UNIFAC model this can be treated. Now, at present in this activity coefficient model the groups are available to construct alkanes, alkanes, alkynes, aromatics, water alcohols, ketones, aldehydes, esters, ethers, amine, carboxylic acid, some chlorinated compound, dominated compound and few other groups for specific molecules. Let us talk about the Kumar equation of a state. The Kumar equation of a state is modified modification of the Vera model which we discussed in we have discussed in the previous segment and that was developed to simplify the calculation for multi component mixture. Now, since Vera equation is based on the lattice model with the quasi chemical approach for the non-randomness of the molecules in the mixture the quasi chemical expression must be solved.

So, the Kumar modification to the Vera equation of a state this involves a computing a Taylor series expansion. We all of us are aware about the Taylor series. So, Taylor series expansion of the quasi chemical expression around the point where the interaction energy is 0 and that is the case of complete randomness. Now, this operation produces an explicit result for the non-randomness factor which can then be incorporated into the derivation of the equation of a state and chemical potential expression. So, the resulting thermodynamics expressions are cumbersome but rely only on easily programmed summation.

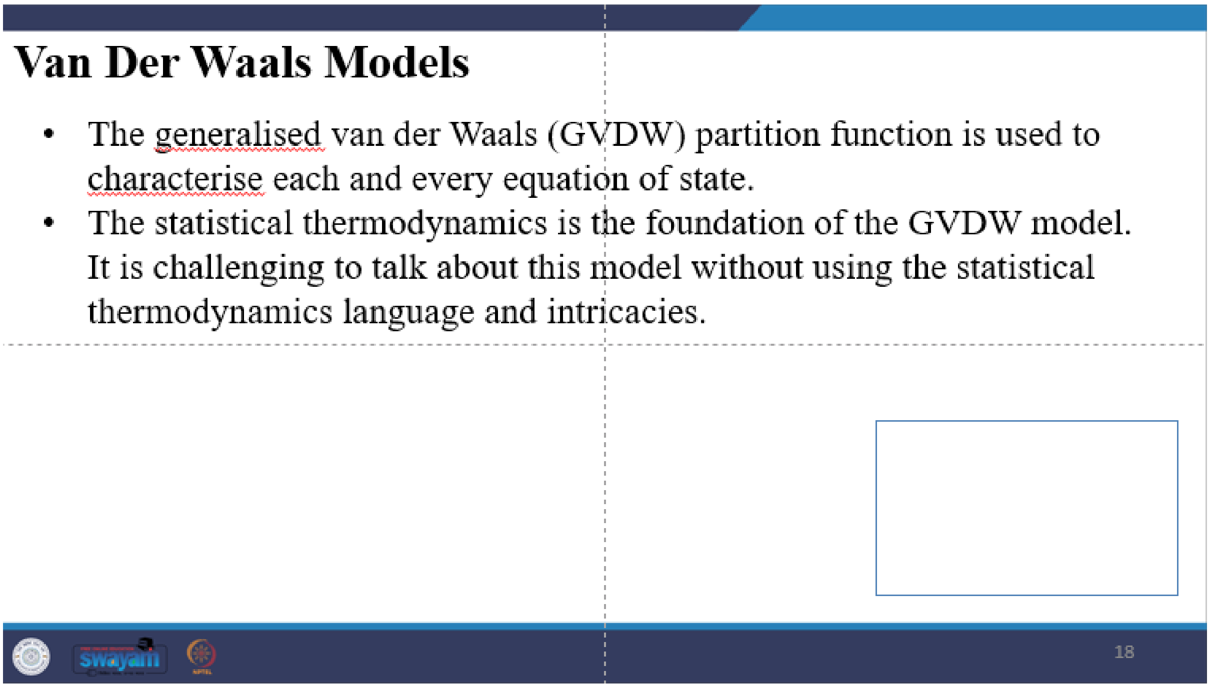


Kumar Equation of State

- The Kumar equation of state is a modification of the Panayiotou-Vera model (discussed in pervious chapter) that was developed to simplify the calculations for multicomponent mixtures.
- Since the Panayiotou-Vera equation is based on the lattice model with the quasi chemical approach for the non randomness of the molecules in the mixture, the quasi chemical expressions must be solved.

So, the advantages of Kumar equation of a state they are purely computational and the resulting expression they are approximation of the Vera equation of a state and that will reduce the proper form of for random equation. So, the Kumar they stated that the expression of Vara differ because of errors in their work. Now, thus the discrepancy between the Kumar equation of a state and the Vara equation of a state must occur in the approximation due to the Taylor series. Let us talk about the Van der Waal models. Now the generalized Van der Waals model or Van der Waal partition fraction is used to characterize each and every equation of a state.

The statistical thermodynamic is the foundation of generalized Van der Waal model and it is challenging to talk about the model without using the statistical thermodynamic language and intricacies. Now, this generalized Van der Waal model this relies on the concept of the partition function and the partition function relates the most probable distribution of energy states in a system of molecules to the macroscopic thermodynamic properties of the system. The energy modes these can be divided into translational or rotational vibrational electronic and attractive models. The translational energy state depends directly upon the volume or a density of the fluid that is more specifically on the free volume and for small molecules the rotational vibrational and electronic mode that depends only on temperature. For large molecules however, the rotational vibrational modes also depend on the density.



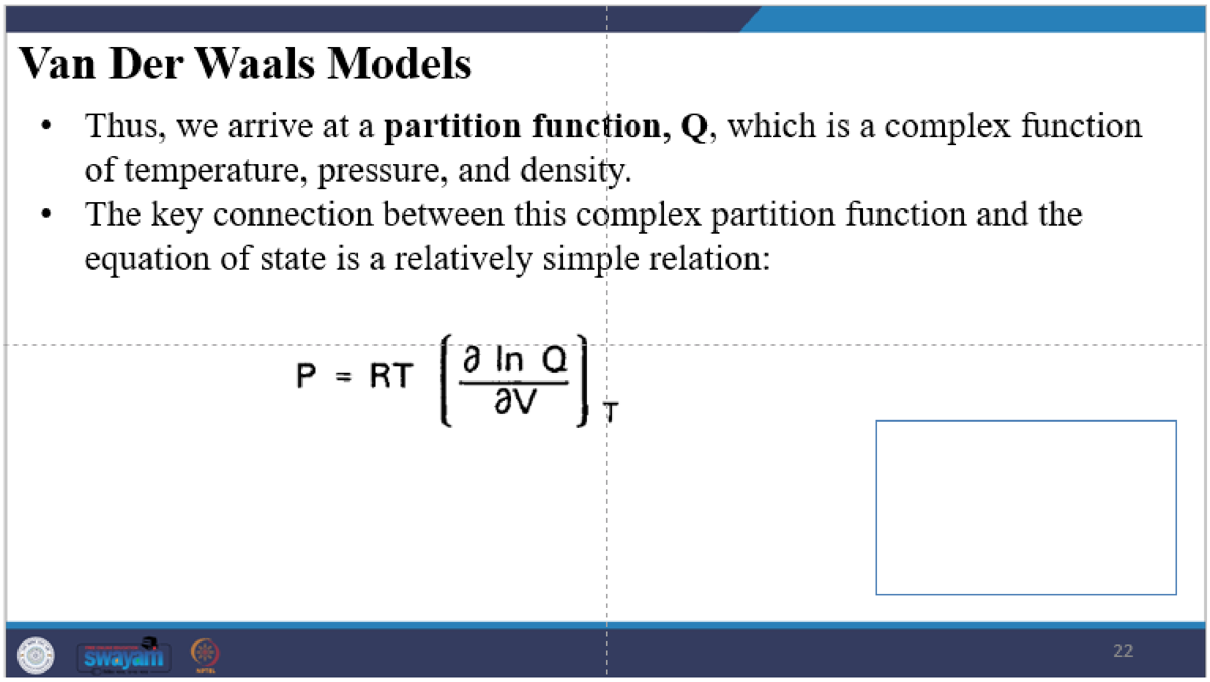
Van Der Waals Models

- The generalised van der Waals (GVDW) partition function is used to characterise each and every equation of state.
- The statistical thermodynamics is the foundation of the GVDW model. It is challenging to talk about this model without using the statistical thermodynamics language and intricacies.

The attractive energy of the system depends upon the intermolecular forces between the molecules which in turn depends on the density and temperature. The density is usually dependent on the molecules positioning and average spacing distance. So, the generalized Van der Waal theory this makes use of the radial distribution function and whereas the lattice model specifies the placement of the molecules or polymer segments in terms of places on the lattice. The likelihood of discovering the centre of another molecule is expressed mathematically as a function of the distance from the centre of the first molecule using the radial distribution function. Now, it is depending on the system's temperature and density.

Now, thus we arrived the partition function Q this one which is a complex function of temperature, pressure and density. The key connection between the complex partition function and the equation of state is a relatively simple relation and this is a very common relation which is equal to P is equal to RT del ln Q over del V at constant temperature.

$$P = RT \left[\frac{\partial \ln Q}{\partial V} \right]_T$$

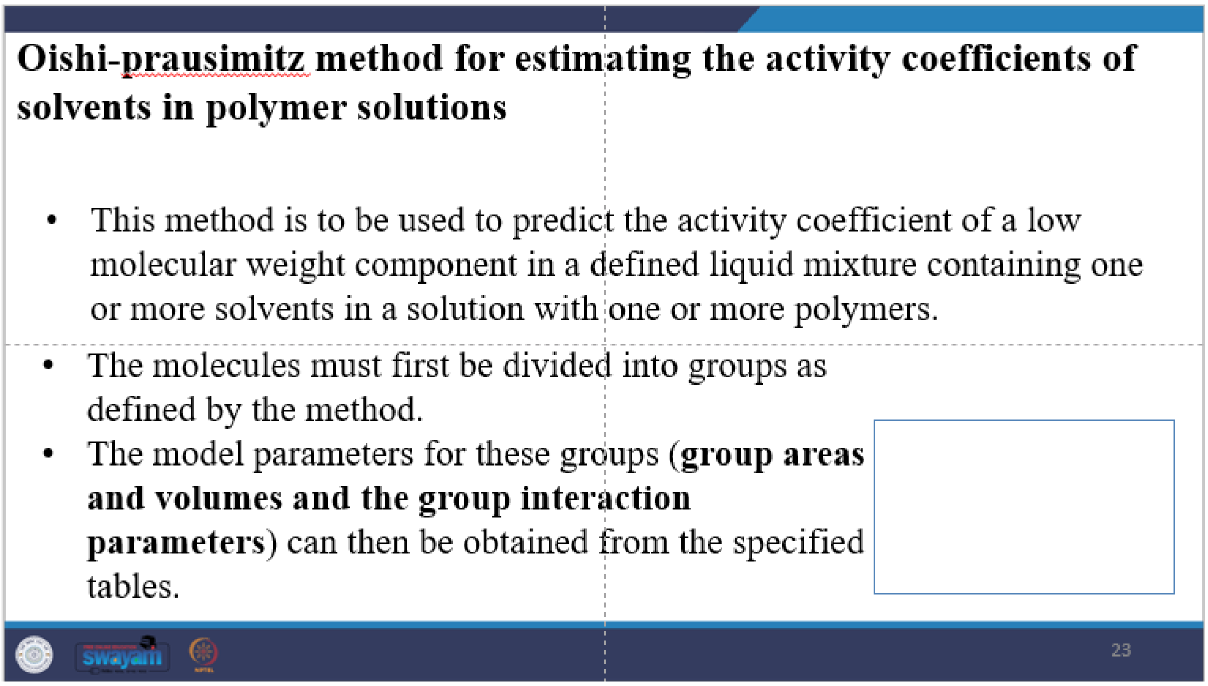


Van Der Waals Models

- Thus, we arrive at a **partition function, Q**, which is a complex function of temperature, pressure, and density.
- The key connection between this complex partition function and the equation of state is a relatively simple relation:

$$P = RT\left[\frac{\partial \ln Q}{\partial V}\right]_T$$

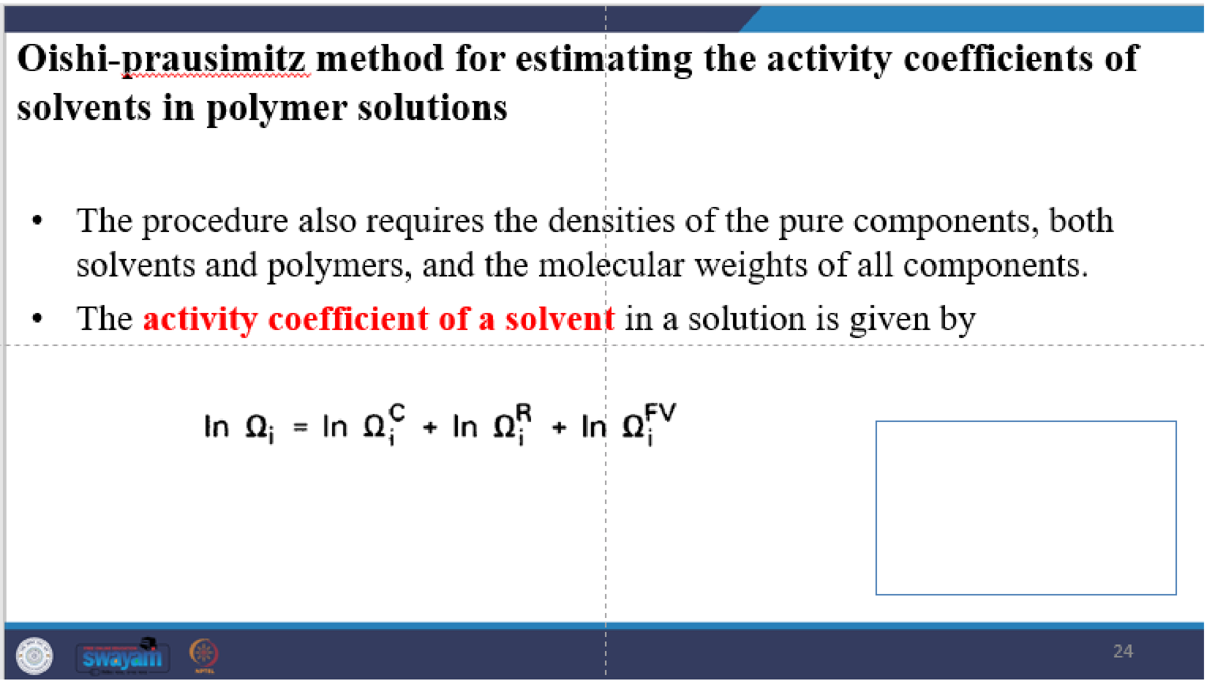
Now, this OISHI method for estimating the activity coefficient of solvent in a polymer solution Now, this method is to be used to predict the activity coefficient of a low molecule weight component in a defined liquid mixture containing one or more solvents in a solution with one or more polymer. The molecules must first be divided into groups as defined by the method and the model parameter for these groups or group area sometimes referred as a group volume and the group interaction parameter. These can be obtained from specified tables.



Oishi-prausimitz method for estimating the activity coefficients of solvents in polymer solutions

- This method is to be used to predict the activity coefficient of a low molecular weight component in a defined liquid mixture containing one or more solvents in a solution with one or more polymers.
- The molecules must first be divided into groups as defined by the method.
- The model parameters for these groups (**group areas and volumes and the group interaction parameters**) can then be obtained from the specified tables.

So, the procedure also requires the densities of the pure component, both solvent and polymer and the molecular weight of all components and the activity coefficient because ultimately the activity coefficient is needed. So, the activity coefficient of the solvent in the solution is given by ln omega i is equal to ln omega i C plus ln omega i R plus ln omega i free volume where this ln omega i this is the activity coefficient of solvent i at temperature T and this is the ln omega i C the combinatorial contribution to the activity coefficient.



Oishi-prausimitz method for estimating the activity coefficients of solvents in polymer solutions

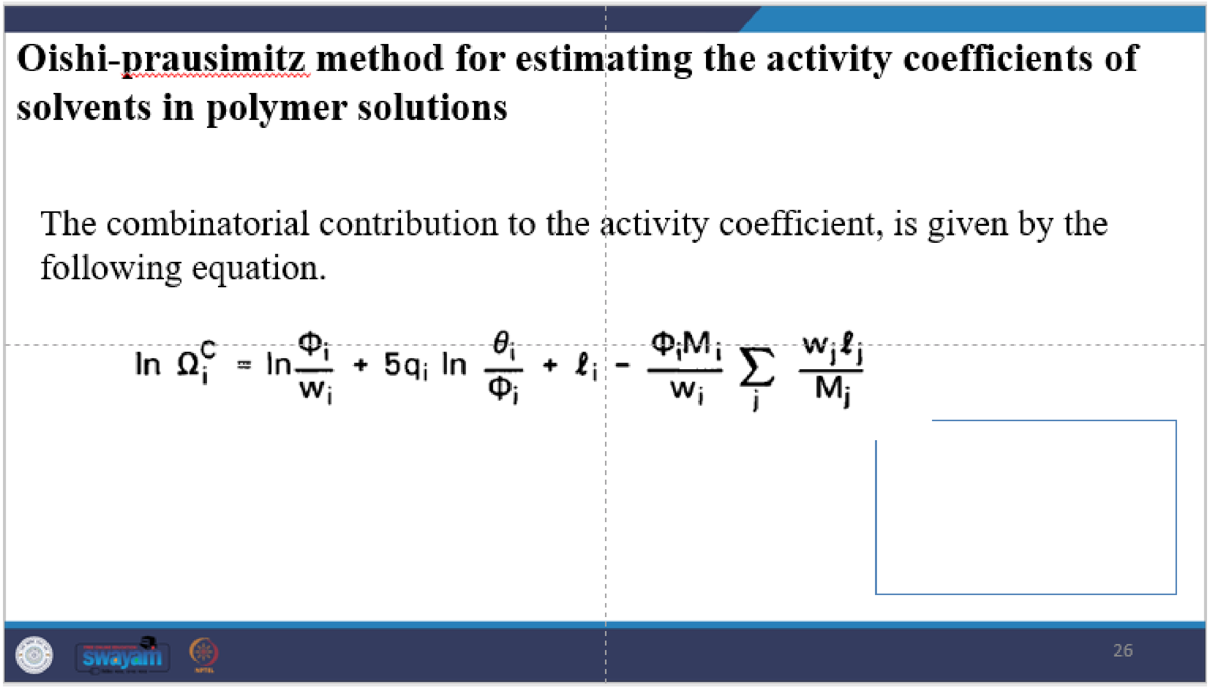
- The procedure also requires the densities of the pure components, both solvents and polymers, and the molecular weights of all components.
- The **activity coefficient of a solvent** in a solution is given by

$$\ln \Omega_i = \ln \Omega_i^C + \ln \Omega_i^R + \ln \Omega_i^{FV}$$

$$\ln \Omega_i = \ln \Omega_i^C + \ln \Omega_i^R + \ln \Omega_i^{FV}$$

This one is the residual contribution to the activity coefficient and this one is the free volume contribution to the activity coefficient and temperature T which is in the kelvins. Now the combinatorial combination contribution of the activity coefficient is usually given by this particular equation ln omega i C is equal to ln phi i y plus phi qi ln theta 1 phi i plus l i minus phi i m i summation j W j l i over m j. Where i j is equal to 1 to 3 m that is number of components in the solution phi i is equal to the number the molecular volume fraction of component i W j is the weight fraction of component i in the polymer solution qi is the surface area parameter of component i theta i the molecular area fraction of component i, l i a parameter for component i, m i is the molecular weight of component i number average is recommended and that is in the kilogram per kilo mole.

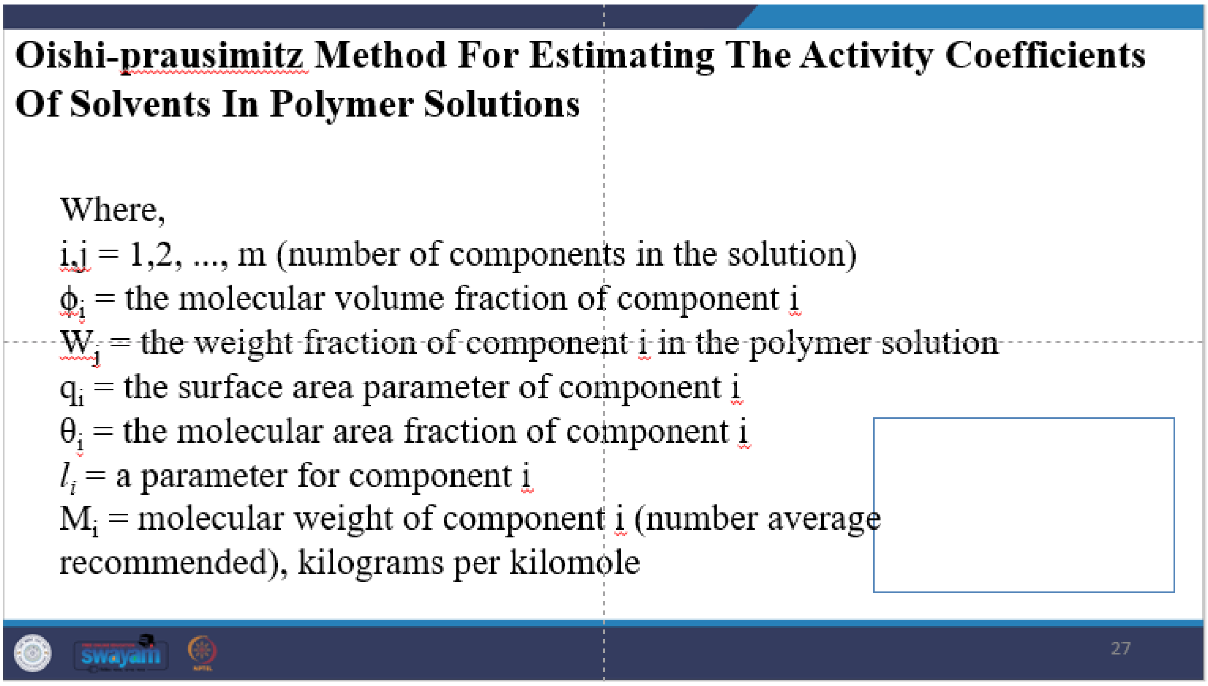
$$\ln \Omega_i^C = \ln \frac{\Phi_i}{w_i} + 5q_i \ln \frac{\theta_i}{\Phi_i} + \ell_i - \frac{\Phi_i M_i}{w_i} \sum_j \frac{w_j \ell_j}{M_j}$$



Oishi-prausimitz method for estimating the activity coefficients of solvents in polymer solutions

The combinatorial contribution to the activity coefficient, is given by the following equation.

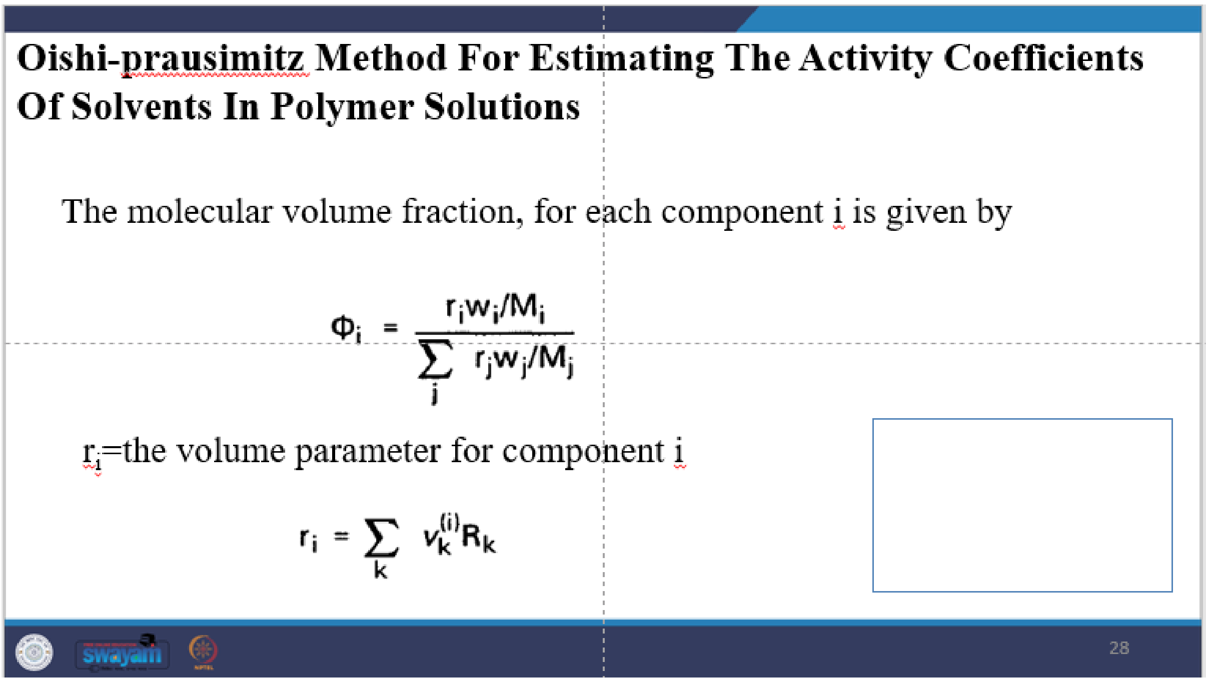
$$\ln \Omega_i^C = \ln\frac{\Phi_i}{w_i} + 5q_i \ln\frac{\theta_i}{\Phi_i} + \ell_i - \frac{\Phi_i M_i}{w_i}\sum_j \frac{w_j \ell_j}{M_j}$$



Oishi-prausimitz Method For Estimating The Activity Coefficients Of Solvents In Polymer Solutions

Where,
i,j = 1,2, ..., m (number of components in the solution)
ϕ_i = the molecular volume fraction of component i
W_j = the weight fraction of component i in the polymer solution
q_i = the surface area parameter of component i
θ_i = the molecular area fraction of component i
l_i = a parameter for component i
M_i = molecular weight of component i (number average recommended), kilograms per kilomole

The molecular volume fraction for each component i is usually given by phi i is equal to r i W i over m i summation j r j W j over m j. So, r i is the volume parameter for component i. So, r i can be given as summation k k i r k. Now, here the V i k is the number of groups of type k in molecule i r k is the group volume parameter for a group k and k is equal to 1 to n which is the number of groups in the solution. So, the molecular area fraction for each component i is given by theta i is equal to q i W i over m i summation i q j W j over m j.



Oishi-prausimitz Method For Estimating The Activity Coefficients Of Solvents In Polymer Solutions

The molecular volume fraction, for each component i is given by

$$\Phi_i = \frac{r_i w_i / M_i}{\sum_j r_j w_j / M_j}$$

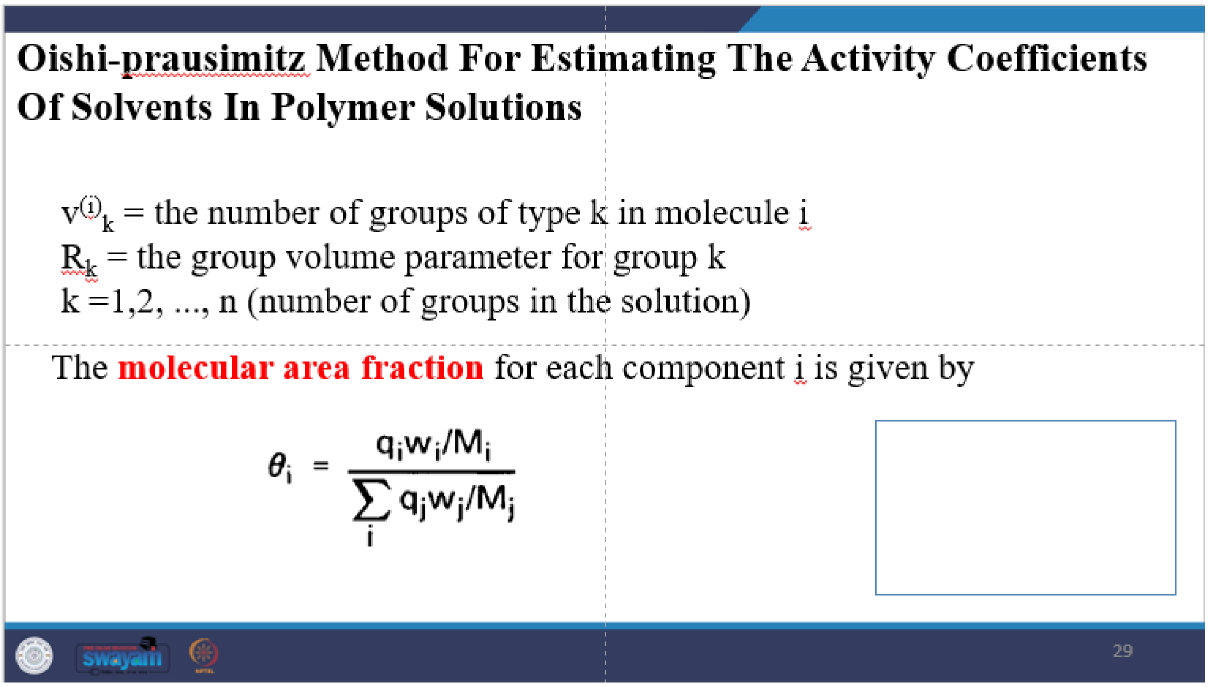
r_i=the volume parameter for component i

$$r_i = \sum_k v_k^{(i)} R_k$$

$$\Phi_i = \frac{r_i w_i / M_i}{\sum_j r_j w_j / M_j}$$

$$r_i = \sum_k v_k^{(i)} R_k$$

So, the area parameter for each component i is determined by q i summation k V k i q k, where q k is the group area parameter for group k. The residual activity contribution to the activity coefficient for each component is given by l n summation k k i l n k i. Now, this l n omega i r is equal to k V k i l n l n a i. This is the residual activity coefficient of group k in the defined solution at the given temperature T. And this is the residual activity coefficient of group k in the reference solution containing pure component i at the temperature T.



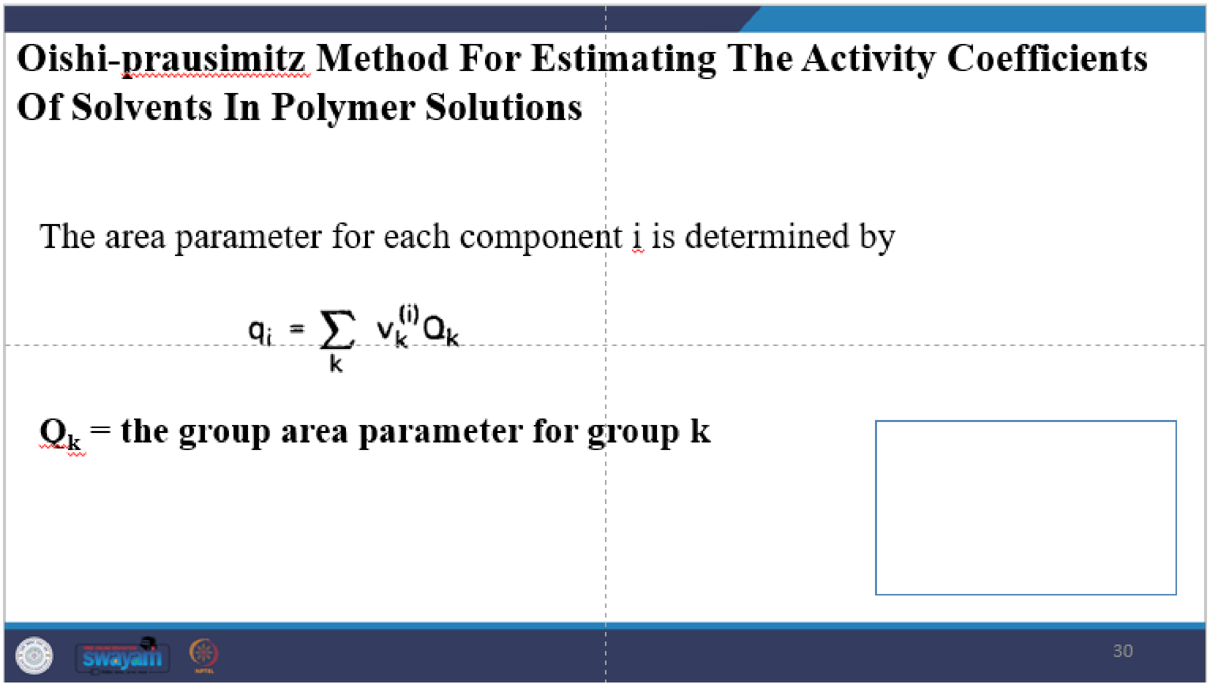
Oishi-prausimitz Method For Estimating The Activity Coefficients Of Solvents In Polymer Solutions

$v^{(i)}_k$ = the number of groups of type k in molecule i
R_k = the group volume parameter for group k
k =1,2, ..., n (number of groups in the solution)

The **molecular area fraction** for each component i is given by

$$\theta_i = \frac{q_i w_i/M_i}{\sum_i q_j w_j/M_j}$$

$$\theta_i = \frac{q_i w_i/M_i}{\sum_i q_j w_j/M_j}$$



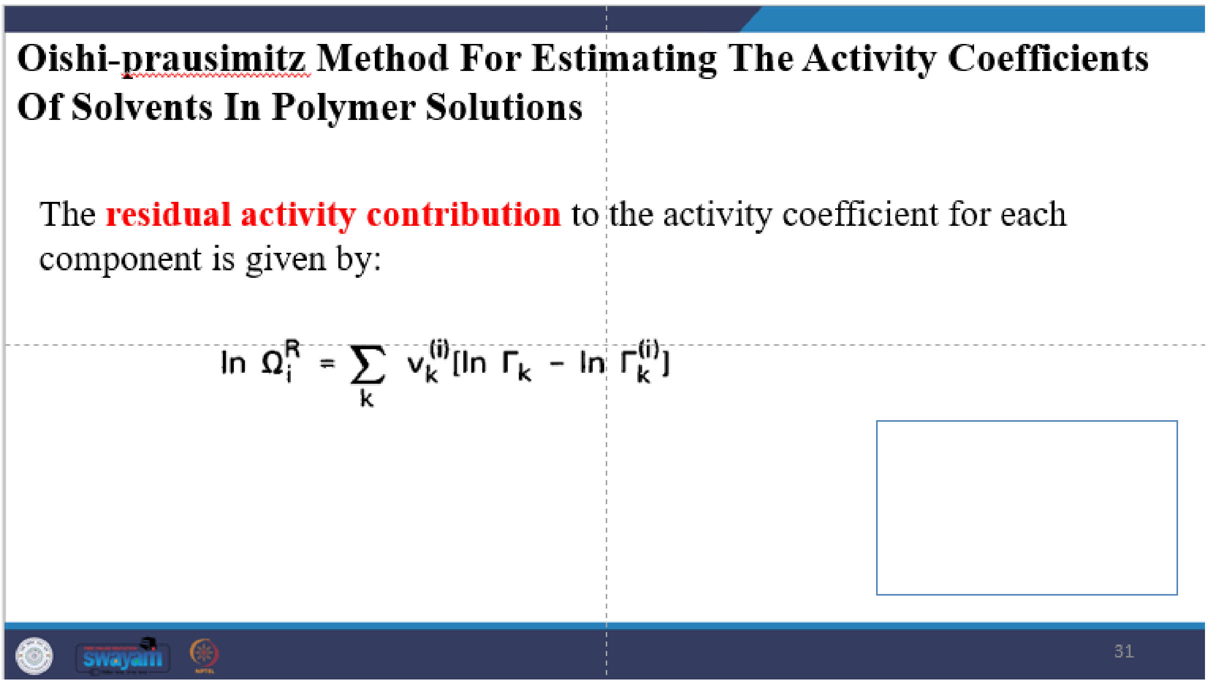
Oishi-prausimitz Method For Estimating The Activity Coefficients Of Solvents In Polymer Solutions

The area parameter for each component i is determined by

$$q_i = \sum_k v_k^{(i)} Q_k$$

Q_k = the group area parameter for group k

$$q_i = \sum_k v_k^{(i)} Q_k$$



Oishi-prausimitz Method For Estimating The Activity Coefficients Of Solvents In Polymer Solutions

The **residual activity contribution** to the activity coefficient for each component is given by:

$$\ln \Omega_i^R = \sum_k v_k^{(i)}[\ln \Gamma_k - \ln \Gamma_k^{(i)}]$$

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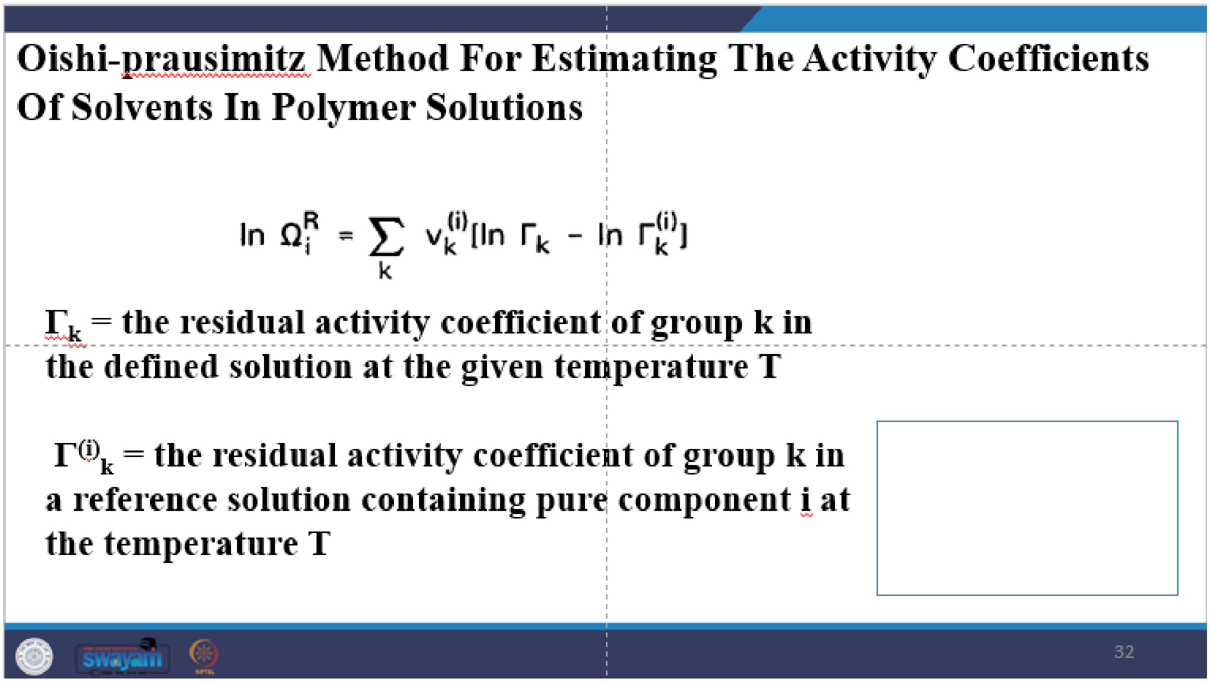

Oishi-prausimitz Method For Estimating The Activity Coefficients Of Solvents In Polymer Solutions

$$\ln \Omega_i^R = \sum_k v_k^{(i)}[\ln \Gamma_k - \ln \Gamma_k^{(i)}]$$

Γ_k = the residual activity coefficient of group k in the defined solution at the given temperature T

$\Gamma^{(i)}{}_k$ = the residual activity coefficient of group k in a reference solution containing pure component i at the temperature T

So, dear friends, in this particular segment, we discussed the different models and equations of state pertaining to the polymeric system, especially when dealing with the thermodynamic system. For your convenience, we have enlisted several references that you can utilize as per your needs. Thank you very much.