Chemical Engineering Thermodynamics
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Lecture – 42
Conclusion

Alright hello and welcome back to this concluding lecture on Chemical Engineering Thermodynamics. What we will do today is sort of summarize everything we have discussed about so far in this course and try to look at how we put all the pieces of the puzzle together; so, that the loss of thermodynamics can be applied to chemical engineering problems. So, let me quickly summarize what we have done in this course then.

We started off with first law, we define internal energy of a system, we related it to heat and work requirements in a reversible process and then we define the efficiency if the process is irreversible. Then we define the second law, defined quantity known as the entropy and then related the heat exchange along a reversible path to entropy change.

Once we define entropy, I can go back and use it along with the first law to form what is known as a fundamental property relation for a closed system that involves only state variables such as du, dv, ds etcetera. We also looked at simple scenarios where there is an ideal gas how I calculate the change in internal energy, change in enthalpy, change in entropy etcetera. If the gas is not ideal then we define quantities known as the residual properties that are deviations from the ideal gas behavior and we looked at how we can calculate these residual properties from pvt relations or what we call as the equations of state.

The various equations of state we looked at are virial equation of state; how we looked at cubic equations of state which are essentially cubic in volume and then we looked at a bunch of generalized correlations such as leak has tables or pits or correlations. So, once I know how to calculate these residual properties even for real fluids, I can calculate the change in thermodynamic properties and hence the heat and work requirements for real fluids as well. So, far we were talking about pure components and how I can calculate the thermodynamic properties for pure components. Moment we move on to mixtures things become a little bit more difficult. So, we defined what are known as partial molar properties for the mixtures. And we are the sum ability relation the total property of a mixture can be calculated once I know the partial molar properties.

It turns out that the partial molar properties are also related to one another via Gibbs-Duhem equation etcetera. Once, I define the partial molar properties, we also defined chemical potential and for a phase equilibrium problem we should have shown that the chemical potential needs to be equal for each of the species in all the phases that are at equilibrium. However, chemical potential is not a convenient quantity to work with its not well defined at the zero pressure limit sorry, we define what is known as the fugacity. Once we define fugacity we need to calculate it and the way we have done that is by relating fugacity to an equation of state model or the compressibility factor c.

So, if I am given an equation of state we looked at a bunch of expressions and how to use them to calculate fugacity of the species in a mixture or fugacity of a pure species. Along the way we also looked at alternate ways to calculate fugacity of liquids other than involving equations of state. Once I know how to calculate fugacity of pure species, fugacity of species in the mixture, I can go back to the phase equilibrium problem and try to use these expressions for fugacities of the species in the mixture and obtain the relationships among various thermodynamic variables at equilibrium right at phase equilibrium.

And, based on that given a certain thermodynamic variables, I can calculate the other thermodynamic variables right. But to be able to do that we also need to calculate the fugacity of the liquid mixture; let us say I have a vapor liquid equilibrium it is not enough only if I know the fugacity of the vapor mixture, I also need to know the fugacity of the liquid mixture. And, to be able to quantify the fugacity of the liquid mixture, one way to do that is calculate the fugacity using cubic equation of state which allows us, to calculate the conditions or properties for a liquid as well.

But then it is not very convenient and sometimes it is not easy to find an equation of state that is applicable and the liquid like conditions or throughout the entire range from 0 to the pressure of interest. So, what we have done is define what are known as ideal solutions, that have the same Gibbs free energy change as in case of ideal gases, but then we have accounted for non-ideal solutions using a quantity known as the excess property.

And excess properties are related to activity coefficients and we have used a set of models for activity coefficients such as Margules equation, Van Laar's equation and more sophisticated models such as NRTL or Wilson's equation are also available. Once we have a model for activity coefficients I can express the fugacity of the liquid mixture or fugacity of species in the liquid mixture using the activity coefficient models.

And, I already know how to calculate the fugacity of the vapor mixture using equations of state. So, now I can put both of them together and solve the phase equilibrium problem. For special case if the liquid mixture is ideal solution then of course and the gas is ideal gas like then of course, everything boils down to what we call as the Raoult's law. Otherwise we can use models for activity coefficients, models for fugacity coefficients and then solve the phase equilibrium problem.

Then we also looked at the condition for stability of liquid mixtures which is minimization of the Gibbs free energy, various expressions that are applicable to solve the liquid-liquid-equilibrium and vapor-liquid-liquid-equilibrium. And finally, the reaction equilibrium problem wherein we define what is known as the reaction coordinate that alone is sufficient to quantify the progress of a reaction.

And, how to express the fugacities in terms of these reaction coordinates and how to obtain the equilibrium reaction coordinate from the reaction equilibrium criteria. Along the way we define what is known as the equilibrium constant k, that is related to the Gibbs free energy change upon the reaction. If we have Gibbs free energy change upon the reaction at the desired temperature then we are good otherwise we have to correct this equilibrium constant using the specific heat capacities and enthalpy change upon the reaction as well.

So, as you can see we have built up a case from a simple first law scenario, used it to expand and understand how we can calculate heat and work requirements. We are the state variables or thermodynamic variables such as internal energy, entropy etcetera and then how we can calculate these thermodynamic variables for gaseous mixtures, for liquid mixtures. And, once I calculate these thermodynamic variables how I can apply it to chemical engineering problems, such as phase equilibrium problems, reaction equilibrium problems etcetera. I hope you have enjoyed the course so far.

Thanks for tuning in to this course bye.