Thermodynamics (Classical) for Biological Systems

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Module No # 06
Reaction Equilibria
Lecture No. # 40
Course Review

Welcome! to the last lecture of this particular course on thermodynamics or essentially, on the application of classical thermodynamics to biological systems. In this course, or in this lecture, I am just going to review whatever we have done in the entire course and that way, it will probably improve some understanding of a few things. If you see things in perspective, it will help at different level of understanding, that is one and also, it is nice to look at everything together at one time. This lecture is going to be just speech or I am just going to continue talking, we probably would not have any gaps in between, those nice things, that we had when we could re-orient and think of something else or do something else and then come back. Those things were used as techniques to improve the learning process itself, bring an active learning, and so on and so forth … towards improved learning process during the lectures. This is just a review, so we will not have any breaks during the review.

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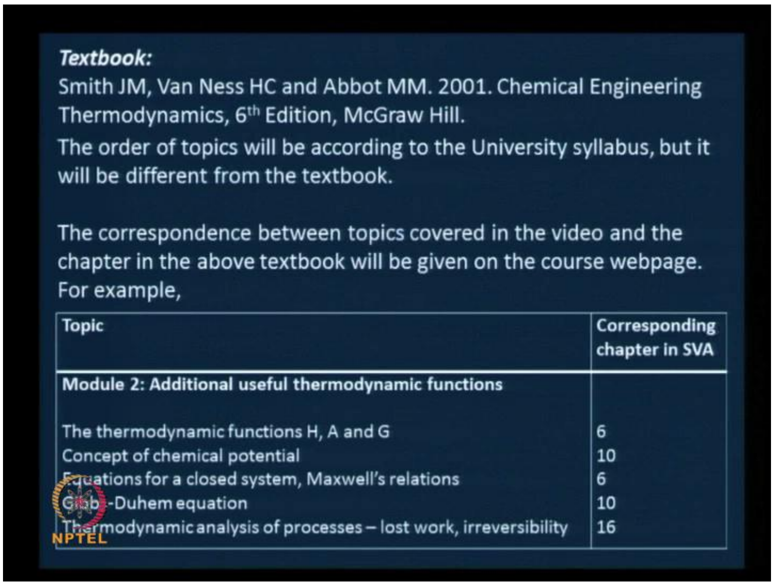

Textbook:
Smith JM, Van Ness HC and Abbot MM. 2001. Chemical Engineering Thermodynamics, 6th Edition, McGraw Hill.
The order of topics will be according to the University syllabus, but it will be different from the textbook.

The correspondence between topics covered in the video and the chapter in the above textbook will be given on the course webpage. For example,

Topic	**Corresponding chapter in SVA**
Module 2: Additional useful thermodynamic functions	
The thermodynamic functions H, A and G	6
Concept of chemical potential	10
Equations for a closed system, Maxwell's relations	6
Gibbs-Duhem equation	10
Thermodynamic analysis of processes – lost work, irreversibility	16

The textbook for this course, of course, was Smith Van Ness and Abbot. I have given you the edition that I have used; probably there is a more recent edition. And the order of topics, I said, would be according to the university syllabus, but it will be different from that given in the textbook. The textbook has an order of its own for its own reasons, but for the given university syllabus, I think the order followed in this particular course is better for better understanding, and seeing things in perspective. The correspondence between the topics covered in the video and the chapter, chapter or chapters in the textbook will be available on the course webpage.

And, I had given you an example also for module 2, that the thermodynamic functions H, A and G would be from chapter 6. Now, we are directly jumping to 6 here; concept of a chemical potential is chapter 10; equations for a closed systems, Maxwell's relations, again from chapter 6; Gibbs-Duhem equation from chapter 10 and thermodynamic analysis of processes including lost work and irreversibility was from chapter16. So, we would jump about in the textbook, but since you have this, if you want to read further from the textbook you can go to the appropriate chapters and read them. But I think, the ordering given in this particular set of lectures would be probably better if you need to understand the various aspects given here.

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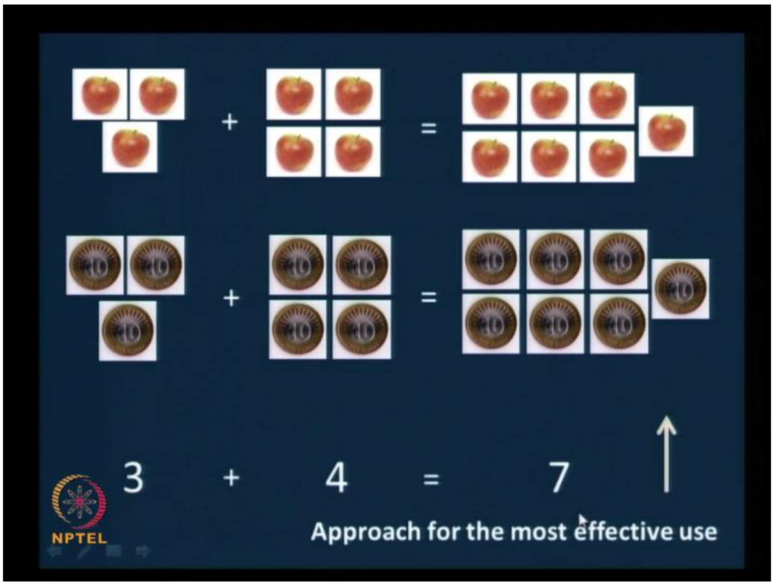

3 + 4 = 7

Approach for the most effective use

Then, I said, the approach for the most effective use of thermodynamics, that I see here, is as follows. We said, if you are looking at apples, three apples in a basket and you add them with four apples, then you get seven apples. You know … you could see this as three apples, if you add them with four apples, you could get seven apples. Similarly, if you take three coins, three 10 rupee coins and add them with four other 10 rupee coins, you get seven 10 rupee coins. … This is in the level of specifics. I could introduce things in the level of specifics, but that makes it very limited. A probably comprehensive approach would be to abstract this into a number 3 and abstract this into a number 4 and we know from 1st standard mathematics, that if you add 3 and 4 together, you will always get 7, therefore you will get 7 of that kind. So, we said, that this is the approach that we are going to follow in this particular course.

We will present the abstractions first and then take up specific cases. We said, that would make things a lot more complete. Otherwise, … especially in thermodynamics, and I believe, that that is a reason for a lot of confusions … while following certain ways of exposure to thermodynamics. You take specific cases, then you understand things a certain way, which may not be complete, and then you try to apply the same understanding to something else, it will not be valid. Therefore, it is best to, to understand it at the abstract level and then apply it to specific cases. This is called the axiomatic approach. We will do this. At least, I believe in that.

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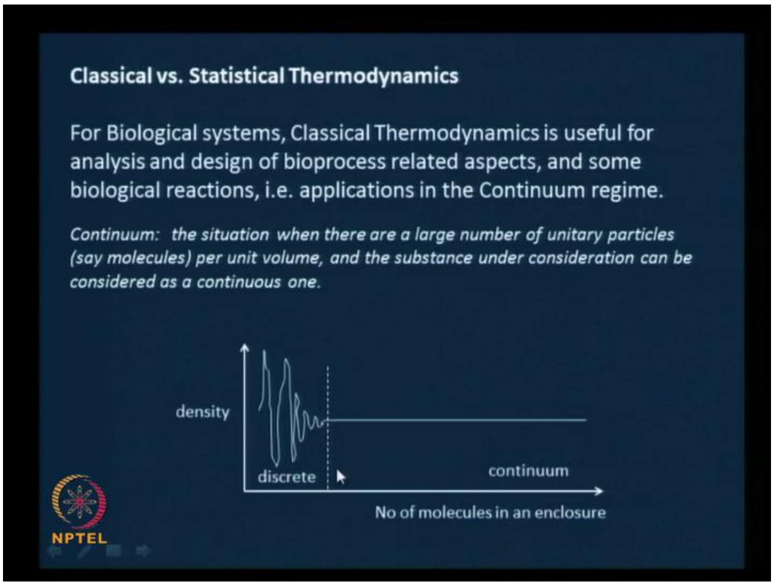

Classical vs. Statistical Thermodynamics

For Biological systems, Classical Thermodynamics is useful for analysis and design of bioprocess related aspects, and some biological reactions, i.e. applications in the Continuum regime.

Continuum: the situation when there are a large number of unitary particles (say molecules) per unit volume, and the substance under consideration can be considered as a continuous one.

Then, we talked about classical versus statistical thermodynamics. We said that for biological systems, classical thermodynamics is useful for analysis and design of bioprocess related aspects, some biological relations and so on, even inside the cells, as long as, the applications are in the continuum regime.

… We saw what a continuum was. It is a situation where … there are large number of unitary particles, say molecules, per unit volume and the substance under consideration can be considered as a continuous one. Or in other words, for example, if you plot the density of the substance versus the number of molecules, say, in an enclosure, here till it reaches a certain point, it is going to remain a constant density assuming, that the temperature, pressure conditions are constant, and so on. And then, after which the number of molecules are so less, that its density at a particular point will start fluctuating. So, this is the discrete region, which we are not concerned with in this particular course. In fact, classical thermodynamics cannot handle that. It can handle only the continuum regime. … To handle this regime, which is very relevant for biological systems, we need statistical thermodynamics, which we will not cover as a part of this course.

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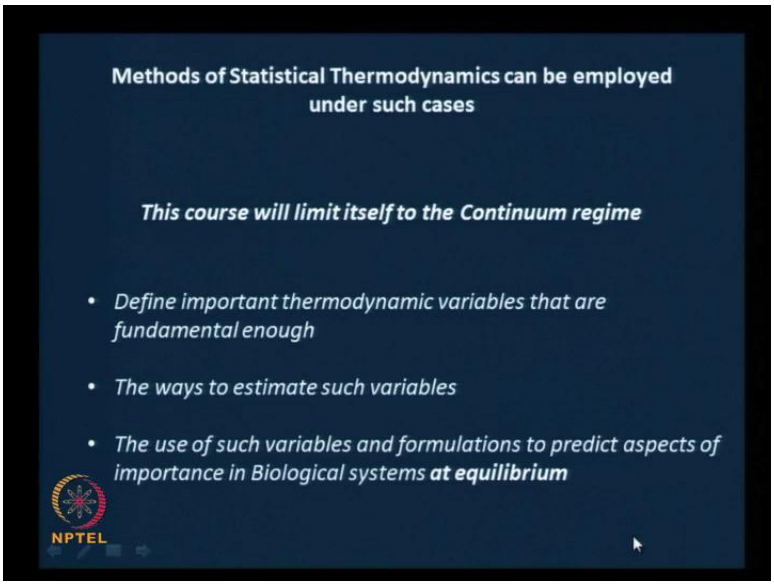

Methods of Statistical Thermodynamics can be employed under such cases

This course will limit itself to the Continuum regime

- *Define important thermodynamic variables that are fundamental enough*
- *The ways to estimate such variables*
- *The use of such variables and formulations to predict aspects of importance in Biological systems **at equilibrium***

Therefore, this course will limit itself to the continuum regime. It will define important thermodynamic variables that are fundamental enough. It will also look at ways to estimate such variables, and it will also look at the use of such variables and formulations to predict aspects of importance in biological systems, especially at equilibrium. This was the scope of the course.

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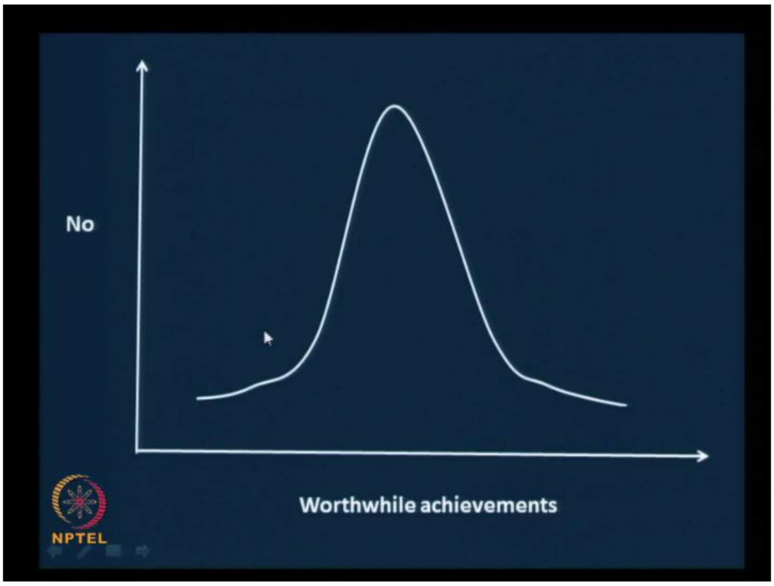

With this background, I also told you something about the course philosophy, you know, that it is good to know this to know where exactly I am pitching the course. In fact, we did this sometime in the beginning of the 4th module. Since this is a review and probably the place for this is here, I thought I will present this here. If you look at the number of students in a class on the y-axis versus worthwhile achievements – you know, worthwhile achievements does not necessarily mean achievements in an exam, … closed kind of an exam or defined exam or something like that; I am using this to represent something really worthwhile – then you find, that you typically have a Gaussian distribution in a class of a reasonable size, say, about twenty. This distribution, you find time and again. Sometimes the tails are little skewed, and so on and so forth, but more or less, this distribution remains.

I have pitched the course at this level, at the level of the average, so that an average student in terms of whatever achievements the person has done, which reflects a certain level of application of that student, that student will be able to get it with reasonable ease. People here, of course, will feel bored, people here would need to do a lot more work. For people here I did assign an exercise. It could be done over many months, and it will challenge your curiosity, and so on and so forth … whatever you could do, and I will talk about that exercise in a minute.

But unfortunately, in a situation like this, when it is across a medium, it is a little difficult to handle people here; at least I do not know how to handle this, in this particular kind of a medium. In a class, what I do is I use cooperative learning techniques where I combine students of different achievement levels together. I have my own, own way of doing that. I have my own algorithm to do that. I use, you know, the group average CGPA is plus or minus 0.25 of the class average CGPA and so on. That works very well for students of lower achievements to pick-up from students of higher achievements. And, students with higher achievements also get benefited through a better understanding, and so on. That typically works well for me here, but unfortunately here, I do not know how to do it.

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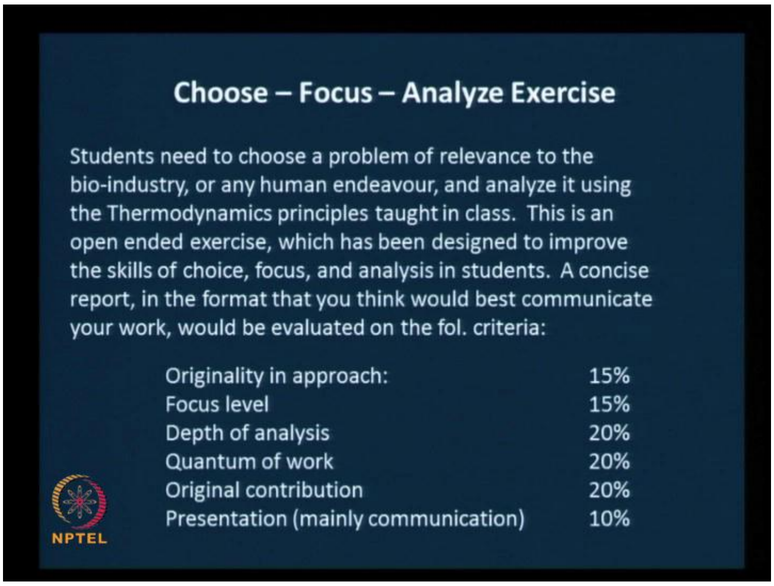

Choose – Focus – Analyze Exercise

Students need to choose a problem of relevance to the bio-industry, or any human endeavour, and analyze it using the Thermodynamics principles taught in class. This is an open ended exercise, which has been designed to improve the skills of choice, focus, and analysis in students. A concise report, in the format that you think would best communicate your work, would be evaluated on the fol. criteria:

Originality in approach:	15%
Focus level	15%
Depth of analysis	20%
Quantum of work	20%
Original contribution	20%
Presentation (mainly communication)	10%

To handle people here I have, I had given an exercise, you can take the exercise for this course also. That is, the choose-focus-analyze exercise. Students need to choose a problem of relevance to the bio-industry or any human endeavor, and analyze it using the thermodynamics principles taught in class. This is an open ended exercise, which has been designed to improve the skills of choice, focus and analysis in students.

A concise report in the format, that you think would best communicate your work, can be submitted to me at anytime and by email. That would be evaluated on the following criteria, which is: originality in approach, 15 percent; focus level, 15 percent; depth of analysis, 20 percent; quantum of work, 20 percent; original contribution, 20 percent and presentation, which is, if I read it once with reasonable concentration, I must be able to understand it, that is communication. That carries 8 percent maybe, and of course, it goes without saying that a shoddy looking report is not professional. Therefore, it has to look professional, and that will carry 2 percent for a total of 10 percent.

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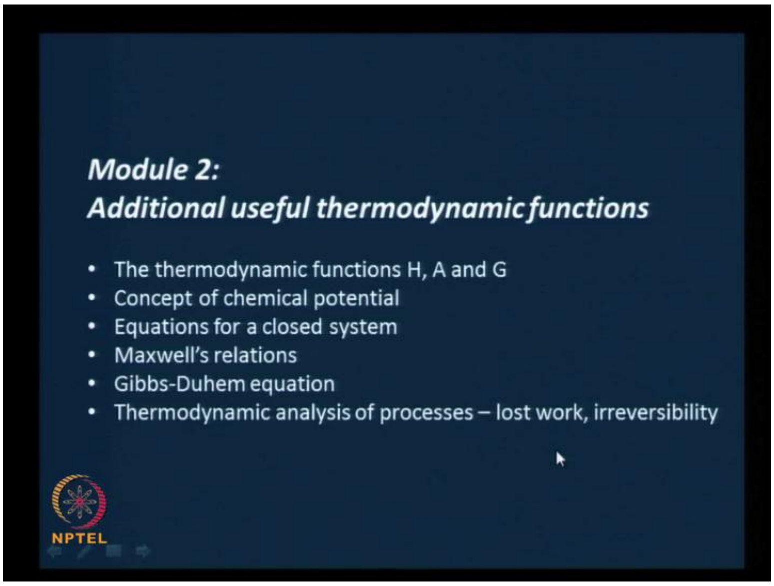

Module 2:
Additional useful thermodynamic functions

- The thermodynamic functions H, A and G
- Concept of chemical potential
- Equations for a closed system
- Maxwell's relations
- Gibbs-Duhem equation
- Thermodynamic analysis of processes – lost work, irreversibility

Those were the preliminaries and then we reviewed whatever you would have picked up in higher secondary school, as well as, in your 1st year of engineering. We reviewed that in one class, and then, we went on to module 2.

Module 2 was on additional useful thermodynamic functions. We looked at the thermodynamic functions: enthalpy, Helmholtz free energy and Gibbs' free energy. Then we looked at the concept of chemical potential, equations for a closed system, … Maxwell's relations, Gibbs-Duhem equation, and thermodynamic analysis of processes in terms of lost work and irreversibility. We will see some of these as we rush along here in the review.

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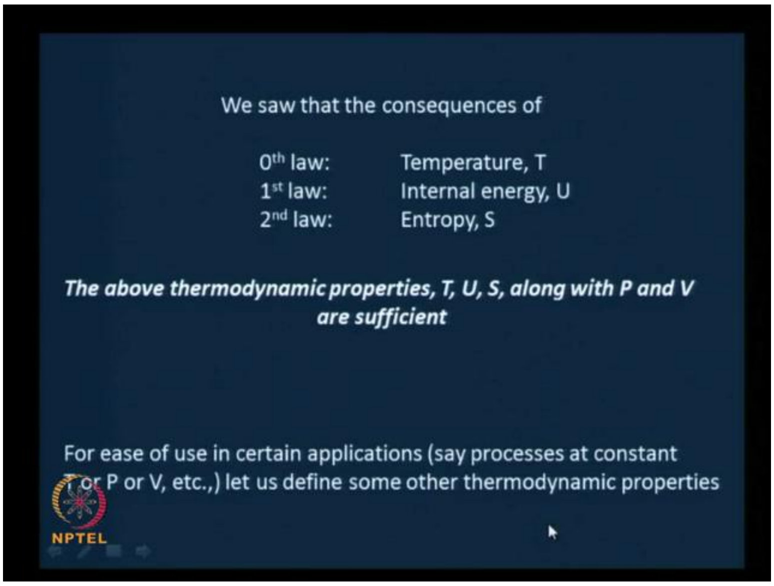

We saw that the consequences of

0^{th} law:	Temperature, T
1^{st} law:	Internal energy, U
2^{nd} law:	Entropy, S

The above thermodynamic properties, T, U, S, along with P and V are sufficient

For ease of use in certain applications (say processes at constant T or P or V, etc.,) let us define some other thermodynamic properties

We saw, that the consequence of the 0th law was temperature; it resulted in the useful variable temperature. The consequence of the 1st law is internal energy and the consequence of the 2nd law is entropy.

And we said that T, U, S along with P and V are actually sufficient to thermodynamically describe a system. Whereas for the ease of use in certain applications, say processes at constant T or P or specific volume, let us define some other thermodynamic properties, is what we said.

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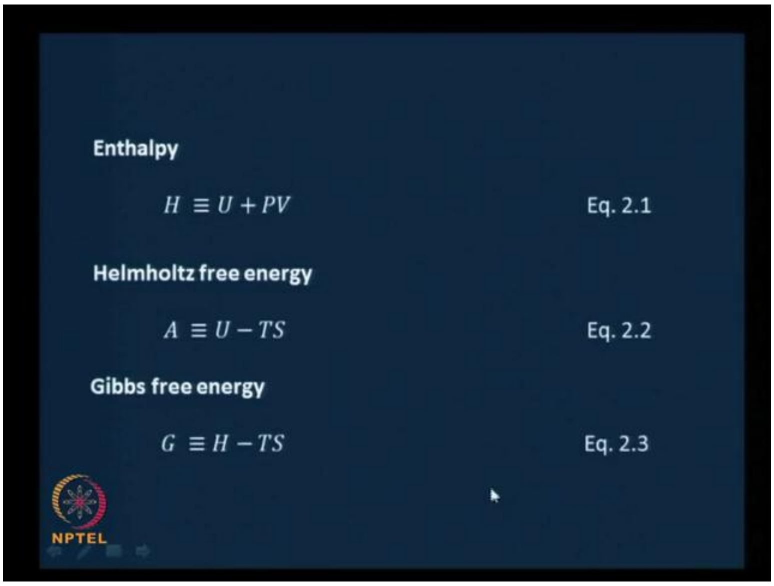

Enthalpy

$$H \equiv U + PV \qquad \text{Eq. 2.1}$$

Helmholtz free energy

$$A \equiv U - TS \qquad \text{Eq. 2.2}$$

Gibbs free energy

$$G \equiv H - TS \qquad \text{Eq. 2.3}$$

And with that motivation, we defined enthalpy as a combination of internal energy and PV. We defined Helmholtz free energy as a combination of internal energy minus TS and Gibbs free energy as H minus TS.

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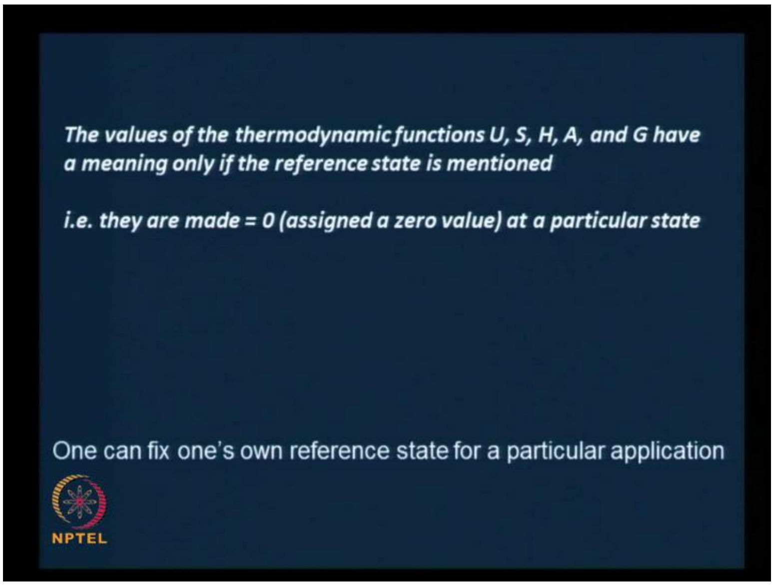

The values of the thermodynamic functions U, S, H, A, and G have a meaning only if the reference state is mentioned

i.e. they are made = 0 (assigned a zero value) at a particular state

One can fix one's own reference state for a particular application

And we said, the values of the thermodynamic functions U, S, H, A ,and G, this is a mnemonic based on the name … U, S, H, A and G, have a meaning only if the reference state is mentioned. This is, again, a kind of a review thing, you know this already. In other words, there is a certain set of conditions at which they are assigned a value zero. Of course, one can fix one's own reference state for a particular application.

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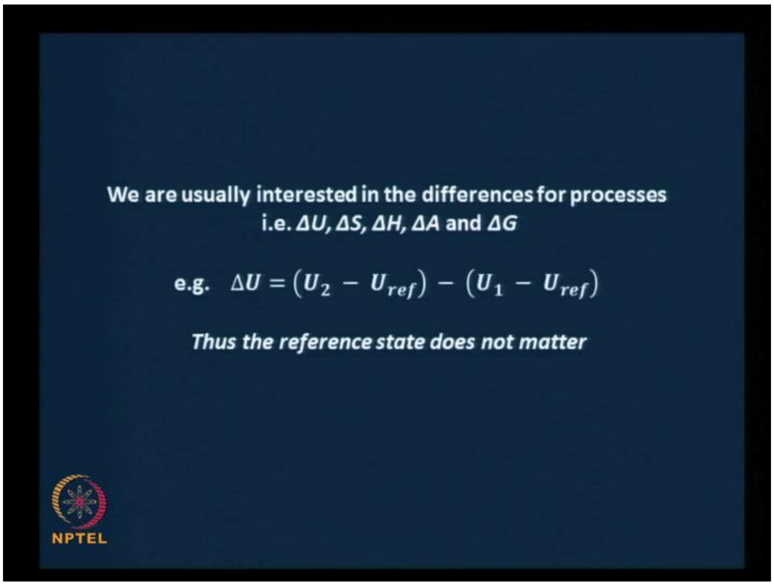

We are usually interested in the differences for processes
i.e. $\Delta U, \Delta S, \Delta H, \Delta A$ and ΔG

e.g. $\Delta U = (U_2 - U_{ref}) - (U_1 - U_{ref})$

Thus the reference state does not matter

If you are interested in a process, it does not really matter. … what reference state you take does not really matter because of this reason. Because, in a process we are interested in delta U, delta S, delta H, delta A and delta G, delta referring to the value at a final state minus the value at an initial state. For example, delta U would be the value at the final state is, U 2 minus U reference. You know, taking the reference value along and the value or the initial state of state 1 is U 1 minus U reference. If you take this value, it becomes U 2 minus U 1, anyway. U reference values get cancelled out. Therefore, it does not really matter what reference value you choose. But, for any of the values at any point to make sense, you need a reference value. In fact, you need to know where it has been assigned the value zero.

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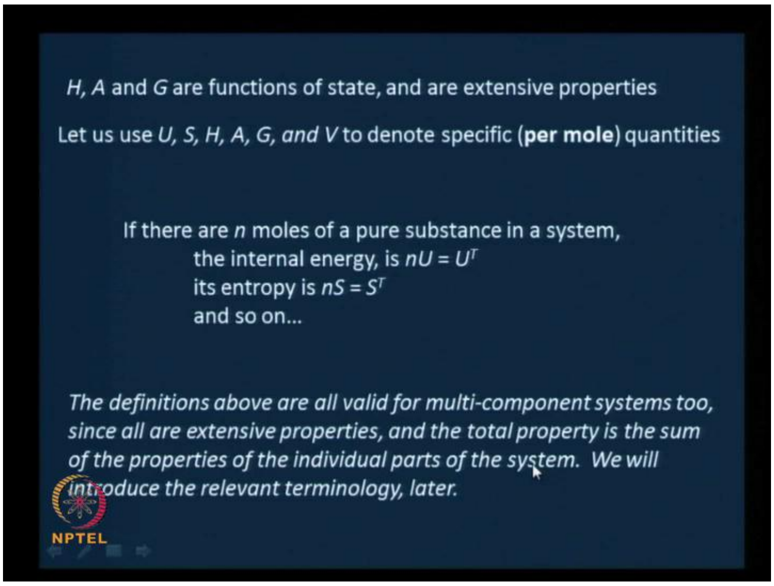

H, A and G are functions of state, and are extensive properties

Let us use $U, S, H, A, G,$ and V to denote specific (**per mole**) quantities

If there are n moles of a pure substance in a system,
the internal energy, is $nU = U^T$
its entropy is $nS = S^T$
and so on…

The definitions above are all valid for multi-component systems too, since all are extensive properties, and the total property is the sum of the properties of the individual parts of the system. We will introduce the relevant terminology, later.

We know that H, A and G, the additional functions are functions of state, which means, they depend only on the state of a system, not on the path taken to achieve … state 2 from state 1. And also, we said, for terminology purposes we will use the capitals U, S, H, A, G and V … to denote specific or per mole quantities. And therefore, if there are n moles of a pure substance in a system, the internal energy will be nU, which is also represented as U T and I think, we finally went with U T. Its entropy is nS, the number of moles into molar entropy or S T, and so on.

And the definitions above, U T, S T and so on, are all valid for multi-component systems too, since all are extensive properties and the total property is the sum of properties of individual parts of the system.

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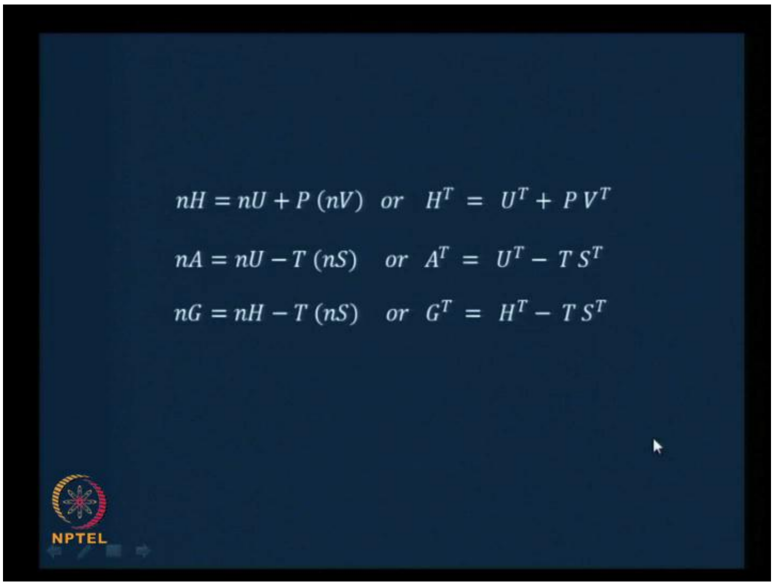

$nH = nU + P\,(nV)$ or $H^T = U^T + P\,V^T$

$nA = nU - T\,(nS)$ or $A^T = U^T - T\,S^T$

$nG = nH - T\,(nS)$ or $G^T = H^T - T\,S^T$

Going by that, we said nH equals nU plus P times nV or we are using this terminology, or we use this terminology in the later parts of the course. H T, the total enthalpy is U T plus P V T. This is intrinsic, so there is no T here.

Similarly, A T is U T minus T S T and G T equals H T minus T S T.

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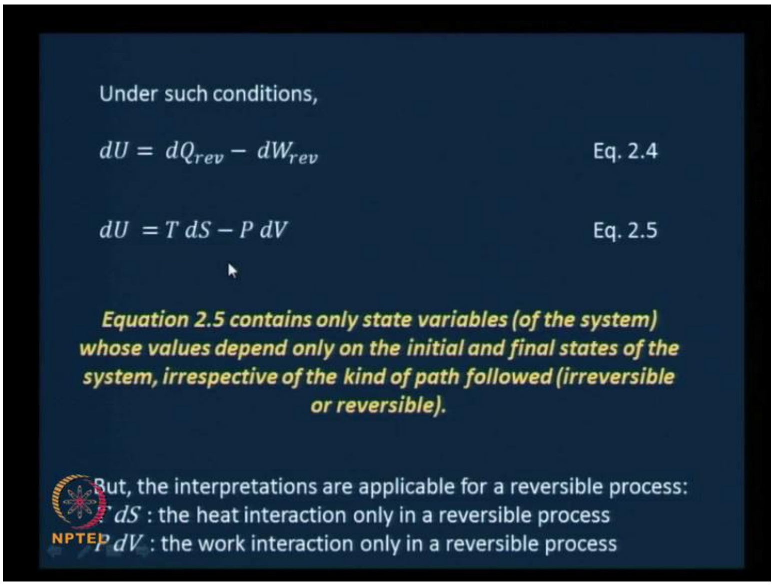

Under such conditions,

$dU = dQ_{rev} - dW_{rev}$ Eq. 2.4

$dU = T\,dS - P\,dV$ Eq. 2.5

Equation 2.5 contains only state variables (of the system) whose values depend only on the initial and final states of the system, irrespective of the kind of path followed (irreversible or reversible).

But, the interpretations are applicable for a reversible process:

$T\,dS$: the heat interaction only in a reversible process

$P\,dV$: the work interaction only in a reversible process

Then, we looked at single-component, single phase systems and we said, we could derive this equation, dU equals T dS minus P dV for a single phase, single-component system. And we also recognized, that this equation 2.5 contains only state variables, you know, U, T, S, P and V, state variables of the system whose values depend only on the initial and final states of the system, irrespective of the kind of path followed to … reach state 2 from state 1. And therefore, you know, we had used some … reversible process arguments to get at this, and we said that this equation is valid for any closed system irrespective of the assumptions that we made regarding the kind of process to achieve this. For example, this could be valid for either irreversible or reversible processes.

Whereas, the interpretation of T dS as the heat interaction is applicable only to a reversible process, the interpretation of P dV as work interaction is possible only for a reversible process. You take these two terms, two terms separately, then it is not valid, whereas the whole equation is valid for any process.

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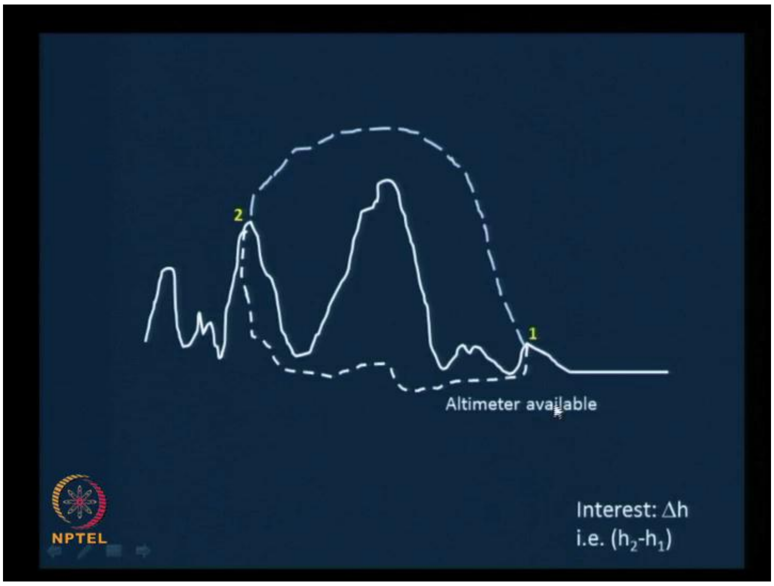

Altimeter available

Interest: Δh
i.e. (h_2-h_1)

… We had used this nice example of being interested in the difference in heights between points 1 and 2. We said that there could be some paths through which it would be easier to measure the heights as we go along. Therefore, we can choose that path and for example, probably only on this path an altimeter is available. Altimeter is used to measure heights. Therefore, we could measure heights as we go along this path and therefore, we could measure height here and irrespective of this, we could measure height here. And therefore, we could get h 1 minus h 2 or h 2 minus h 1.

Whereas, the altimeters may not be available on the other paths, maybe, you could take a helicopter and so on and so forth, or trek through an unchartered territory from 1 to 2. In those paths, maybe, a way of measurement of the height is not available, but it does not really matter what path you choose, as long as, you are interested in the difference in heights. That is going to remain the same irrespective of the path used to go from 1 to 2. This is essentially, a central argument in the ways we went about deriving a few useful relationships in thermodynamics.

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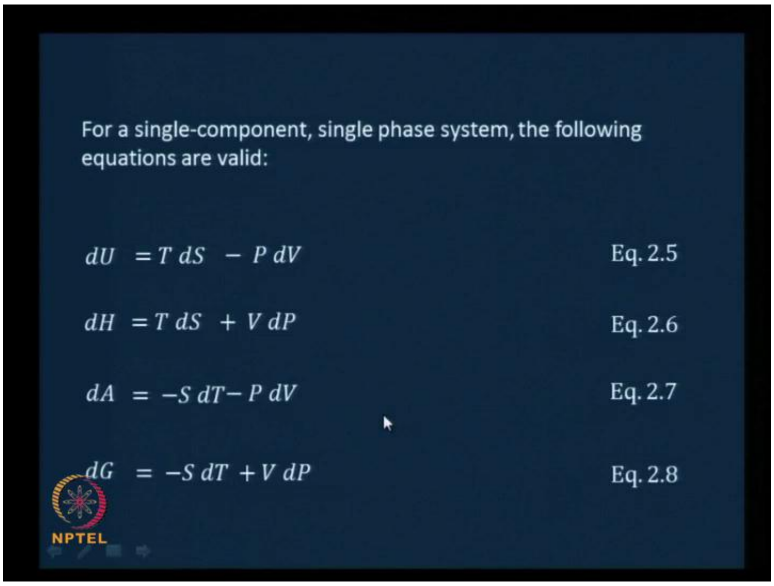

For a single-component, single phase system, the following equations are valid:

$dU = T\,dS - P\,dV$ Eq. 2.5

$dH = T\,dS + V\,dP$ Eq. 2.6

$dA = -S\,dT - P\,dV$ Eq. 2.7

$dG = -S\,dT + V\,dP$ Eq. 2.8

Therefore, these equations are valid for a single-component, single phase system, closed system. dU equals T dS minus P dV; dH equals T dS plus V dP; dA equals minus S dT minus P dV and dG equals minus S dT plus V dP.

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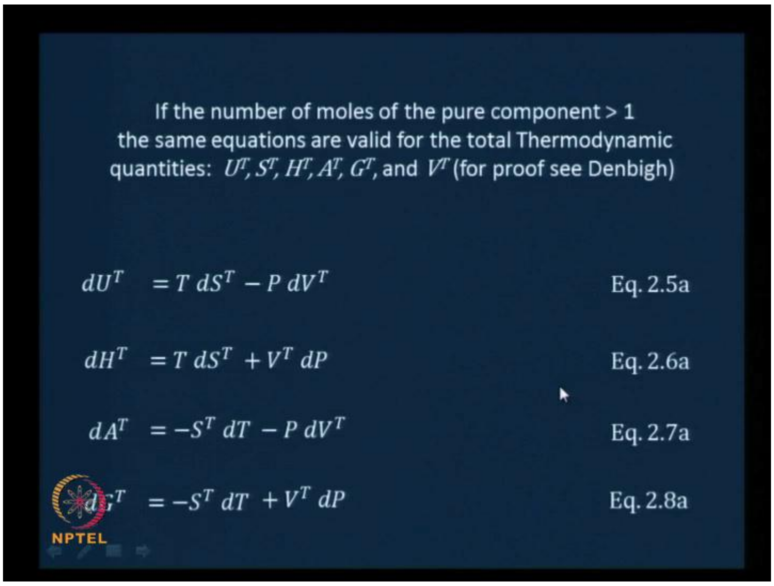

If the number of moles of the pure component > 1 the same equations are valid for the total Thermodynamic quantities: U^T, S^T, H^T, A^T, G^T, and V^T (for proof see Denbigh)

$$dU^T = T\,dS^T - P\,dV^T \quad \text{Eq. 2.5a}$$

$$dH^T = T\,dS^T + V^T\,dP \quad \text{Eq. 2.6a}$$

$$dA^T = -S^T\,dT - P\,dV^T \quad \text{Eq. 2.7a}$$

$$dG^T = -S^T\,dT + V^T\,dP \quad \text{Eq. 2.8a}$$

We also said that those are for 1 mole. Even … if the number of moles increases, as long as it is a … pure component closed system, you could write the same kind of equations for U T, S T, H T, A T and G T and V T; proof is given in Denbigh. Therefore, dU T equals T dS T minus P dV T; dH T equals T dS T plus V T dP; dA T equals minus S T dT minus P dV T and dG T equals minus S T dT plus V T dP.

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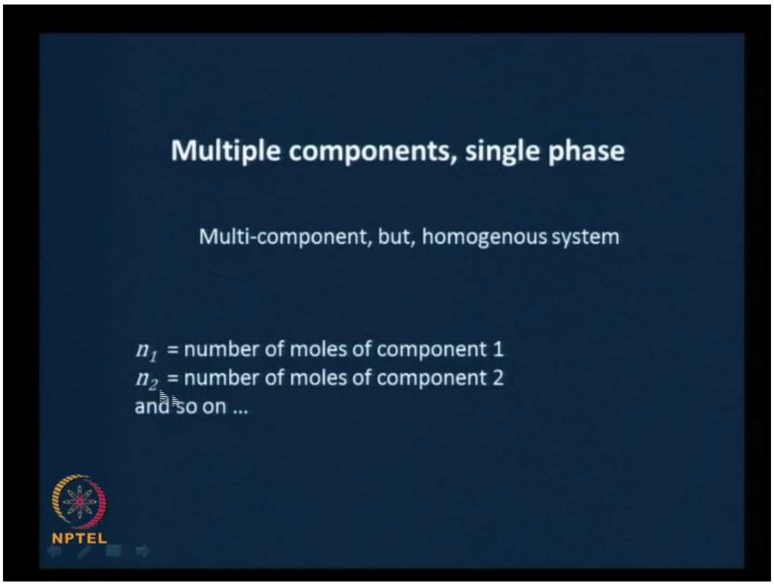

Multiple components, single phase

Multi-component, but, homogenous system

n_1 = number of moles of component 1
n_2 = number of moles of component 2
and so on …

Then we looked at multi-component, single phase system, … or multi-component homogeneous system. We said n 1 would be the number of moles of component 1, n 2 would be the number of moles of component 2, and so on.

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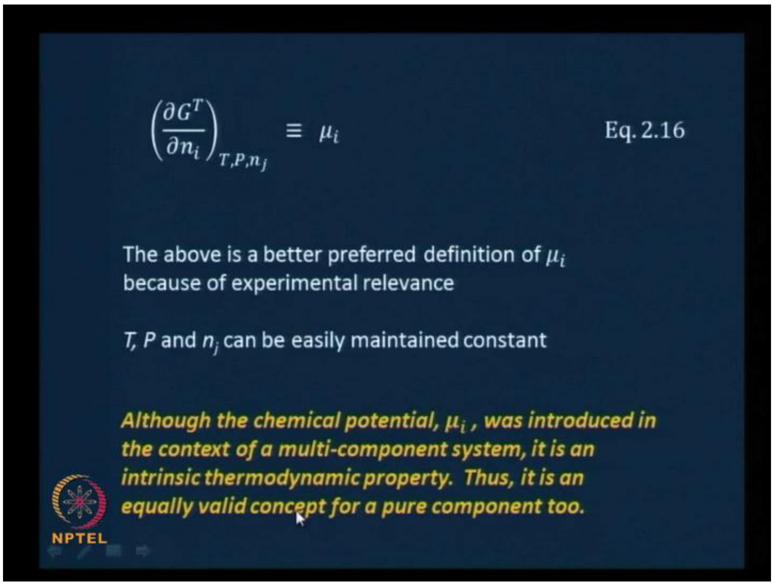

$$\left(\frac{\partial G^T}{\partial n_i}\right)_{T,P,n_j} \equiv \mu_i \qquad \text{Eq. 2.16}$$

The above is a better preferred definition of μ_i because of experimental relevance

T, P and n_j can be easily maintained constant

Although the chemical potential, μ_i, was introduced in the context of a multi-component system, it is an intrinsic thermodynamic property. Thus, it is an equally valid concept for a pure component too.

… We saw this very fundamental definition, dou G T dou n i at constant T, P, n j is defined as a chemical potential. This is pretty much the way it is predominantly used, although there could be other definitions of the chemical potential, because it is much easier to keep T, P and n j constant while doing an experiment to probably measure this. … Also, we saw, that although the chemical potential has been introduced in the context of a multi-component system, it is an intrinsic thermodynamic quantity, a very basic quantity and it is an equally valid concept for a pure component also.

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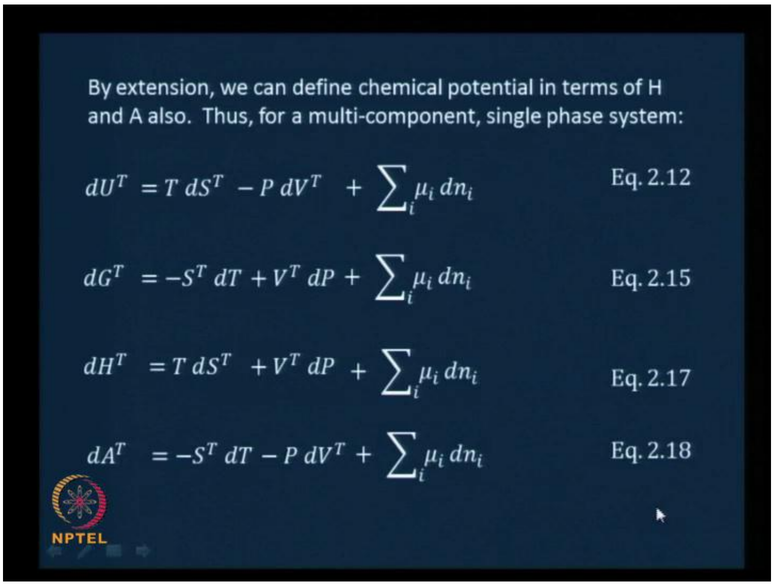

By extension, we can define chemical potential in terms of H and A also. Thus, for a multi-component, single phase system:

$$dU^T = T\,dS^T - P\,dV^T + \sum_i \mu_i\,dn_i \qquad \text{Eq. 2.12}$$

$$dG^T = -S^T\,dT + V^T\,dP + \sum_i \mu_i\,dn_i \qquad \text{Eq. 2.15}$$

$$dH^T = T\,dS^T + V^T\,dP + \sum_i \mu_i\,dn_i \qquad \text{Eq. 2.17}$$

$$dA^T = -S^T\,dT - P\,dV^T + \sum_i \mu_i\,dn_i \qquad \text{Eq. 2.18}$$

Therefore, for a multi-component, single phase system, we extended the argument to come up with these equations that are valid. dU T equals T dS T minus P dV T plus sum over all i mu i dn i. Similar expressions for dG T, dH T and dA T. It is good to have all these things together, so that you can always go back and refer to this. And, by repeated use, you might remember some of these.

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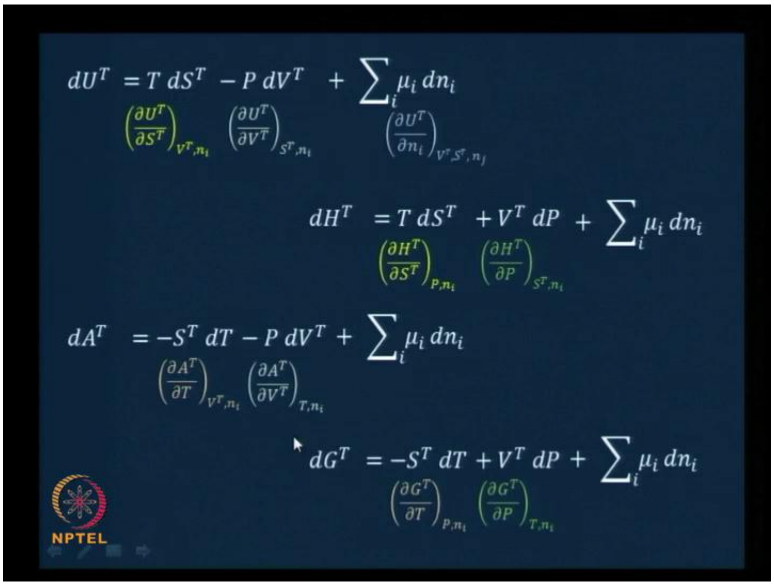

$$dU^T = \underset{\left(\frac{\partial U^T}{\partial S^T}\right)_{V^T,n_i}}{T\,dS^T} - \underset{\left(\frac{\partial U^T}{\partial V^T}\right)_{S^T,n_i}}{P\,dV^T} + \underset{\left(\frac{\partial U^T}{\partial n_i}\right)_{V^T,S^T,n_j}}{\sum_i \mu_i\,dn_i}$$

$$dH^T = \underset{\left(\frac{\partial H^T}{\partial S^T}\right)_{P,n_i}}{T\,dS^T} + \underset{\left(\frac{\partial H^T}{\partial P}\right)_{S^T,n_i}}{V^T\,dP} + \sum_i \mu_i\,dn_i$$

$$dA^T = \underset{\left(\frac{\partial A^T}{\partial T}\right)_{V^T,n_i}}{-S^T\,dT} - \underset{\left(\frac{\partial A^T}{\partial V^T}\right)_{T,n_i}}{P\,dV^T} + \sum_i \mu_i\,dn_i$$

$$dG^T = \underset{\left(\frac{\partial G^T}{\partial T}\right)_{P,n_i}}{-S^T\,dT} + \underset{\left(\frac{\partial G^T}{\partial P}\right)_{T,n_i}}{V^T\,dP} + \sum_i \mu_i\,dn_i$$

And then, by comparison of the various partial derivatives, for example, this is nothing but dU T equals dou U T dou S T dS T plus dou U T dou V T dV T, and so on.

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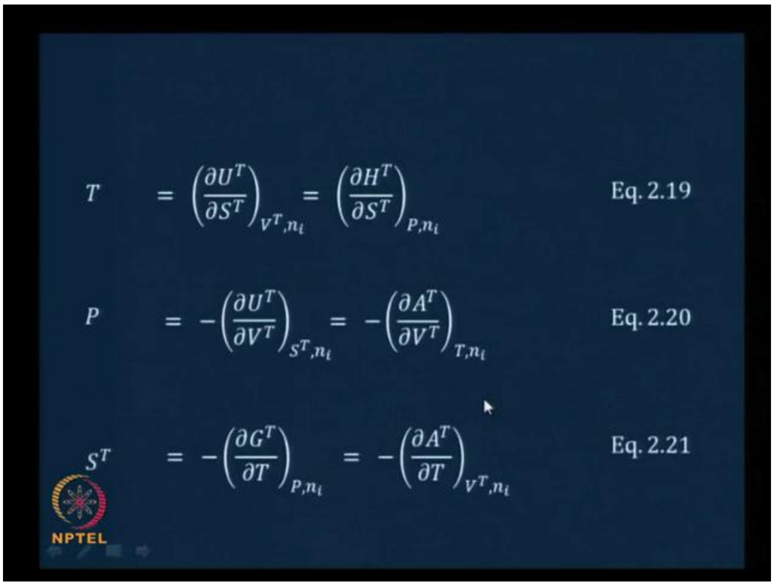

$$T = \left(\frac{\partial U^T}{\partial S^T}\right)_{V^T,n_i} = \left(\frac{\partial H^T}{\partial S^T}\right)_{P,n_i} \qquad \text{Eq. 2.19}$$

$$P = -\left(\frac{\partial U^T}{\partial V^T}\right)_{S^T,n_i} = -\left(\frac{\partial A^T}{\partial V^T}\right)_{T,n_i} \qquad \text{Eq. 2.20}$$

$$S^T = -\left(\frac{\partial G^T}{\partial T}\right)_{P,n_i} = -\left(\frac{\partial A^T}{\partial T}\right)_{V^T,n_i} \qquad \text{Eq. 2.21}$$

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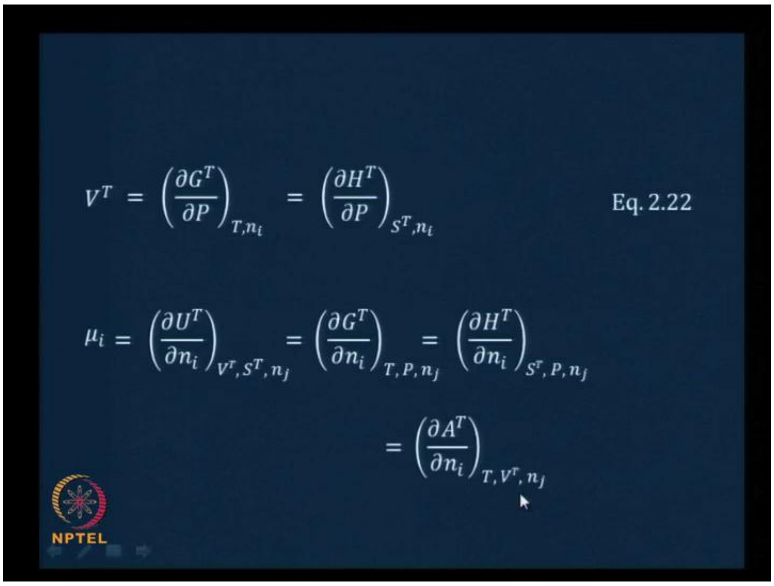

$$V^T = \left(\frac{\partial G^T}{\partial P}\right)_{T,n_i} = \left(\frac{\partial H^T}{\partial P}\right)_{S^T,n_i} \qquad \text{Eq. 2.22}$$

$$\mu_i = \left(\frac{\partial U^T}{\partial n_i}\right)_{V^T,S^T,n_j} = \left(\frac{\partial G^T}{\partial n_i}\right)_{T,P,n_j} = \left(\frac{\partial H^T}{\partial n_i}\right)_{S^T,P,n_j}$$

$$= \left(\frac{\partial A^T}{\partial n_i}\right)_{T,V^T,n_j}$$

Going by the expansion or the total derivative in terms of the partial derivatives, we could write the various expressions as, temperature as this, pressure as this, enthalpy as this, specific volume as this and the chemical potential as dou U T, dou n i at constant V T, S T, n j or dou G T dou n i at constant T, P, n j, more commonly used or dou H T dou n i at constant S T, P, n j or dou A T dou n i at constant T, V T, n j.

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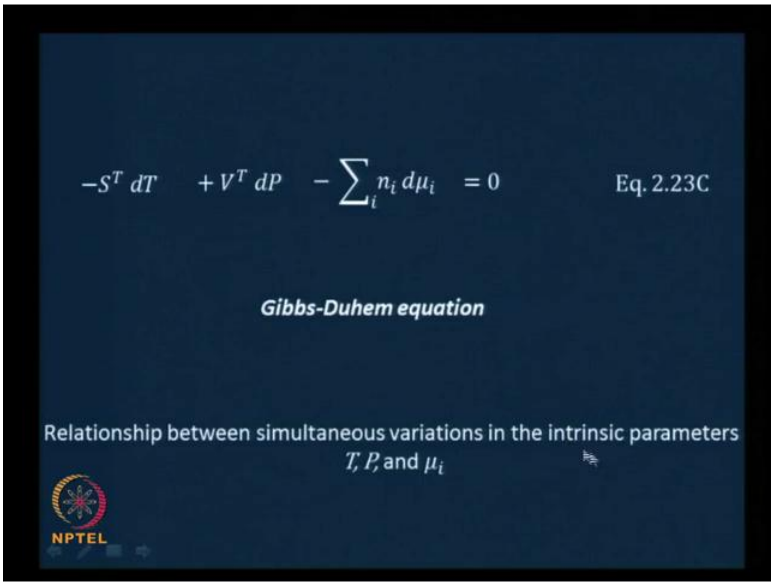

$$-S^T\,dT \quad + V^T\,dP \quad - \sum_i n_i\,d\mu_i \quad = 0 \qquad \text{Eq. 2.23C}$$

Gibbs-Duhem equation

Relationship between simultaneous variations in the intrinsic parameters $T, P,$ and μ_i

Then, we derived a fundamental equation, the Gibbs-Duhem equation, which says, minus S T dT plus V T dP minus sum over i n i d mu i equals 0. This gives relationship between simultaneous variations of temperature, pressure and chemical potential.

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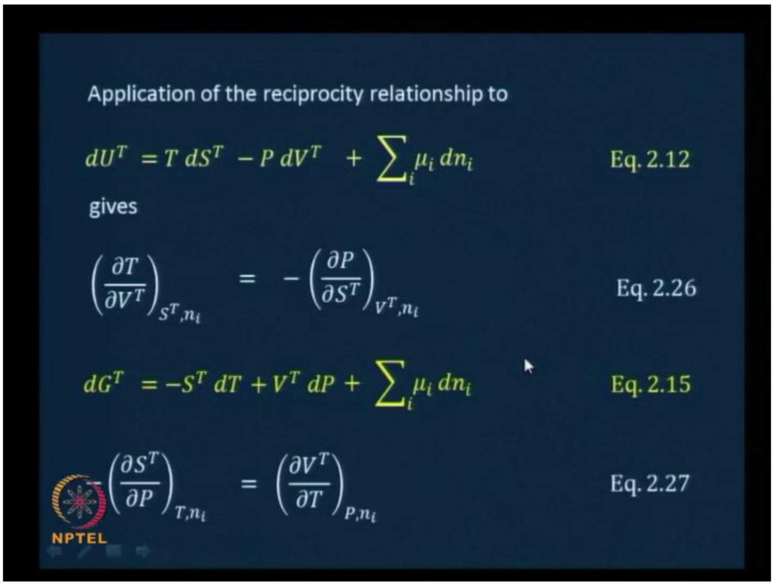

Application of the reciprocity relationship to

$$dU^T = T\,dS^T - P\,dV^T + \sum_i \mu_i\,dn_i \qquad \text{Eq. 2.12}$$

gives

$$\left(\frac{\partial T}{\partial V^T}\right)_{S^T,n_i} = -\left(\frac{\partial P}{\partial S^T}\right)_{V^T,n_i} \qquad \text{Eq. 2.26}$$

$$dG^T = -S^T\,dT + V^T\,dP + \sum_i \mu_i\,dn_i \qquad \text{Eq. 2.15}$$

$$-\left(\frac{\partial S^T}{\partial P}\right)_{T,n_i} = \left(\frac{\partial V^T}{\partial T}\right)_{P,n_i} \qquad \text{Eq. 2.27}$$

… Then, applying the reciprocity relationship, you know, taking two at a time and the reciprocity relationship given by the mathematics, mathematical theorem, we could get very useful relationships, which was dou T dou V T at constant S T, n i equals minus dou P dou S T at constant V T, n i and so on.

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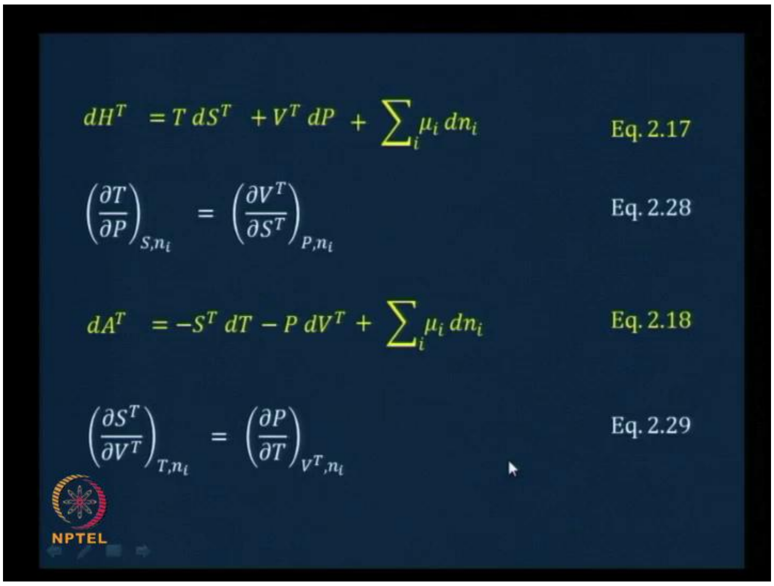

$$dH^T = T\,dS^T + V^T\,dP + \sum_i \mu_i\,dn_i$$ Eq. 2.17

$$\left(\frac{\partial T}{\partial P}\right)_{S,n_i} = \left(\frac{\partial V^T}{\partial S^T}\right)_{P,n_i}$$ Eq. 2.28

$$dA^T = -S^T\,dT - P\,dV^T + \sum_i \mu_i\,dn_i$$ Eq. 2.18

$$\left(\frac{\partial S^T}{\partial V^T}\right)_{T,n_i} = \left(\frac{\partial P}{\partial T}\right)_{V^T,n_i}$$ Eq. 2.29

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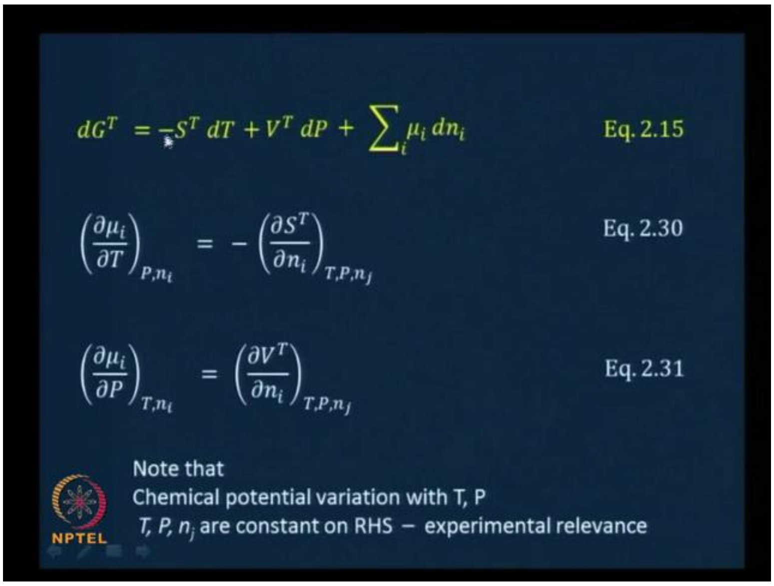

$$dG^T = -S^T\,dT + V^T\,dP + \sum_i \mu_i\,dn_i$$ Eq. 2.15

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_i} = -\left(\frac{\partial S^T}{\partial n_i}\right)_{T,P,n_j}$$ Eq. 2.30

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_i} = \left(\frac{\partial V^T}{\partial n_i}\right)_{T,P,n_j}$$ Eq. 2.31

Note that
Chemical potential variation with T, P
T, P, n_j are constant on RHS − experimental relevance

I am not going to read those out they are useful expressions which can be used to represent not so easy to measure thermodynamic variables in terms of easy to measure thermodynamic variables, such as P, T and V.

And these equations, 2.26 to 2.31, which we obtained through application of the reciprocity relationship to equations that are applicable to a closed system, are called Maxwell’s relations.

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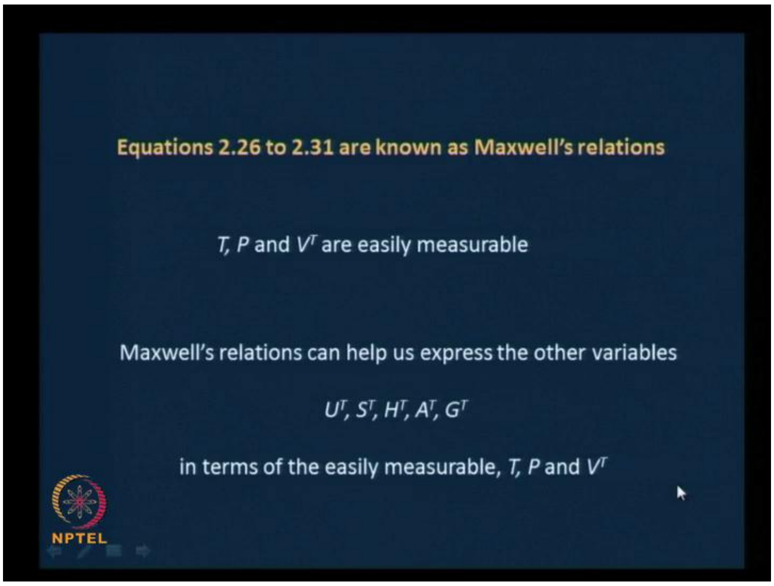

Equations 2.26 to 2.31 are known as Maxwell's relations

T, P and V^T are easily measurable

Maxwell's relations can help us express the other variables

U^T, S^T, H^T, A^T, G^T

in terms of the easily measurable, T, P and V^T

This is what I just mentioned. We could represent U T, S T, H T, A T, G T which are not so easily measurable in terms of T, P and V T, which are easily measurable by using these Maxwell's relations.

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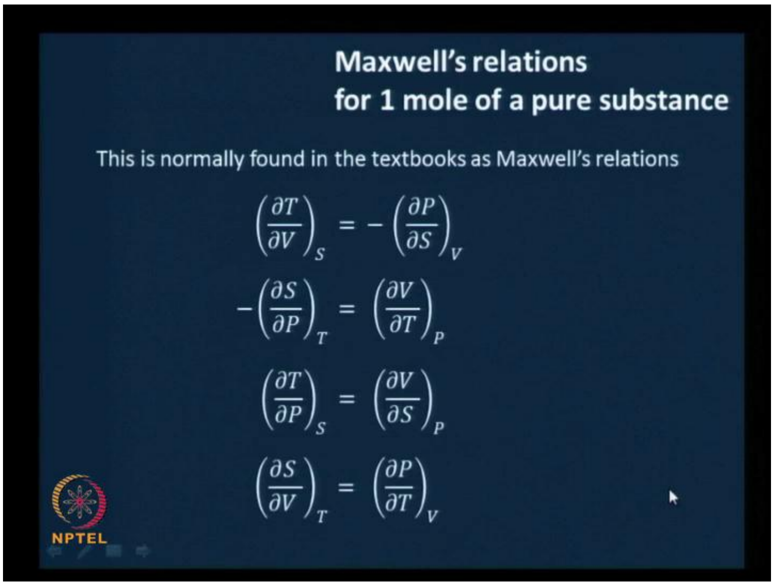

Maxwell's relations
for 1 mole of a pure substance

This is normally found in the textbooks as Maxwell's relations

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

And what you will find in your textbook predominantly … are Maxwell's relations for 1 mole of a pure substance. And that is this, which you can also get by the earlier relations that we gave, except that we do not consider n i and T as the total values and so on, since this is 1 mole of a pure substance.

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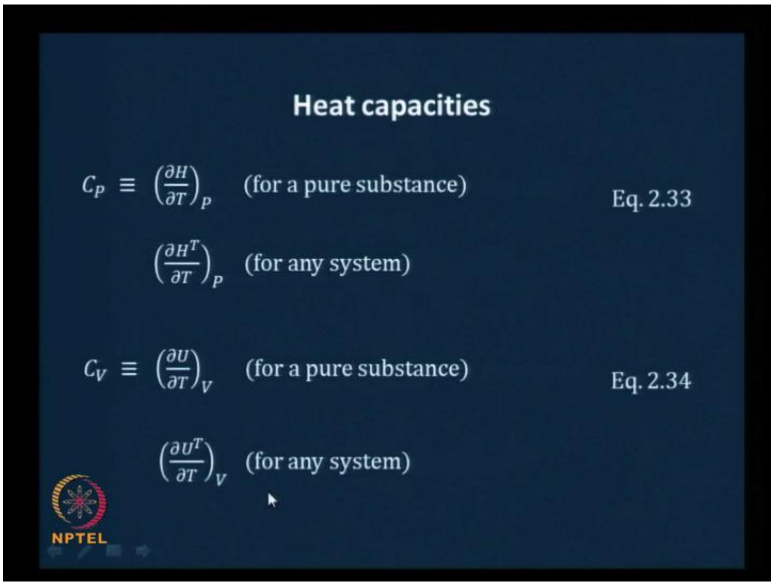

Heat capacities

$C_P \equiv \left(\frac{\partial H}{\partial T}\right)_P$ (for a pure substance) Eq. 2.33

$\left(\frac{\partial H^T}{\partial T}\right)_P$ (for any system)

$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V$ (for a pure substance) Eq. 2.34

$\left(\frac{\partial U^T}{\partial T}\right)_V$ (for any system)

Apart from these, other useful thermodynamic variables or measurable thermodynamic variables are heat capacities. This we already know, C P is dou H dou T at constant P or dou H T dou T at constant P for any system. This is for a pure substance molar value. Similarly, C V is dou U dou T at constant V for a pure substance or dou U T dou T at constant V for any system.

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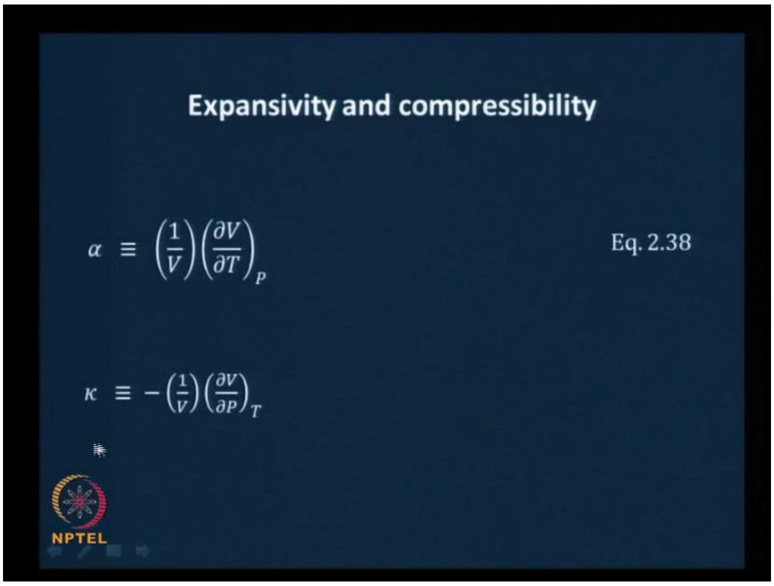

Expansivity and compressibility

$\alpha \equiv \left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial T}\right)_P$ Eq. 2.38

$\kappa \equiv -\left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial P}\right)_T$

Similarly, we would also have expansivity and compressibility as useful thermodynamic variables. Expansivity, alpha, defined as 1 by V dou V dou T at constant P and isothermal compressibility, as it is called, because T is constant here, is defined as minus 1 by V dou V dou P, how the volume changes with pressure at constant temperature, that is, kappa.

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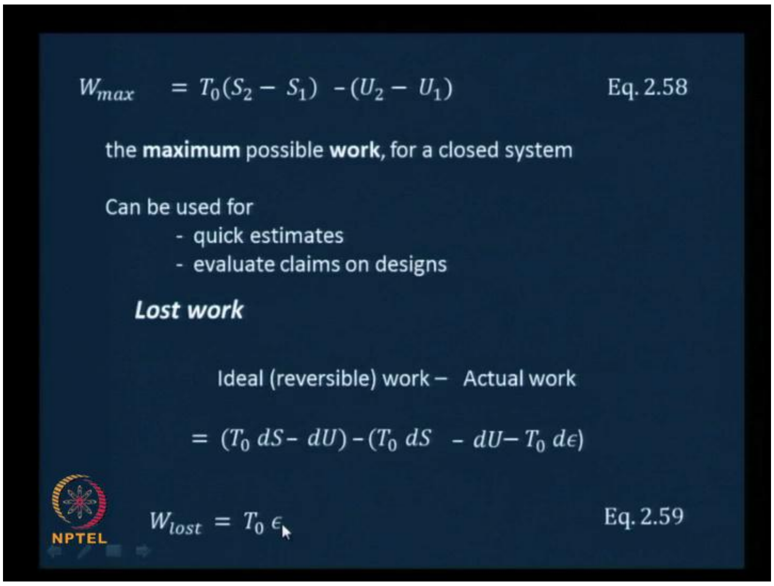

$W_{max} = T_0(S_2 - S_1) - (U_2 - U_1)$ Eq. 2.58

the **maximum** possible **work**, for a closed system

Can be used for
- quick estimates
- evaluate claims on designs

Lost work

Ideal (reversible) work – Actual work

$= (T_0\, dS - dU) - (T_0\, dS - dU - T_0\, d\epsilon)$

$W_{lost} = T_0\, \epsilon$ Eq. 2.59

Then, we looked at maximum work and lost work. We saw, that maximum work could be expressed as T 0, the temperature of the surroundings, times S 2 minus S 1 minus of U 2 minus U 1. And the maximum possible work for a closed system is this expression; it can be used for making some quick estimates, and to evaluate back of the envelope and to do back of the envelope evaluations for claims on certain designs, and so on and so forth. If somebody is saying, that they can get so much work, you can just quickly do a calculation, if you know these values, rules of thumb values, and use that to make a quick decision and so on. Since this is the maximum work, the lost work was ideal or reversible work minus the actual work, … which we derived as T 0 times epsilon, which is the entropy, that is created; epsilon is the entropy created.

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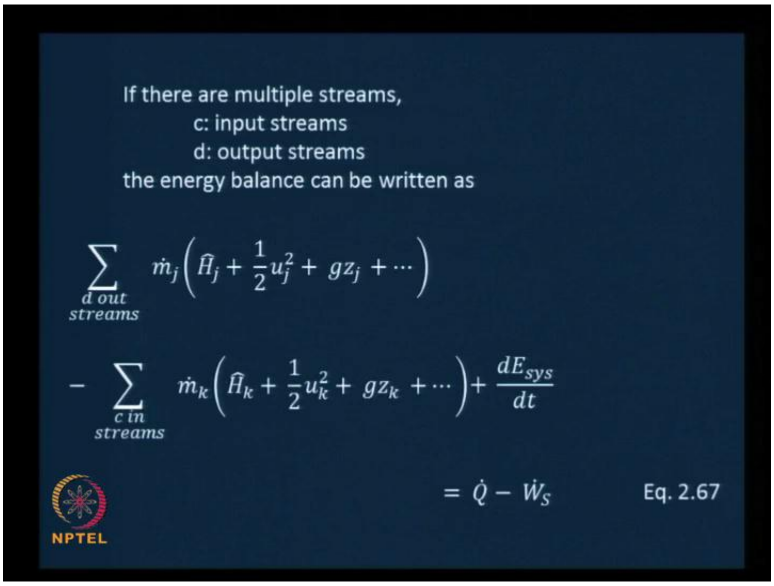

If there are multiple streams,
c: input streams
d: output streams
the energy balance can be written as

$$\sum_{\substack{d\ out \\ streams}} \dot{m}_j\left(\hat{H}_j + \frac{1}{2}u_j^2 + gz_j + \cdots\right) - \sum_{\substack{c\ in \\ streams}} \dot{m}_k\left(\hat{H}_k + \frac{1}{2}u_k^2 + gz_k + \cdots\right) + \frac{dE_{sys}}{dt} = \dot{Q} - \dot{W}_S \qquad \text{Eq. 2.67}$$

Then, we looked at open systems and we came up with an energy balance equation for open systems. This is for the output streams, enthalpy, this is the internal energy term velocity squared term, and the potential energy term, and the other energies here. This is for the inlet streams, outlet minus inlet, plus the time variation of the system energy equals Q dot minus … W S dot. And for each of these cases we had worked out examples to see how you can apply or use these expressions in practical situations.

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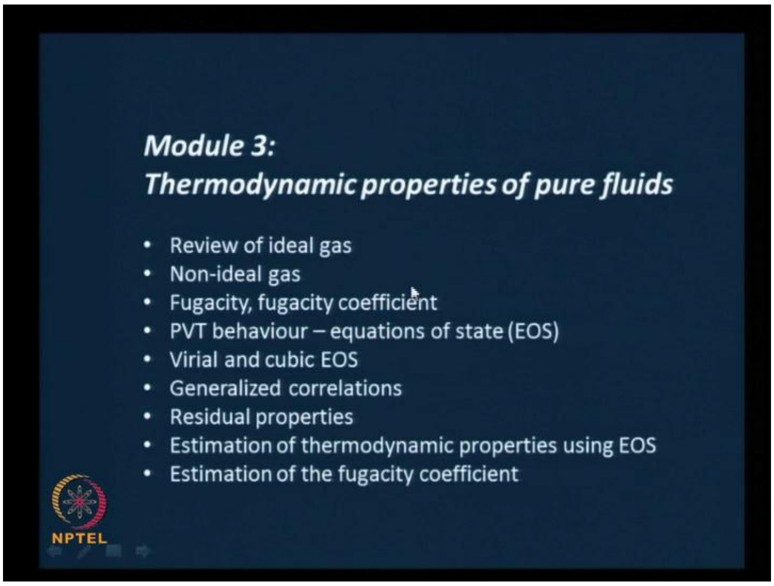

Module 3:
Thermodynamic properties of pure fluids

- Review of ideal gas
- Non-ideal gas
- Fugacity, fugacity coefficient
- PVT behaviour – equations of state (EOS)
- Virial and cubic EOS
- Generalized correlations
- Residual properties
- Estimation of thermodynamic properties using EOS
- Estimation of the fugacity coefficient

Then module 3 was on thermodynamic properties of pure fluids. We first reviewed an ideal gas. We looked at non-ideal gas, fugacity, fugacity coefficient, then equations of state or PVT behavior, and various equations of state, such as virial and cubic equations of state. Then, we looked at generalized correlations, residual properties, estimation of thermodynamic properties using equations of state and estimation of fugacity coefficient.

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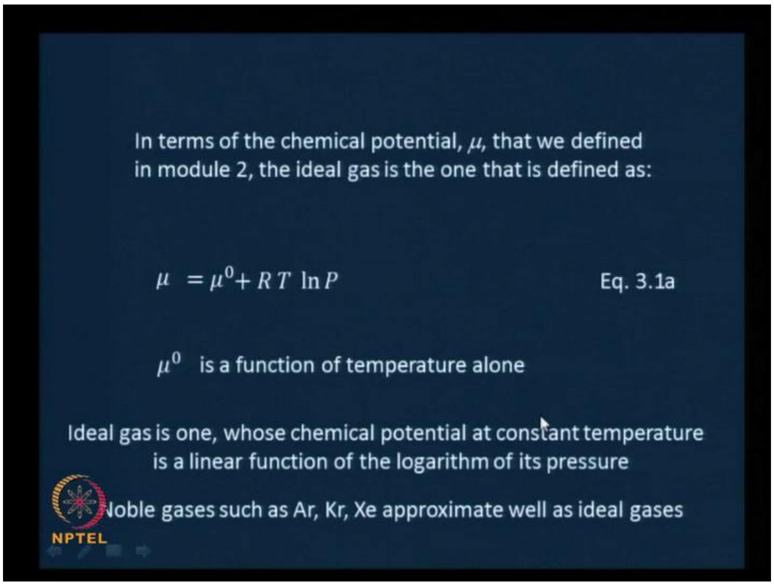

In terms of the chemical potential, μ, that we defined in module 2, the ideal gas is the one that is defined as:

$$\mu = \mu^0 + R\,T\,\ln P \qquad \text{Eq. 3.1a}$$

μ^0 is a function of temperature alone

Ideal gas is one, whose chemical potential at constant temperature is a linear function of the logarithm of its pressure

Noble gases such as Ar, Kr, Xe approximate well as ideal gases

Let me just point out a few as we go along this. This was our definition of an ideal gas in terms of the chemical potential, and hopefully, you would have realized that this is pretty much the backbone of this course. We have written all in terms of the chemical potential and used that to relate various aspects. Here, mu equals mu naught plus R T ln P is that for an ideal gas; mu naught is a function of temperature alone. And ideal gas is therefore, one whose chemical potential at constant temperature is a linear function of the logarithm of its pressure. There are some gases, as we know, that approximate well to ideal gases.

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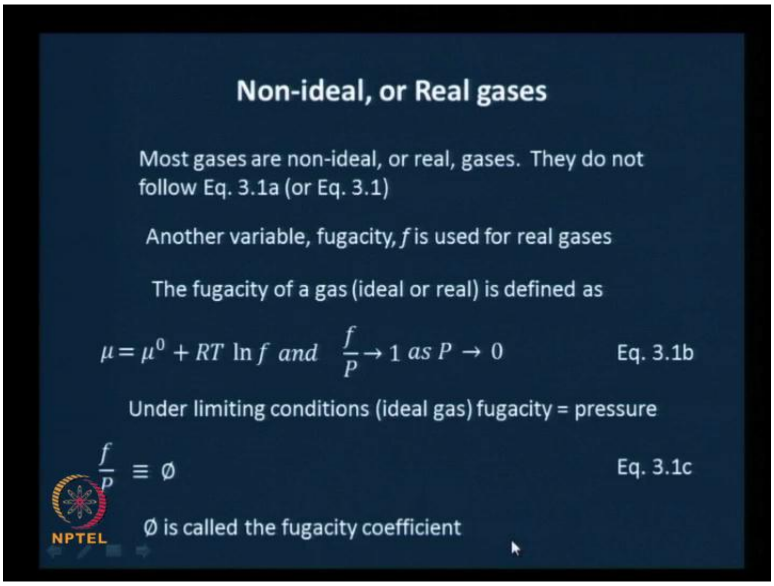

Non-ideal, or Real gases

Most gases are non-ideal, or real, gases. They do not follow Eq. 3.1a (or Eq. 3.1)

Another variable, fugacity, *f* is used for real gases

The fugacity of a gas (ideal or real) is defined as

$$\mu = \mu^0 + RT \ln f \ and \ \frac{f}{P} \rightarrow 1 \ as \ P \rightarrow 0 \qquad \text{Eq. 3.1b}$$

Under limiting conditions (ideal gas) fugacity = pressure

$$\frac{f}{P} \equiv \emptyset \qquad \text{Eq. 3.1c}$$

$\emptyset$ is called the fugacity coefficient

Most gases do not; they are all non-ideal or real. For them mu equals mu naught plus R T ln f, where f is the fugacity; and, to complete the definition we need to say f by P tends to 1 as P tends to 0. … f by P is actually the fugacity coefficient phi.

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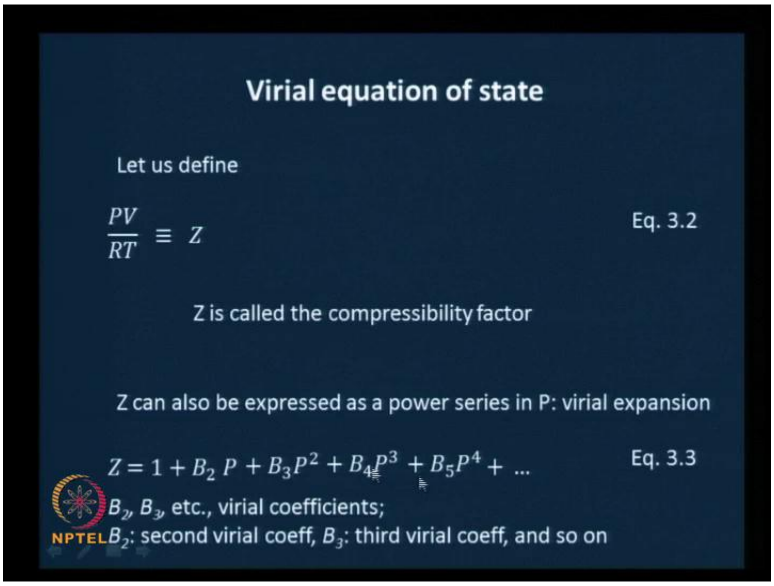

Virial equation of state

Let us define

$$\frac{PV}{RT} \equiv Z \qquad \text{Eq. 3.2}$$

Z is called the compressibility factor

Z can also be expressed as a power series in P: virial expansion

$$Z = 1 + B_2 P + B_3 P^2 + B_4 P^3 + B_5 P^4 + \ldots \qquad \text{Eq. 3.3}$$

B_2, B_3, etc., virial coefficients;

B_2: second virial coeff, B_3: third virial coeff, and so on

Now, the equations of state, equations of state is nothing but the relationship between P V and T for a pure substance. If we define P V by R T as Z, the compressibility factor, then this is one of the virial equations of state in terms of pressure, Z equals 1 plus B 2 P plus B 3 P squared plus B 4 P cubed plus B 5 P power 4 and so on. It is a power series expansion.

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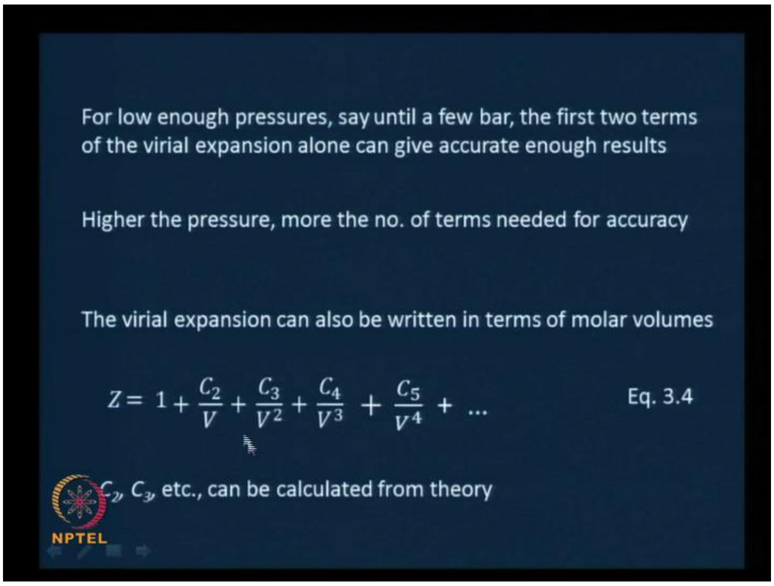

For low enough pressures, say until a few bar, the first two terms of the virial expansion alone can give accurate enough results

Higher the pressure, more the no. of terms needed for accuracy

The virial expansion can also be written in terms of molar volumes

$$Z = 1 + \frac{C_2}{V} + \frac{C_3}{V^2} + \frac{C_4}{V^3} + \frac{C_5}{V^4} + \ldots \qquad \text{Eq. 3.4}$$

C_2, C_3, etc., can be calculated from theory

And you could also write the expansion in terms of specific volumes …. Since the pressures were directly related, the specific volumes would be inversely related. Z equals 1 plus C 2 by V plus C 3 by V squared plus C 4 by V cubed, and so on. These coefficients can actually be calculated from statistical mechanics theory.

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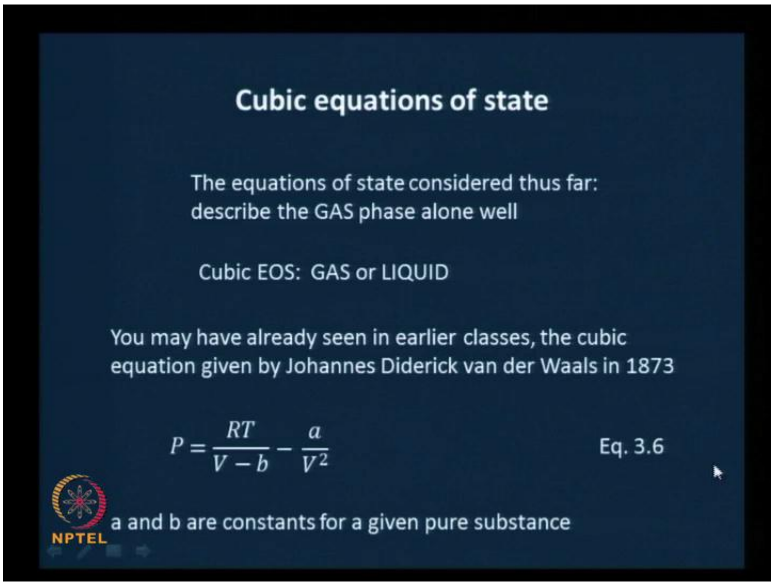

Cubic equations of state

The equations of state considered thus far: describe the GAS phase alone well

Cubic EOS: GAS or LIQUID

You may have already seen in earlier classes, the cubic equation given by Johannes Diderick van der Waals in 1873

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \qquad \text{Eq. 3.6}$$

a and b are constants for a given pure substance

Then, we saw cubic equations of state. Now, the equations of state, the virial equations can describe the gas phase alone well. The cubic equations can do both, gas phase and liquid phase, well. You could apply it anywhere, but if you are applying the virial equations, then be a little careful, that is all I am trying to say here, across states, that is. The Van der Waals equation, that you have already seen is nothing but a cubic equation P equals RT by V minus b minus a by V squared, and a and b are constants for a pure substance.

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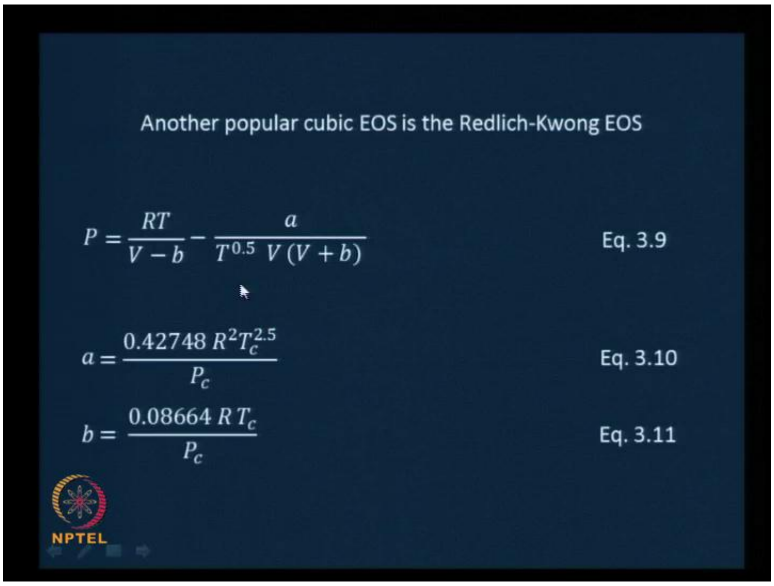

Another popular cubic EOS is the Redlich-Kwong EOS

$$P = \frac{RT}{V-b} - \frac{a}{T^{0.5}\, V\,(V+b)} \qquad \text{Eq. 3.9}$$

$$a = \frac{0.42748\, R^2 T_c^{2.5}}{P_c} \qquad \text{Eq. 3.10}$$

$$b = \frac{0.08664\, R\, T_c}{P_c} \qquad \text{Eq. 3.11}$$

The other popular equation, that we saw somewhat extensively in this course is the Redlich-Kwong equation, P equals R T by V minus b minus a by T power 0.5 V into V plus b, and you have expressions for a and b from which we can calculate that.

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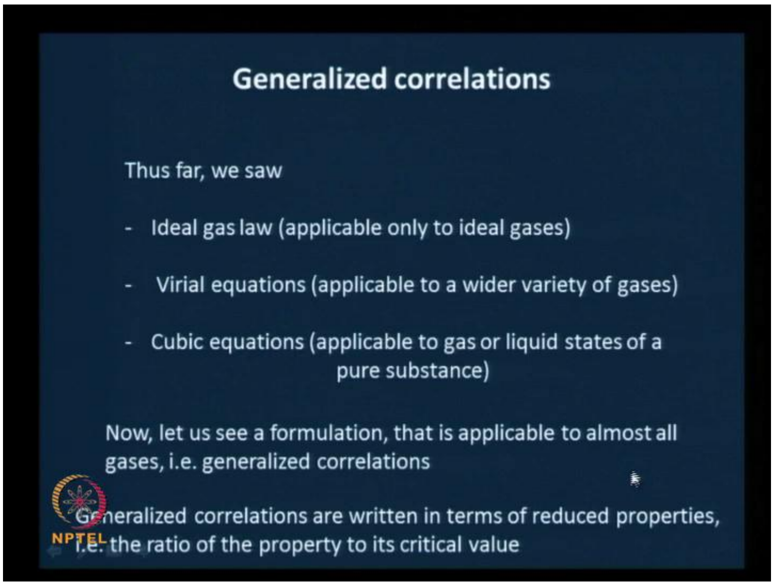

Generalized correlations

Thus far, we saw

- Ideal gas law (applicable only to ideal gases)
- Virial equations (applicable to a wider variety of gases)
- Cubic equations (applicable to gas or liquid states of a pure substance)

Now, let us see a formulation, that is applicable to almost all gases, i.e. generalized correlations

Generalized correlations are written in terms of reduced properties, i.e. the ratio of the property to its critical value

The generalized correlations are … something like this. We have ideal gas law, we have virial equations applicable to a wider variety of gases, typically, and cubic equations applicable to gas or liquid states of a pure substance, with more ease. We apply this too, but this is with more ease. And now, the generalized correlations are something, that are applicable to all gases in general and the generalized correlations are given in terms of reduced properties, which are nothing but the ratio of the actual property to its critical value.

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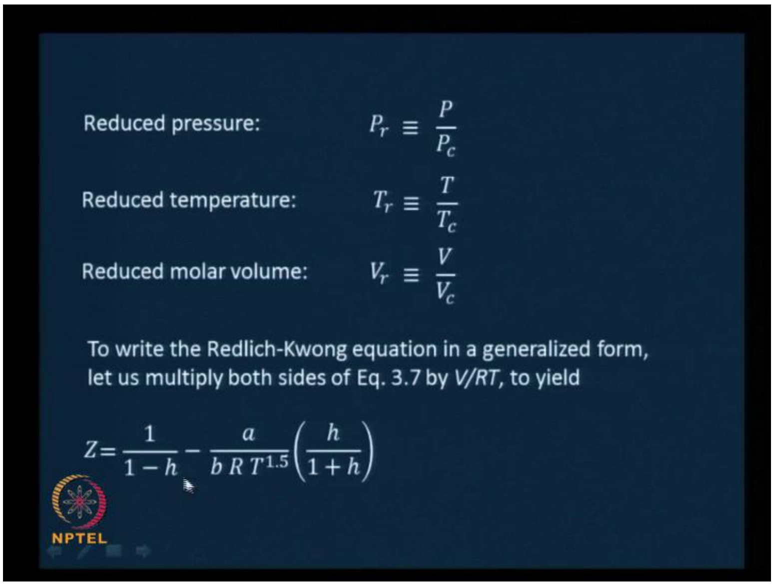

Reduced pressure: $P_r \equiv \frac{P}{P_c}$

Reduced temperature: $T_r \equiv \frac{T}{T_c}$

Reduced molar volume: $V_r \equiv \frac{V}{V_c}$

To write the Redlich-Kwong equation in a generalized form, let us multiply both sides of Eq. 3.7 by *V/RT*, to yield

$$Z = \frac{1}{1-h} - \frac{a}{b\,R\,T^{1.5}}\left(\frac{h}{1+h}\right)$$

For example, reduced pressure P r is P by P c; reduced temperature T r is T by T c and reduced molar volume is V by V c. This is the way to write the Redlich-Kwong equation in a generalized form. We went up about showing how to do this.

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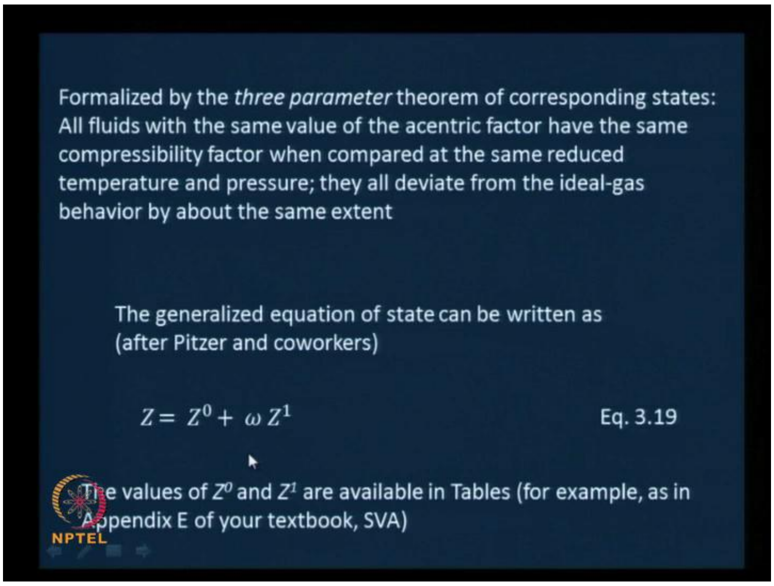

Formalized by the *three parameter* theorem of corresponding states: All fluids with the same value of the acentric factor have the same compressibility factor when compared at the same reduced temperature and pressure; they all deviate from the ideal-gas behavior by about the same extent

The generalized equation of state can be written as (after Pitzer and coworkers)

$$Z = Z^0 + \omega Z^1 \qquad \text{Eq. 3.19}$$

The values of Z^0 and Z^1 are available in Tables (for example, as in Appendix E of your textbook, SVA)

And then, we looked at the three parameter theorem, which essentially says, that three parameters are good enough. To use the three parameter theorem, we have this formulation Z, the compressibility factor, can be written as some Z naught plus omega times Z 1, the values of Z naught and Z 1 and omega, omega for a substance, and Z naught and Z 1 under various conditions are given as tables. Therefore, this becomes easier to use in the real context.

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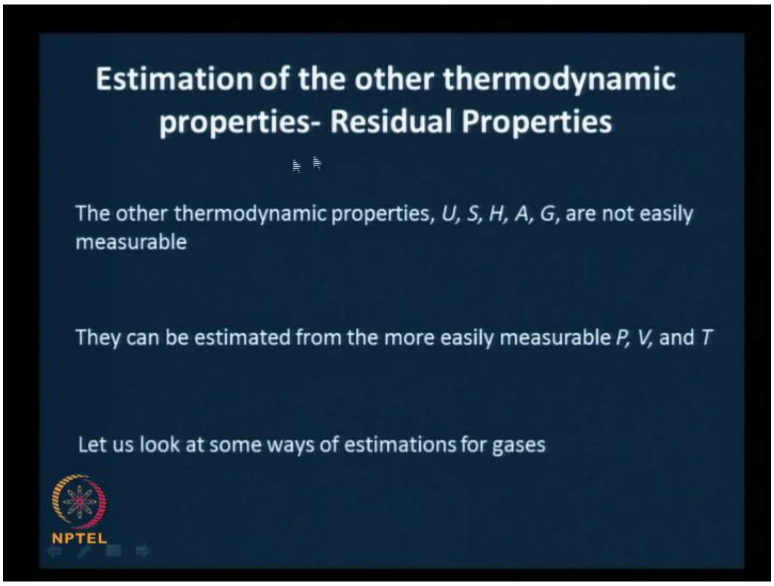

Estimation of the other thermodynamic properties- Residual Properties

The other thermodynamic properties, *U, S, H, A, G*, are not easily measurable

They can be estimated from the more easily measurable *P, V,* and *T*

Let us look at some ways of estimations for gases

We could use something called residual properties to estimate other thermodynamic properties that are not easily measurable.

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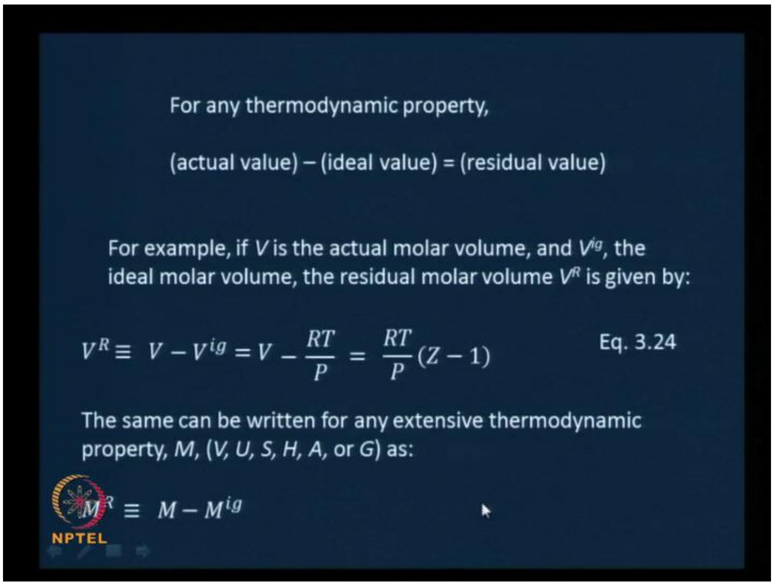

For any thermodynamic property,

(actual value) – (ideal value) = (residual value)

For example, if V is the actual molar volume, and V^{ig}, the ideal molar volume, the residual molar volume V^R is given by:

$$V^R \equiv V - V^{ig} = V - \frac{RT}{P} = \frac{RT}{P}(Z-1) \qquad \text{Eq. 3.24}$$

The same can be written for any extensive thermodynamic property, M, ($V, U, S, H, A,$ or G) as:

$$M^R \equiv M - M^{ig}$$

And the residual properties are nothing, but the difference between the actual value and the ideal value. V R, residual, equals V actual minus V ideal gas. You could write the residual property for any extensive property, U, S, H, A, G or V.

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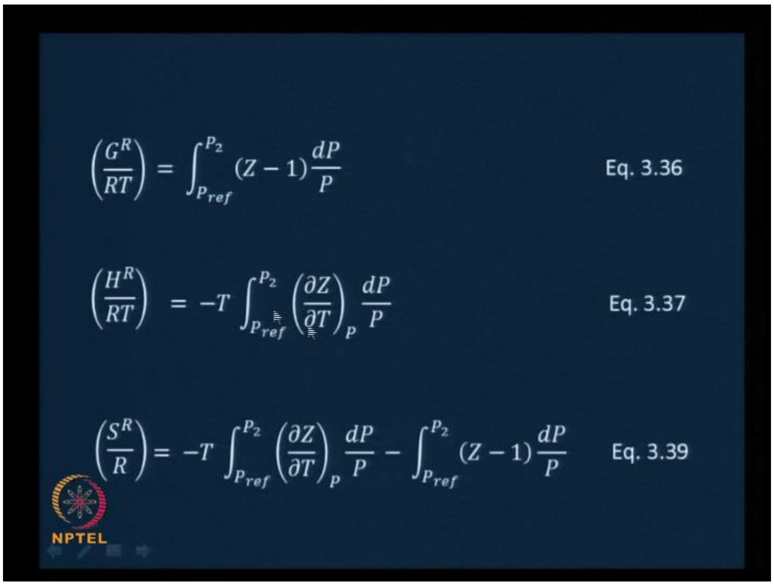

$$\left(\frac{G^R}{RT}\right) = \int_{P_{ref}}^{P_2} (Z-1)\frac{dP}{P} \qquad \text{Eq. 3.36}$$

$$\left(\frac{H^R}{RT}\right) = -T \int_{P_{ref}}^{P_2} \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} \qquad \text{Eq. 3.37}$$

$$\left(\frac{S^R}{R}\right) = -T \int_{P_{ref}}^{P_2} \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_{P_{ref}}^{P_2} (Z-1)\frac{dP}{P} \qquad \text{Eq. 3.39}$$

These are the expressions, that we derived after lengthy derivations. G R by R T is integral P reference to P 2 Z minus 1 d P by P; H R by R T equals minus T integral P reference to P 2 dou Z dou T at constant P dP by P and S R by R equals minus T integral P reference to P 2 dou Z dou T at constant P dP by P minus integral P reference to P 2 Z minus 1 dP by P. Therefore, you can use this to get at the reduced value.

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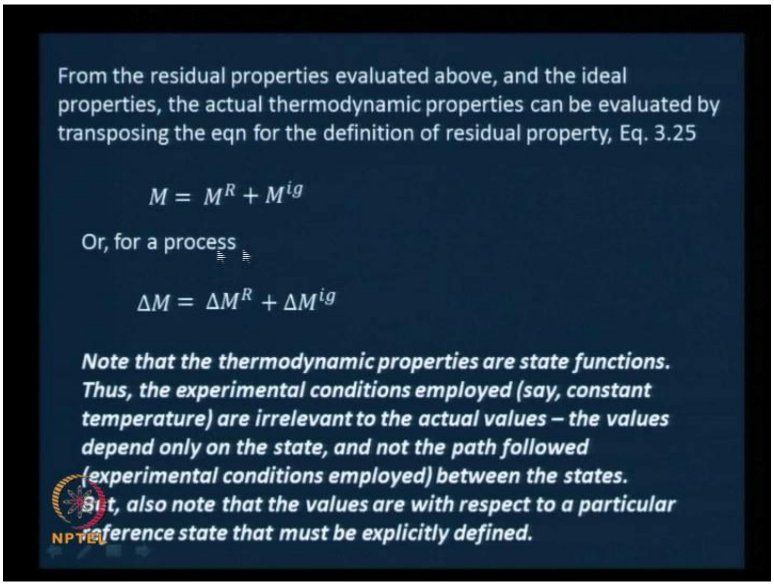

From the residual properties evaluated above, and the ideal properties, the actual thermodynamic properties can be evaluated by transposing the eqn for the definition of residual property, Eq. 3.25

$$M = M^R + M^{ig}$$

Or, for a process

$$\Delta M = \Delta M^R + \Delta M^{ig}$$

Note that the thermodynamic properties are state functions. Thus, the experimental conditions employed (say, constant temperature) are irrelevant to the actual values – the values depend only on the state, and not the path followed (experimental conditions employed) between the states. But, also note that the values are with respect to a particular reference state that must be explicitly defined.

If you know the ideal gas value, to get the actual value, all you need to do is add them both, just by definition. Or for a process, we could do the deltas too.

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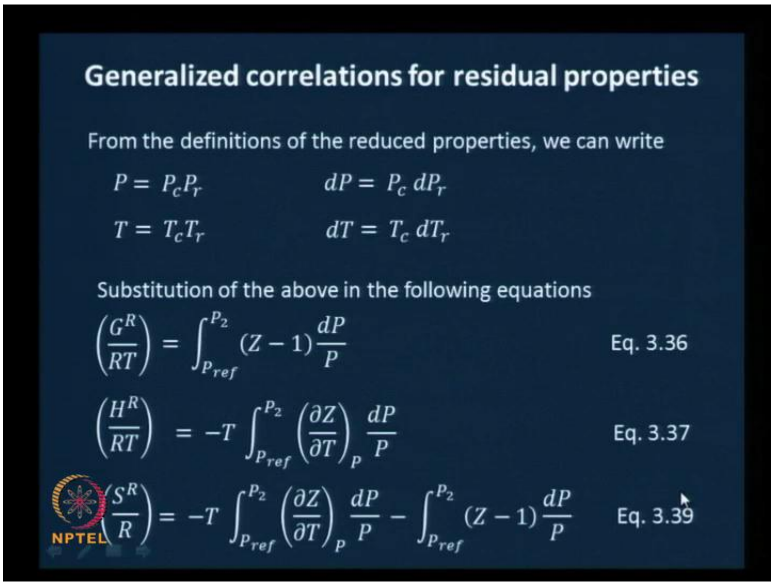

Generalized correlations for residual properties

From the definitions of the reduced properties, we can write

$P = P_c P_r$ $\quad$ $dP = P_c \, dP_r$

$T = T_c T_r$ $\quad$ $dT = T_c \, dT_r$

Substitution of the above in the following equations

$$\left(\frac{G^R}{RT}\right) = \int_{P_{ref}}^{P_2} (Z-1)\frac{dP}{P} \qquad \text{Eq. 3.36}$$

$$\left(\frac{H^R}{RT}\right) = -T\int_{P_{ref}}^{P_2} \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} \qquad \text{Eq. 3.37}$$

$$\left(\frac{S^R}{R}\right) = -T\int_{P_{ref}}^{P_2} \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_{P_{ref}}^{P_2} (Z-1)\frac{dP}{P} \qquad \text{Eq. 3.39}$$

Then you have a generalized correlation based on residual properties. … To do that, we recognize that P equals P c P r and therefore, dP equals P c times dP r. You can do the same thing for temperature.

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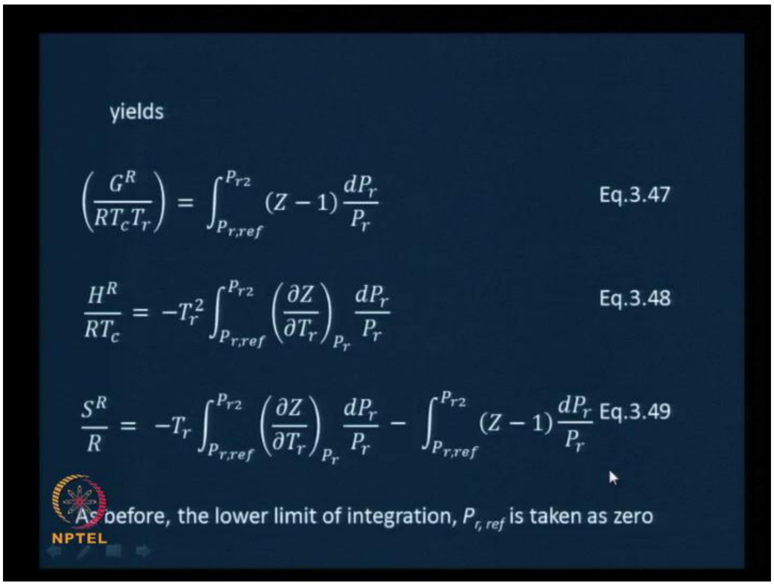

yields

$$\left(\frac{G^R}{RT_cT_r}\right) = \int_{P_{r,ref}}^{P_{r2}} (Z-1)\frac{dP_r}{P_r} \qquad \text{Eq.3.47}$$

$$\frac{H^R}{RT_c} = -T_r^2\int_{P_{r,ref}}^{P_{r2}} \left(\frac{\partial Z}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r} \qquad \text{Eq.3.48}$$

$$\frac{S^R}{R} = -T_r\int_{P_{r,ref}}^{P_{r2}} \left(\frac{\partial Z}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r} - \int_{P_{r,ref}}^{P_{r2}} (Z-1)\frac{dP_r}{P_r} \qquad \text{Eq.3.49}$$

A before, the lower limit of integration, $P_{r,ref}$ is taken as zero

… If you substitute these in the expressions that we had, the residual value expressions that we had derived in the previous slide, shown in the previous slide, you get the generalized correlations in terms of the residual values, which are the same form, but in terms of the residual properties.

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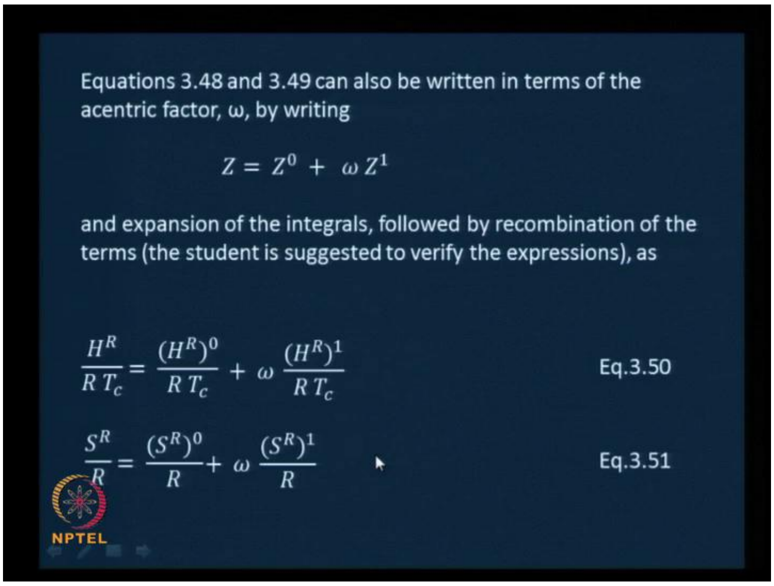

Equations 3.48 and 3.49 can also be written in terms of the acentric factor, ω, by writing

$$Z = Z^0 + \omega Z^1$$

and expansion of the integrals, followed by recombination of the terms (the student is suggested to verify the expressions), as

$$\frac{H^R}{R\,T_c} = \frac{(H^R)^0}{R\,T_c} + \omega\,\frac{(H^R)^1}{R\,T_c} \qquad \text{Eq.3.50}$$

$$\frac{S^R}{R} = \frac{(S^R)^0}{R} + \omega\,\frac{(S^R)^1}{R} \qquad \text{Eq.3.51}$$

…Yyou could use this same formulation to make it more useful in a practical context. Also, H R by R T c is H R naught by R T c plus omega times H R 1 by R T c. You have H R naught by R T c and H R 1 by R T c values tabulated. That is what make it easier to use, especially these tabulations are available in your textbook itself.

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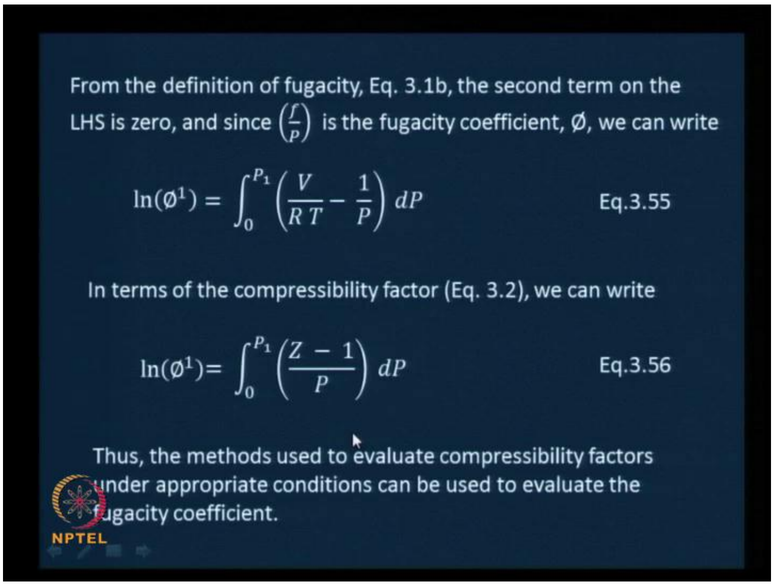

From the definition of fugacity, Eq. 3.1b, the second term on the LHS is zero, and since $\left(\frac{f}{P}\right)$ is the fugacity coefficient, Ø, we can write

$$\ln(\emptyset^1) = \int_0^{P_1}\left(\frac{V}{R\,T} - \frac{1}{P}\right) dP \qquad \text{Eq.3.55}$$

In terms of the compressibility factor (Eq. 3.2), we can write

$$\ln(\emptyset^1) = \int_0^{P_1}\left(\frac{Z-1}{P}\right) dP \qquad \text{Eq.3.56}$$

Thus, the methods used to evaluate compressibility factors under appropriate conditions can be used to evaluate the fugacity coefficient.

Then, we figured out how to get at the fugacity coefficient from the P, V, T data. This is the final expression, ln of phi 1 the fugacity coefficient at 1 is integral of 0 to P 1 V by R

T minus 1 by P dP. This we had derived. In terms of the compressibility factor, it is nothing but integral of 0 to P 1 Z minus 1 by P dP.

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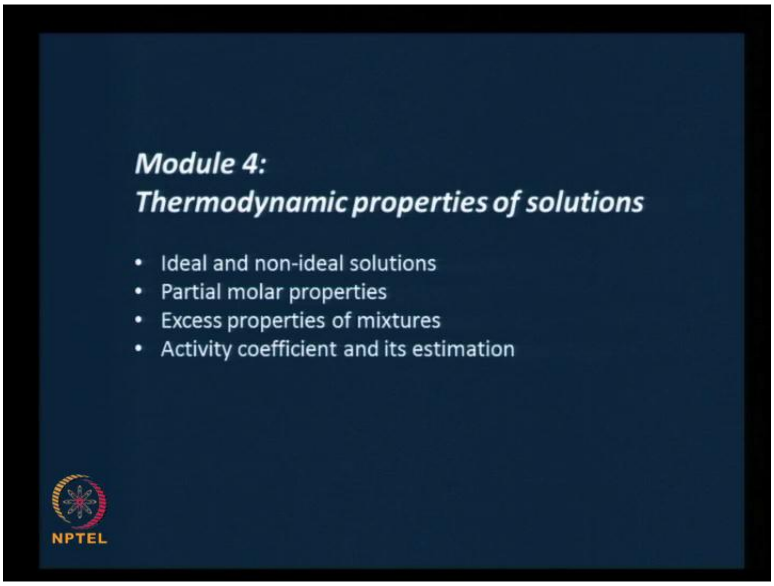

Module 4:
Thermodynamic properties of solutions

- Ideal and non-ideal solutions
- Partial molar properties
- Excess properties of mixtures
- Activity coefficient and its estimation

Then, we went to module 4, which was on thermodynamic properties of solutions. Earlier it was pure substance, now it is solutions, which is nothing but a mixture of pure substances. We looked at the conditions for an ideal and non-ideal solution in terms of chemical potential. Then, partial molar properties, excess properties of mixtures, activity coefficient and its estimation.

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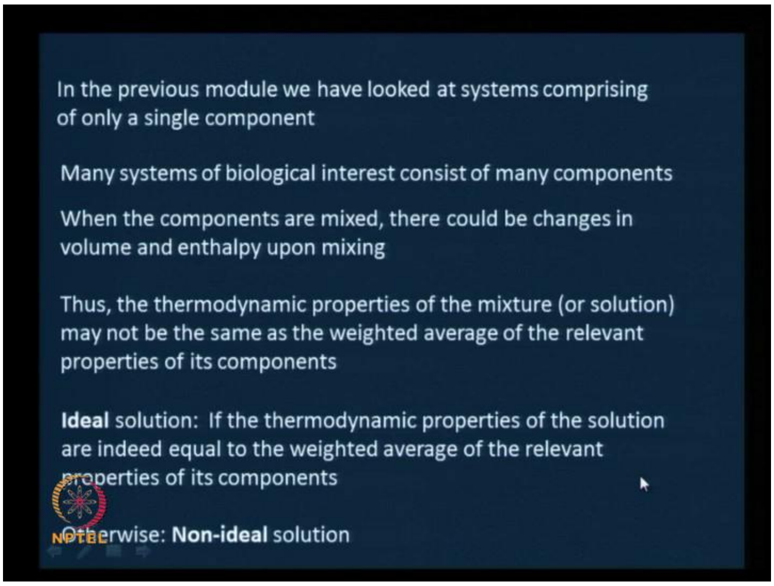

In the previous module we have looked at systems comprising of only a single component

Many systems of biological interest consist of many components

When the components are mixed, there could be changes in volume and enthalpy upon mixing

Thus, the thermodynamic properties of the mixture (or solution) may not be the same as the weighted average of the relevant properties of its components

Ideal solution: If the thermodynamic properties of the solution are indeed equal to the weighted average of the relevant properties of its components

Otherwise: **Non-ideal** solution

When pure substances are mixed together, there could be changes in volume and enthalpy upon mixing. So, that is what makes things either ideal or non-ideal. If there is a change, it becomes a regular solution or non-ideal solution. If there is no change, it becomes … an ideal solution.

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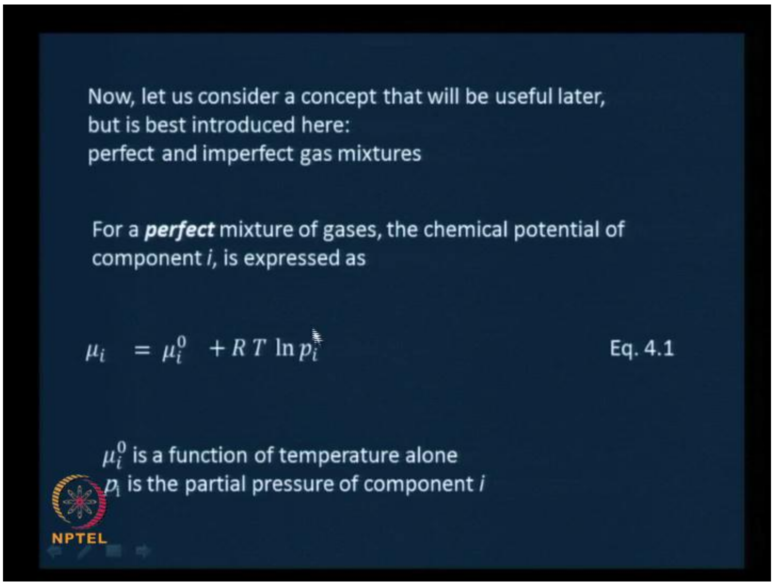

Now, let us consider a concept that will be useful later,
but is best introduced here:
perfect and imperfect gas mixtures

For a ***perfect*** mixture of gases, the chemical potential of component *i*, is expressed as

$$\mu_i = \mu_i^0 + R\,T\,\ln p_i \qquad \text{Eq. 4.1}$$

μ_i^0 is a function of temperature alone
p_i is the partial pressure of component *i*

Then, we introduced the concept of perfect mixture of gases. You know, this is, we said a concept and we have used this concept quite a few times to develop ideas. A perfect mixture of gases is something for which the chemical potential of each of its component can be represented as mu i equals mu i naught plus R T ln p i; p i is the partial pressure. …

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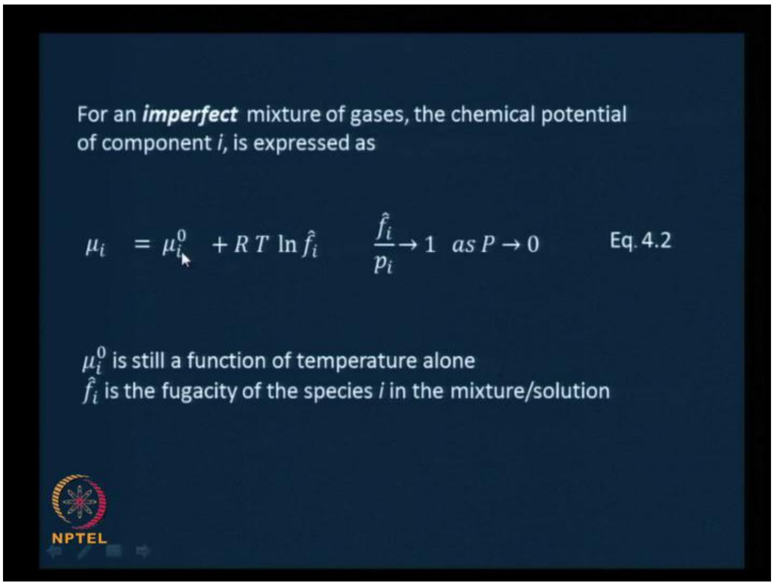

For an ***imperfect*** mixture of gases, the chemical potential of component *i*, is expressed as

$$\mu_i = \mu_i^0 + RT\ln\hat{f}_i \qquad \frac{\hat{f}_i}{p_i}\to 1 \quad as\ P\to 0 \qquad \text{Eq. 4.2}$$

μ_i^0 is still a function of temperature alone
$\hat{f}_i$ is the fugacity of the species *i* in the mixture/solution

Whereas, for an imperfect mixture of gases, the chemical potential of each component i is expressed as mu i equals mu i naught plus R T ln f i hat, which is the fugacity of that component in that mixture; and of course, for completeness, f i hat by p i tends to 1 as the total pressure tends to 0. mu i naught is a function of temperature alone.

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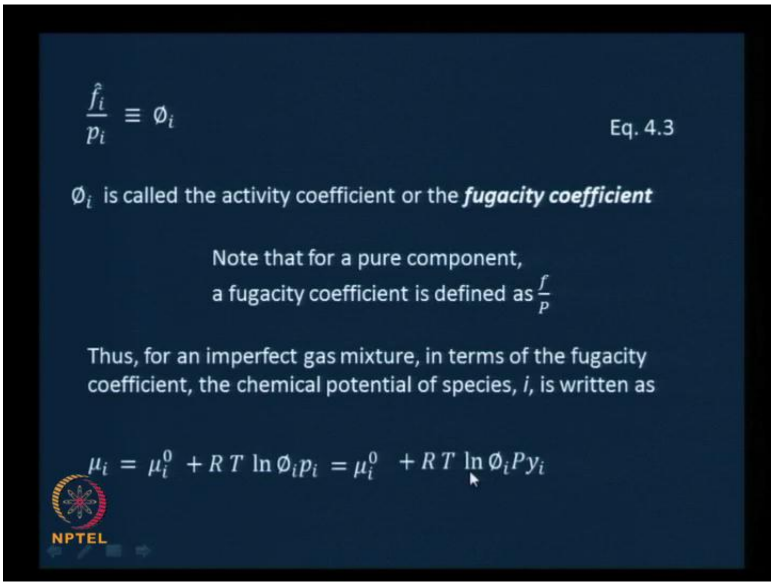

$$\frac{\hat{f}_i}{p_i} \equiv \emptyset_i \qquad \text{Eq. 4.3}$$

$\emptyset_i$ is called the activity coefficient or the ***fugacity coefficient***

Note that for a pure component,
a fugacity coefficient is defined as $\frac{f}{P}$

Thus, for an imperfect gas mixture, in terms of the fugacity coefficient, the chemical potential of species, *i*, is written as

$$\mu_i = \mu_i^0 + RT\ln\emptyset_i p_i = \mu_i^0 + RT\ln\emptyset_i P y_i$$

And f i hat by the partial pressure of i is defined as the fugacity coefficient of i. For an imperfect gas mixture, based on these definitions, you could write mu i equals mu i naught plus R T phi i p i, which …, if you expand p i in terms of P and y i, you get mu i naught plus R T ln phi i p i P y i.

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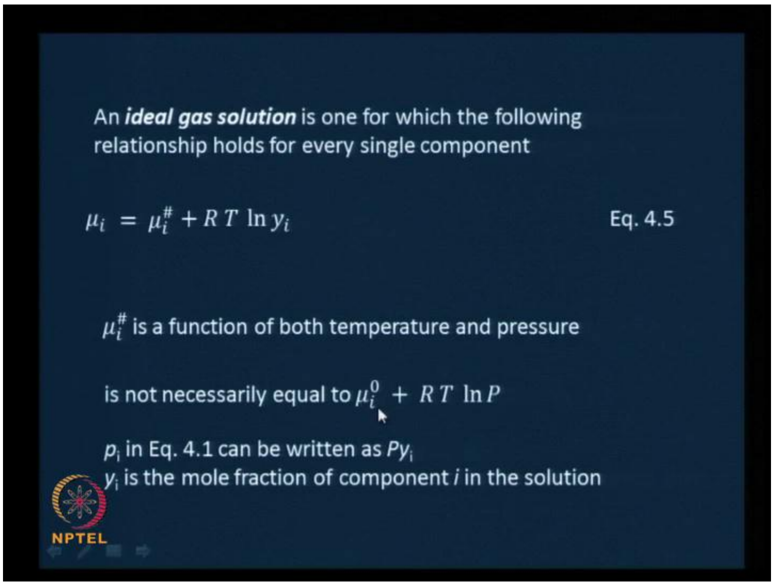

An ***ideal gas solution*** is one for which the following relationship holds for every single component

$\mu_i = \mu_i^{\#} + R\,T\,\ln y_i$ Eq. 4.5

$\mu_i^{\#}$ is a function of both temperature and pressure

is not necessarily equal to $\mu_i^0 + R\,T\,\ln P$

p_i in Eq. 4.1 can be written as Py_i

y_i is the mole fraction of component *i* in the solution

Now, an ideal solution is one for which each component chemical potential can be written as mu i equals mu i hash plus R T ln y i, where y i is the mole fraction of i and mu i hash is both a function of temperature and pressure, the standard value. But in this case, … unlike the cases that we have seen earlier in an ideal gas and perfect mixture and so on, mu i hash is a function of temperature and pressure. Also note, that mu i hash need not necessarily be equal to mu i naught plus R T ln P.

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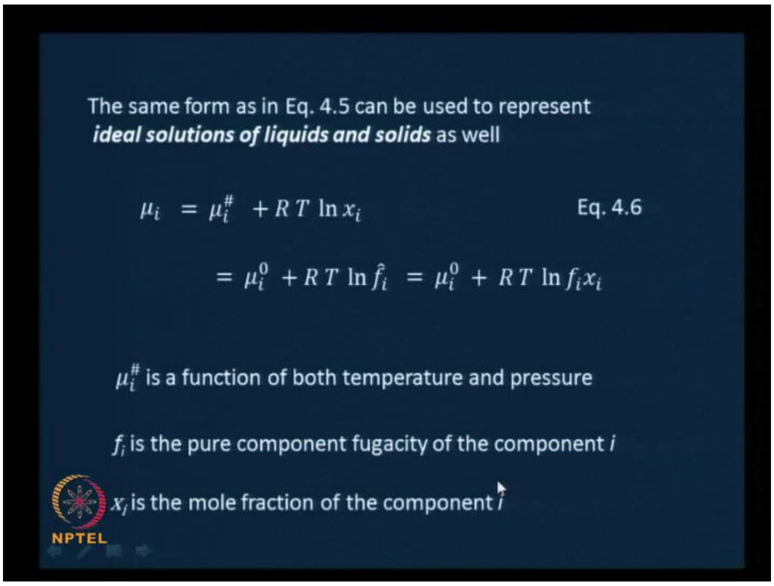

The same form as in Eq. 4.5 can be used to represent ***ideal solutions of liquids and solids*** as well

$$\mu_i = \mu_i^{\#} + RT\ln x_i \qquad \text{Eq. 4.6}$$

$$= \mu_i^0 + RT\ln \hat{f}_i = \mu_i^0 + RT\ln f_i x_i$$

$\mu_i^{\#}$ is a function of both temperature and pressure

f_i is the pure component fugacity of the component *i*

x_i is the mole fraction of the component *i*

For ideal solutions of liquids and solids, you could write, mu i equals mu i hash plus R T ln x i, where x i is the mole fraction of the component in a liquid or a solid mixture. In terms of fugacities, it is mu i naught plus R T f i hat. That is, mu i naught plus R T ln f i x i.

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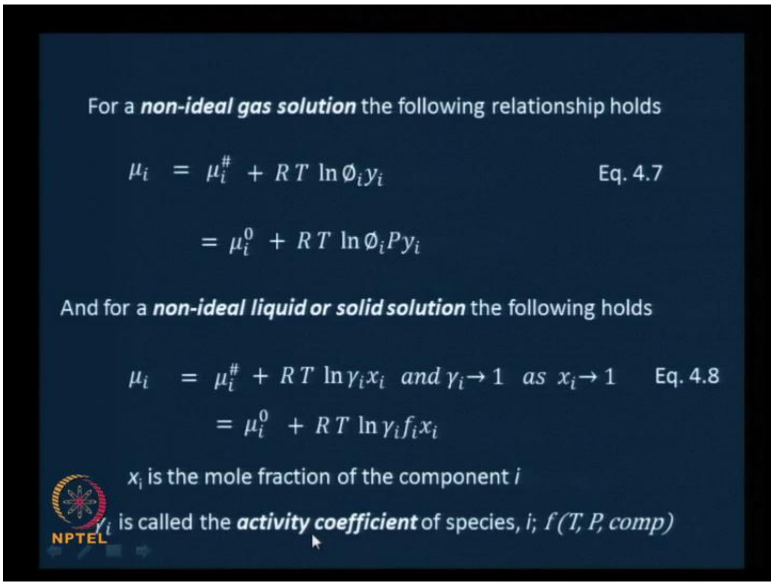

For a ***non-ideal gas solution*** the following relationship holds

$$\mu_i = \mu_i^{\#} + RT\ln \phi_i y_i \qquad \text{Eq. 4.7}$$

$$= \mu_i^0 + RT\ln \phi_i P y_i$$

And for a ***non-ideal liquid or solid solution*** the following holds

$$\mu_i = \mu_i^{\#} + RT\ln \gamma_i x_i \quad \text{and } \gamma_i \rightarrow 1 \text{ as } x_i \rightarrow 1 \qquad \text{Eq. 4.8}$$

$$= \mu_i^0 + RT\ln \gamma_i f_i x_i$$

x_i is the mole fraction of the component *i*

γ_i is called the ***activity coefficient*** of species, *i*; $f(T, P, comp)$

For a non-ideal gas solution, we can write, mu i equals mu i hash plus R T ln phi i y i, which is mu i naught plus R T ln phi i P y i.Ffor a non-ideal liquid or a solid solution, you have a gamma coming in; mu i equals mu i hash plus R T ln gamma i x i and gamma i tends to 1 as x i tends to 1, which is, in terms of the other variables, mu i naught plus R T ln gamma i f i x i. And gamma i, the activity coefficient, is a function of temperature, pressure and composition.

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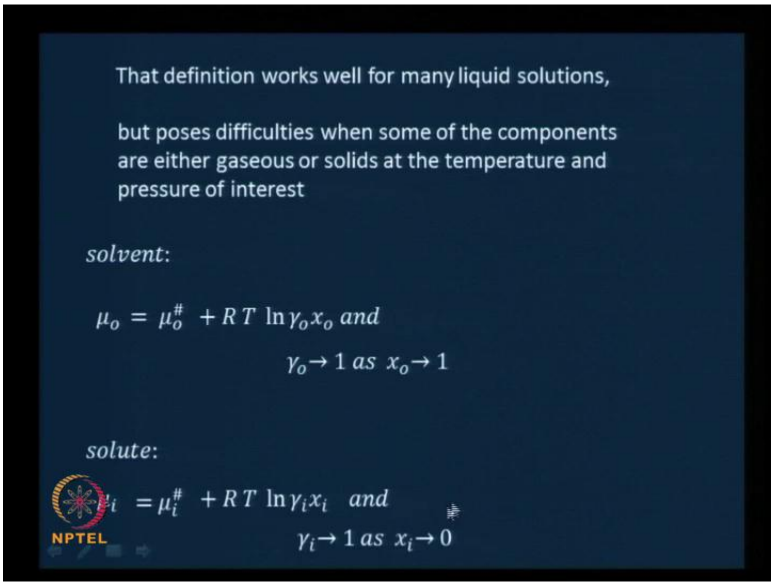

That definition works well for many liquid solutions,

but poses difficulties when some of the components are either gaseous or solids at the temperature and pressure of interest

solvent:

$$\mu_o = \mu_o^{\#} + RT \ln \gamma_o x_o \text{ and}$$

$$\gamma_o \to 1 \text{ as } x_o \to 1$$

solute:

$$\mu_i = \mu_i^{\#} + RT \ln \gamma_i x_i \quad \text{and}$$

$$\gamma_i \to 1 \text{ as } x_i \to 0$$

This works well for many liquid solutions, except if the component is of different phases at different mole fractions. For example, at a low mole fraction it could be a liquid and the solution at a high mole fraction or pure substances, actually a solid, maybe, glucose, or it could be a gas as in oxygen. If that is the case, then we need a special formulation and that formulation was as follows. mu naught equals mu naught hash plus R T ln gamma naught x naught, and gamma naught tends to 1 as x naught tends to 1 for the solvent and for the solute mu i equals mu i hash plus R T ln gamma i x i, and gamma i tends to 1 as x i tends to 0.

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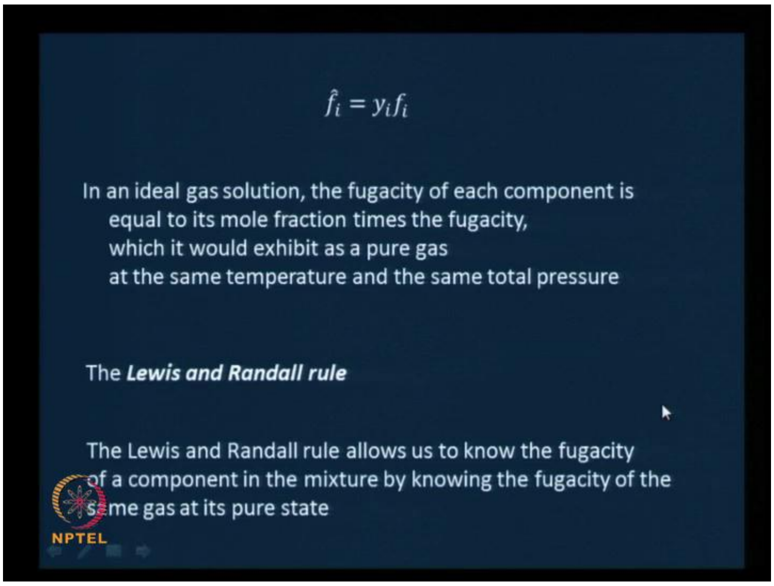

$$\hat{f}_i = y_i f_i$$

In an ideal gas solution, the fugacity of each component is equal to its mole fraction times the fugacity, which it would exhibit as a pure gas at the same temperature and the same total pressure

The ***Lewis and Randall rule***

The Lewis and Randall rule allows us to know the fugacity of a component in the mixture by knowing the fugacity of the same gas at its pure state

This was the Lewis and Randall rule. … This was powerful because the fugacity of the component in solution, f i hat, is nothing but the product of the mole fraction and the fugacity of the pure component, and this can happen only in ideal solutions. This is the Lewis and Randall rule.

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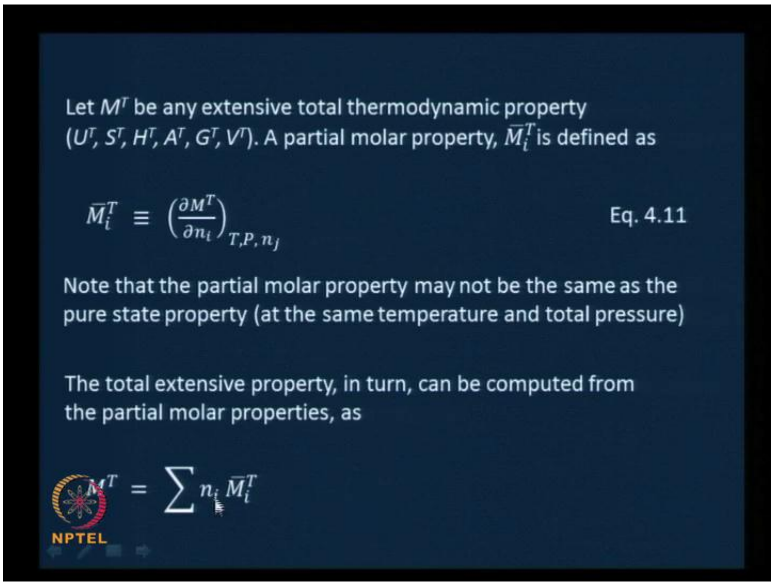

Let M^T be any extensive total thermodynamic property (U^T, S^T, H^T, A^T, G^T, V^T). A partial molar property, $\bar{M}_i^T$ is defined as

$$\bar{M}_i^T \equiv \left(\frac{\partial M^T}{\partial n_i}\right)_{T,P,n_j} \qquad \text{Eq. 4.11}$$

Note that the partial molar property may not be the same as the pure state property (at the same temperature and total pressure)

The total extensive property, in turn, can be computed from the partial molar properties, as

$$M^T = \sum n_i \bar{M}_i^T$$

Since solutions are not ideal, to represent appropriate properties, we need partial molar properties, which are defined as dou M T dou n i at constant T, P and n j. We could define partial molar properties for any of these, and our representation was M i T hash.

… This is the reason why we bring about partial molar properties. The total property is nothing but the weighted sum of the partial molar properties, weighted with its number of moles.

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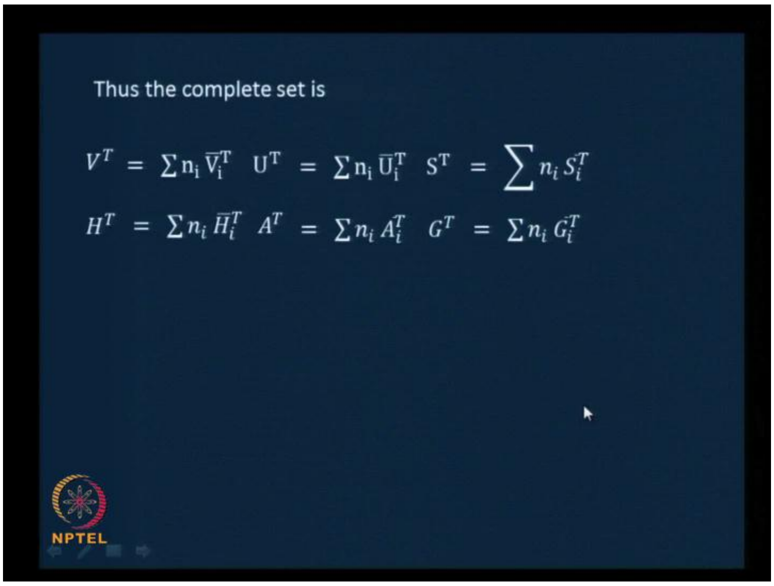

Thus the complete set is

$$V^T = \sum n_i \bar{V}_i^T \quad U^T = \sum n_i \bar{U}_i^T \quad S^T = \sum n_i S_i^T$$

$$H^T = \sum n_i \bar{H}_i^T \quad A^T = \sum n_i A_i^T \quad G^T = \sum n_i G_i^T$$

We had the complete set of partial molar properties here - total volume in terms of the partial molar volume; total internal energy in terms of the partial molar internal energy and so on … till total Gibbs free energy, in terms of the partial molar Gibbs free energy.

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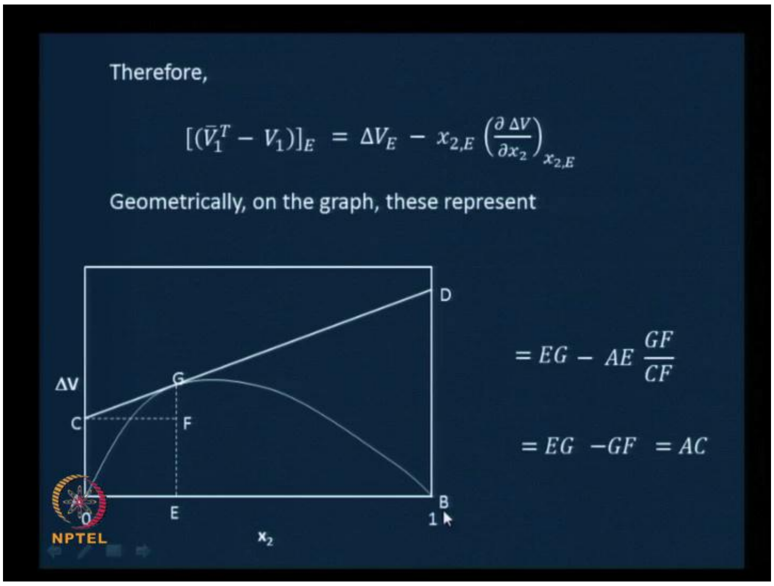

Therefore,

$$[(\bar{V}_1^T - V_1)]_E = \Delta V_E - x_{2,E}\left(\frac{\partial \Delta V}{\partial x_2}\right)_{x_{2,E}}$$

Geometrically, on the graph, these represent

$$= EG - AE\,\frac{GF}{CF}$$

$$= EG - GF = AC$$

And then, we also saw how to estimate partial molar properties from experimental data. We saw that from mixing experiments, which can be represented as change in volume with a certain mole fraction, you get a curve like this. If you are interested in the partial molar volume at E, then you take this point on the curve at E, draw a tangent to the point there, the slope with the intercept here, CA, would actually give us the difference between V 1 T hash, the partial molar property and … the molar property at 1. Since you know the molar property at 1, you could find the partial molar property. Similarly, you could do it for the other, V 2 T hash for a binary system, that is, in terms of this other intercept D B.

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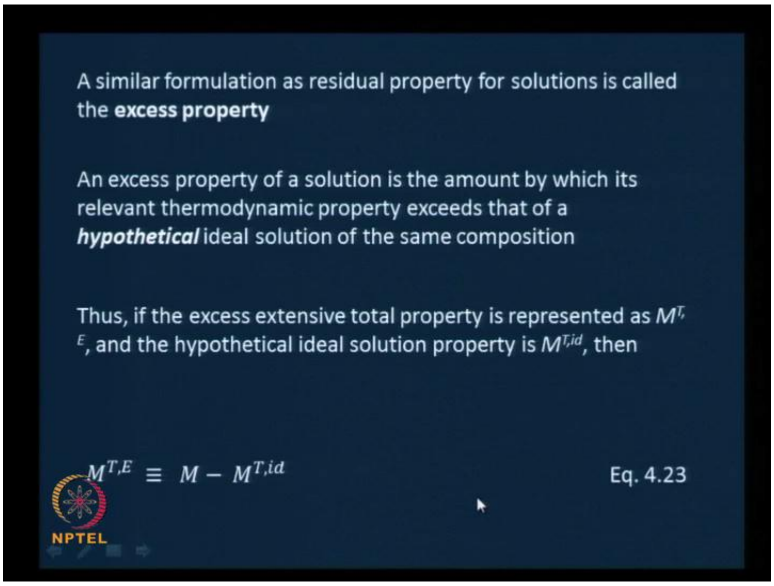

A similar formulation as residual property for solutions is called the **excess property**

An excess property of a solution is the amount by which its relevant thermodynamic property exceeds that of a ***hypothetical*** ideal solution of the same composition

Thus, if the excess extensive total property is represented as $M^{T,E}$, and the hypothetical ideal solution property is $M^{T,id}$, then

$$M^{T,E} \equiv M - M^{T,id} \quad \text{Eq. 4.23}$$

Then, we looked at excess properties and also looked at activity coefficients. Excess properties are nothing but the difference between the actual and the ideal properties. The same way as residual properties were for pure substances, we have excess properties for solutions.

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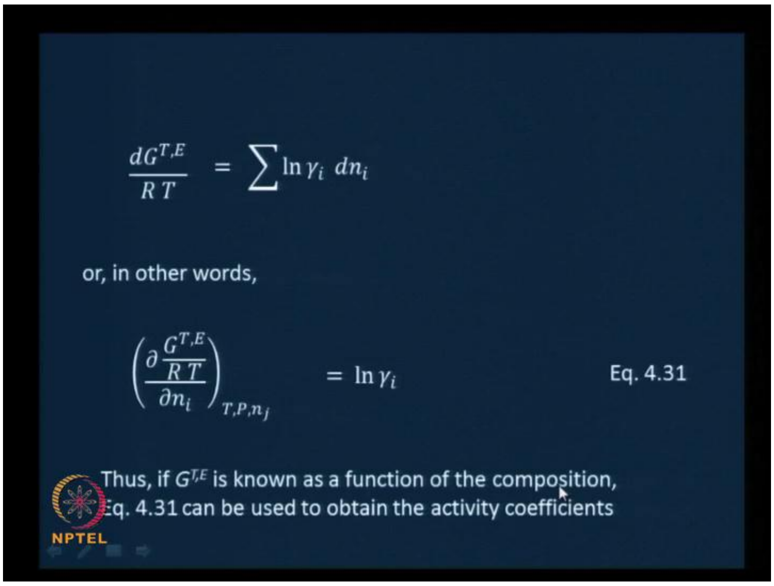

$$\frac{dG^{T,E}}{RT} = \sum \ln \gamma_i \, dn_i$$

or, in other words,

$$\left(\frac{\partial \frac{G^{T,E}}{RT}}{\partial n_i} \right)_{T,P,n_j} = \ln \gamma_i \qquad \text{Eq. 4.31}$$

Thus, if $G^{T,E}$ is known as a function of the composition, Eq. 4.31 can be used to obtain the activity coefficients

We got some useful relationships, dou dou n i of G T E by R T at constant T, P, n j was ln gamma i.

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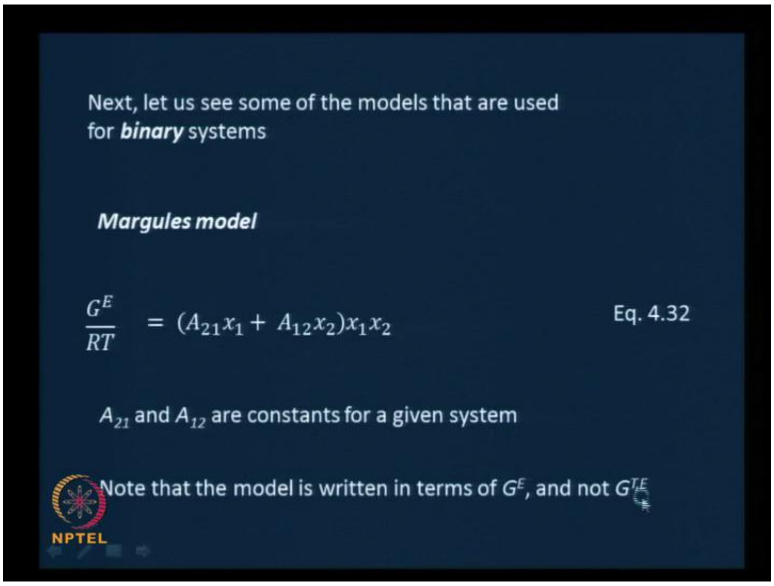

Next, let us see some of the models that are used for ***binary*** systems

Margules model

$$\frac{G^E}{RT} = (A_{21}x_1 + A_{12}x_2)x_1x_2 \qquad \text{Eq. 4.32}$$

A_{21} and A_{12} are constants for a given system

Note that the model is written in terms of G^E, and not $G^{T,E}$

We saw various models, the Margules model, the Redlich-Kister model, van Laar model, and the Wilson model for activity coefficients in a binary system alone.

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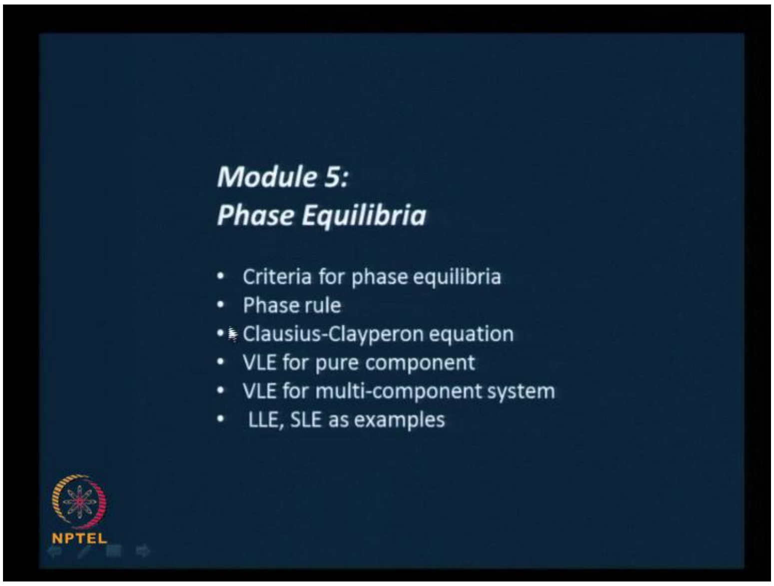

Module 5:
Phase Equilibria

- Criteria for phase equilibria
- Phase rule
- Clausius-Clayperon equation
- VLE for pure component
- VLE for multi-component system
- LLE, SLE as examples

Then, we looked at module 5, which was on phase equilibrium. We looked at the criteria. If there is one take home message, that is the criteria for phase equilibria, from this course. Then, we looked at phase rule, Clausius-Clapeyron equation and the various equilibria, VLE, LLE, SLE, standing for vapour-liquid equilibrium, liquid-liquid equilibrium and solid-liquid equilibrium. In fact, we saw liquid-liquid equilibrium and solid-liquid equilibrium as examples of application of the general criteria for phase equilibrium.

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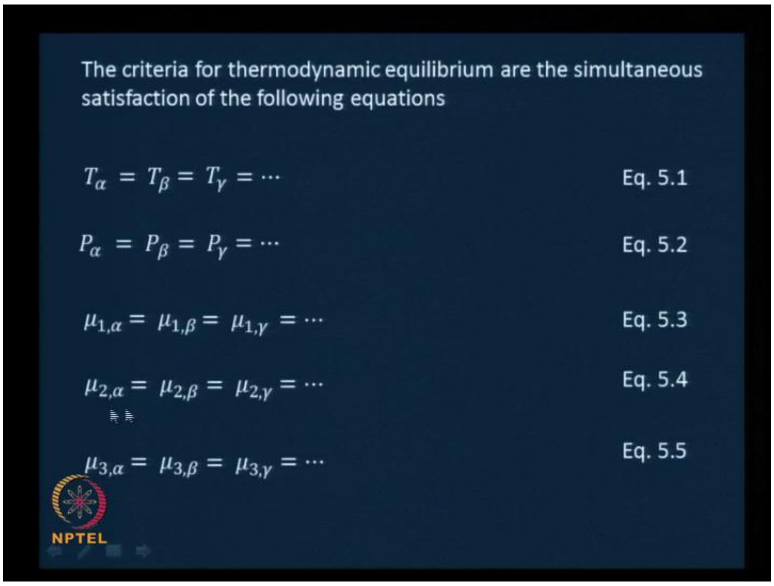

The criteria for thermodynamic equilibrium are the simultaneous satisfaction of the following equations

$$T_\alpha = T_\beta = T_\gamma = \cdots \qquad \text{Eq. 5.1}$$

$$P_\alpha = P_\beta = P_\gamma = \cdots \qquad \text{Eq. 5.2}$$

$$\mu_{1,\alpha} = \mu_{1,\beta} = \mu_{1,\gamma} = \cdots \qquad \text{Eq. 5.3}$$

$$\mu_{2,\alpha} = \mu_{2,\beta} = \mu_{2,\gamma} = \cdots \qquad \text{Eq. 5.4}$$

$$\mu_{3,\alpha} = \mu_{3,\beta} = \mu_{3,\gamma} = \cdots \qquad \text{Eq. 5.5}$$

This is the … one take home message, if you want to remember many years after this course. … At equilibrium, these conditions need to be satisfied, or at thermodynamic equilibrium you need satisfaction of thermal equilibrium, mechanical equilibrium and chemical equilibrium as given from equations 5.3 and so on.

This says that the temperature of the various phases in equilibrium must be equal for thermal equilibrium; the pressures of the various phases in equilibrium must be equal for mechanical equilibrium; and the chemical potential of each of the species in the various phases must be equal. mu 1 alpha equals mu 1 beta equals mu 1 gamma; mu 2 alpha equals mu 2 beta equals mu 2 gamma and so on.

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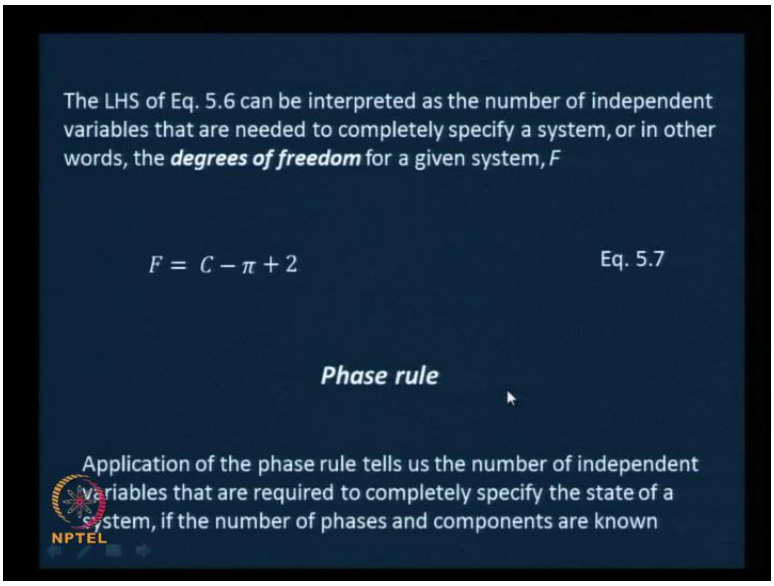

The LHS of Eq. 5.6 can be interpreted as the number of independent variables that are needed to completely specify a system, or in other words, the ***degrees of freedom*** for a given system, F

$$F = C - \pi + 2 \qquad \text{Eq. 5.7}$$

Phase rule

Application of the phase rule tells us the number of independent variables that are required to completely specify the state of a system, if the number of phases and components are known

The degrees of freedom, the number of variables required to specify the state of the system can be obtained from the phase rule, F equals C minus pi plus 2.

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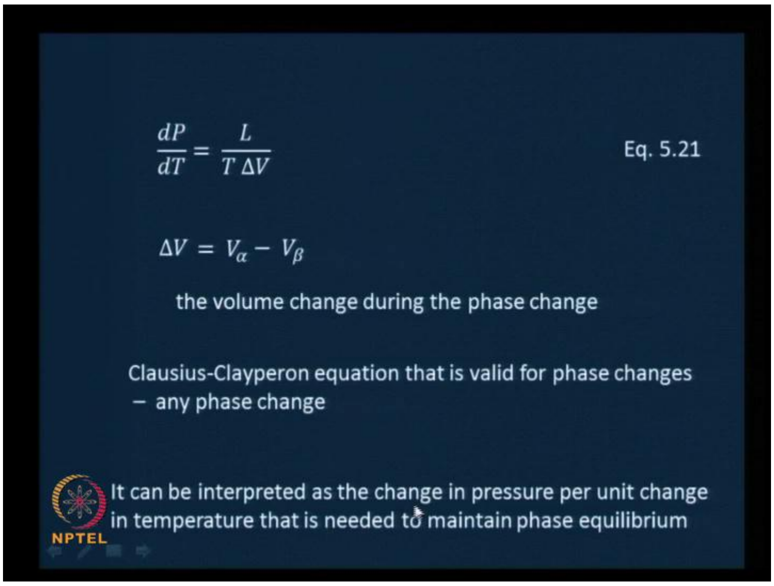

$$\frac{dP}{dT} = \frac{L}{T\,\Delta V} \qquad \text{Eq. 5.21}$$

$$\Delta V = V_\alpha - V_\beta$$

the volume change during the phase change

Clausius-Clayperon equation that is valid for phase changes
– any phase change

It can be interpreted as the change in pressure per unit change in temperature that is needed to maintain phase equilibrium

And this was our Clausius-Clapeyron equation, which is valid for phase changes, dP dT equals L, the latent heat for the phase change by the temperature at which the phase change is occurring by the change in the molar volume of the two phases. It is valid for any phase change, and it can be interpreted as the change in pressure per unit change in temperature that is needed to maintain phase equilibrium.

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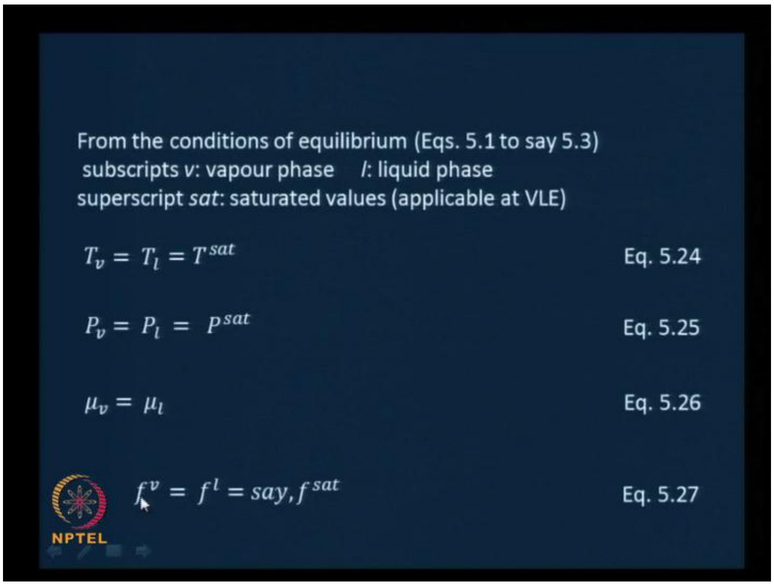

From the conditions of equilibrium (Eqs. 5.1 to say 5.3)
subscripts *v*: vapour phase *l*: liquid phase
superscript *sat*: saturated values (applicable at VLE)

$$T_v = T_l = T^{sat} \qquad \text{Eq. 5.24}$$

$$P_v = P_l = P^{sat} \qquad \text{Eq. 5.25}$$

$$\mu_v = \mu_l \qquad \text{Eq. 5.26}$$

$$f^v = f^l = say, f^{sat} \qquad \text{Eq. 5.27}$$

Then, we saw conditions for vapour-liquid equilibrium from the basic conditions for equilibrium. … For a single component system, it was f, the fugacity of the component in the vapour phase must equal, this is for a pure component, therefore the fugacity of the vapour phase must equal the fugacity of the liquid phase and say, that is equal to f sat.

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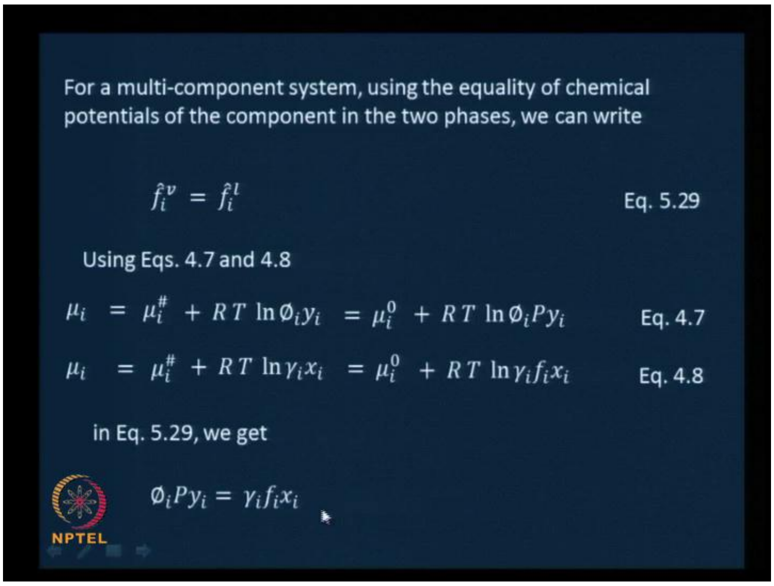

For a multi-component system, using the equality of chemical potentials of the component in the two phases, we can write

$$\hat{f}_i^v = \hat{f}_i^l \qquad \text{Eq. 5.29}$$

Using Eqs. 4.7 and 4.8

$$\mu_i = \mu_i^{\#} + RT \ln \emptyset_i y_i = \mu_i^0 + RT \ln \emptyset_i P y_i \qquad \text{Eq. 4.7}$$

$$\mu_i = \mu_i^{\#} + RT \ln \gamma_i x_i = \mu_i^0 + RT \ln \gamma_i f_i x_i \qquad \text{Eq. 4.8}$$

in Eq. 5.29, we get

$$\emptyset_i P y_i = \gamma_i f_i x_i$$

And in a multi-component system we saw, that the fugacity of the component in the vapour phase, f i V hat, … must equal the fugacity of the component i in the liquid phase. And in terms of the expansions, we could get a useful relationship, that phi i P y i equals gamma i f i x i.

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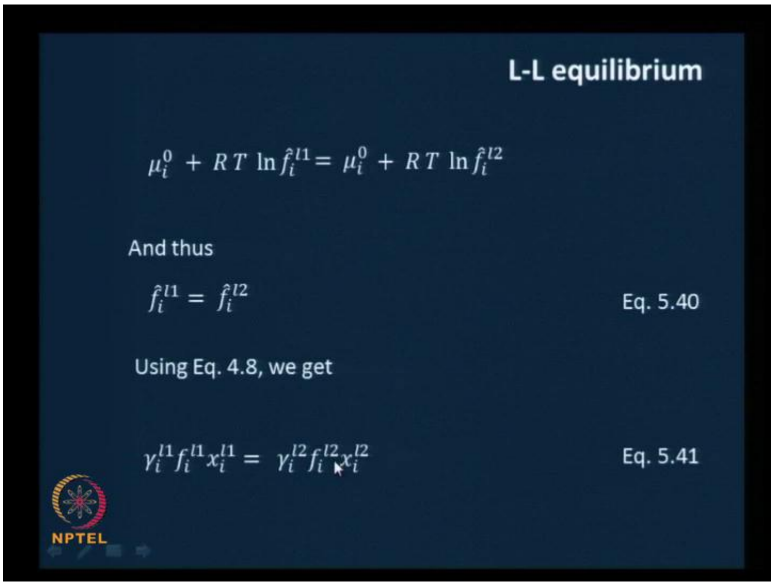

L-L equilibrium

$$\mu_i^0 + RT \ln \hat{f}_i^{l1} = \mu_i^0 + RT \ln \hat{f}_i^{l2}$$

And thus

$$\hat{f}_i^{l1} = \hat{f}_i^{l2} \qquad \text{Eq. 5.40}$$

Using Eq. 4.8, we get

$$\gamma_i^{l1} f_i^{l1} x_i^{l1} = \gamma_i^{l2} f_i^{l2} x_i^{l2} \qquad \text{Eq. 5.41}$$

For liquid-liquid equilibrium, such a relationship is as follows, gamma i in the l1 phase f i l 1 x i l 1 must equal gamma i, the same i, in the l2 phase f i l 2 and x i l 2.

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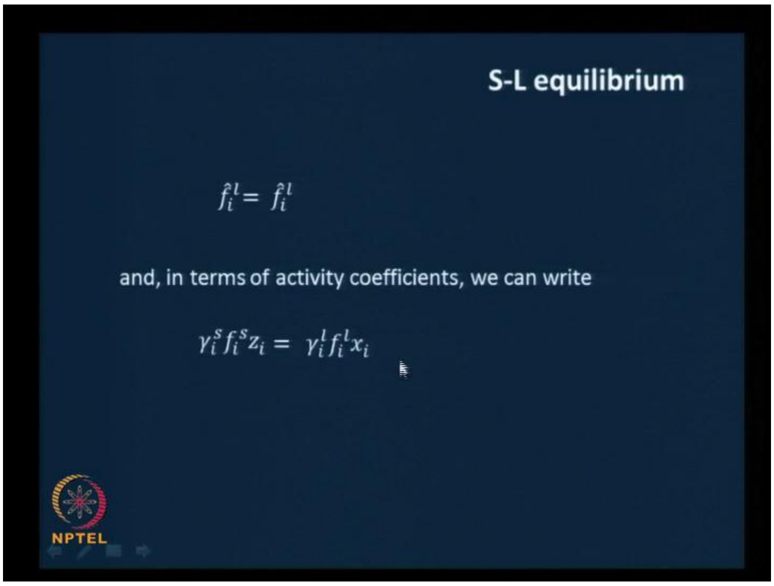

S-L equilibrium

$$\hat{f}_i^l = \hat{f}_i^l$$

and, in terms of activity coefficients, we can write

$$\gamma_i^s f_i^s z_i = \gamma_i^l f_i^l x_i$$

Similarly, in the solid-liquid equilibrium, again from the basic condition, that the fugacities must be equal, we get gamma i of the solid phase, f i solid, z i, the mole fraction in the solid phase, must equal gamma i in the liquid phase, f i in the liquid phase and the mole fraction in the liquid phase.

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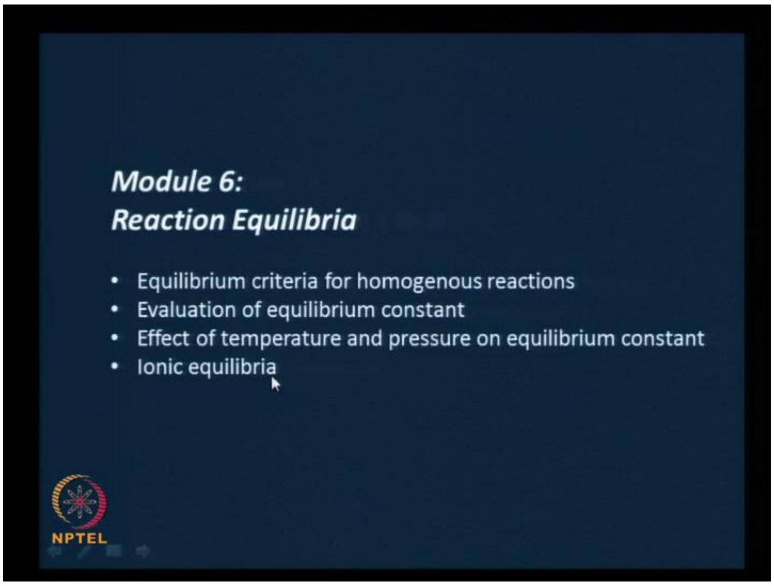

Module 6:
Reaction Equilibria

- Equilibrium criteria for homogenous reactions
- Evaluation of equilibrium constant
- Effect of temperature and pressure on equilibrium constant
- Ionic equilibria

Then, we looked at the conditions for reaction equilibria. This, follows from the phase equilibria, so this could also be a take home message: summation of nu i mu i equals 0. Then, we looked at ways to evaluate the equilibrium constant, effect of pressure and temperature on the equilibrium constant, and something to do with ionic equilibria, the formulation for that, at least, in the last class.

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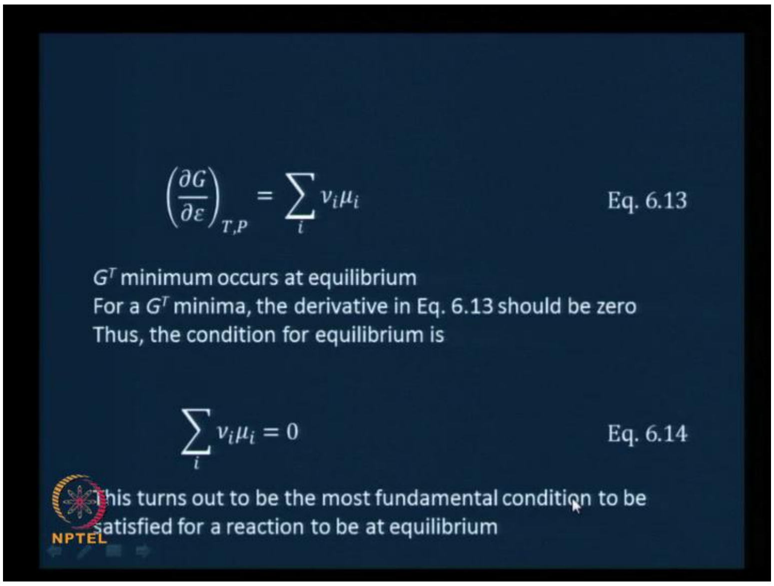

$$\left(\frac{\partial G}{\partial \varepsilon}\right)_{T,P} = \sum_i \nu_i \mu_i \qquad \text{Eq. 6.13}$$

G^T minimum occurs at equilibrium
For a G^T minima, the derivative in Eq. 6.13 should be zero
Thus, the condition for equilibrium is

$$\sum_i \nu_i \mu_i = 0 \qquad \text{Eq. 6.14}$$

This turns out to be the most fundamental condition to be satisfied for a reaction to be at equilibrium

So, this is the condition for equilibrium: If you take the free energy, the Gibbs' free energy as a function of the reaction coordinate at the condition of equilibrium, the slope of that curve must be 0. Therefore, nu i mu i sum over all i that must be 0. This is the basic condition for reaction equilibrium.

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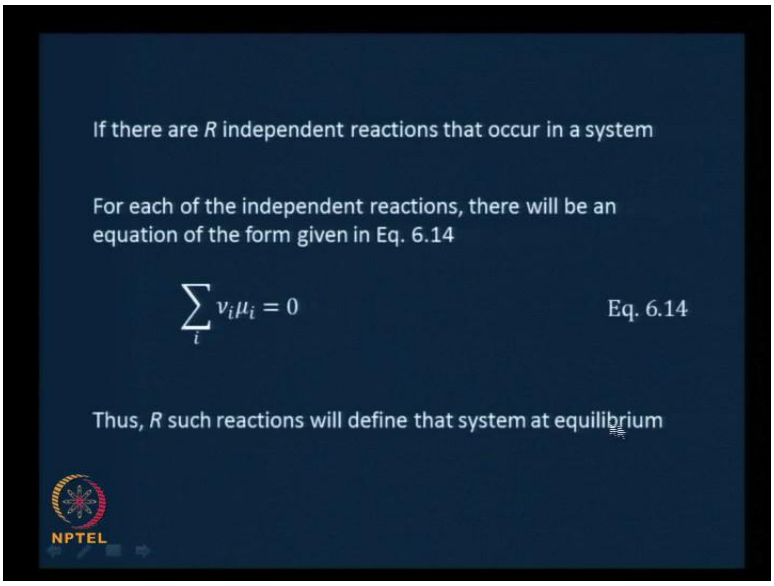

If there are R independent reactions that occur in a system

For each of the independent reactions, there will be an equation of the form given in Eq. 6.14

$$\sum_i \nu_i \mu_i = 0 \qquad \text{Eq. 6.14}$$

Thus, R such reactions will define that system at equilibrium

And if there are R reactions, independent reactions that take place in a system, for each of those R reactions, you could write one such equation. Therefore, R such equations will define the equilibrium of that system.

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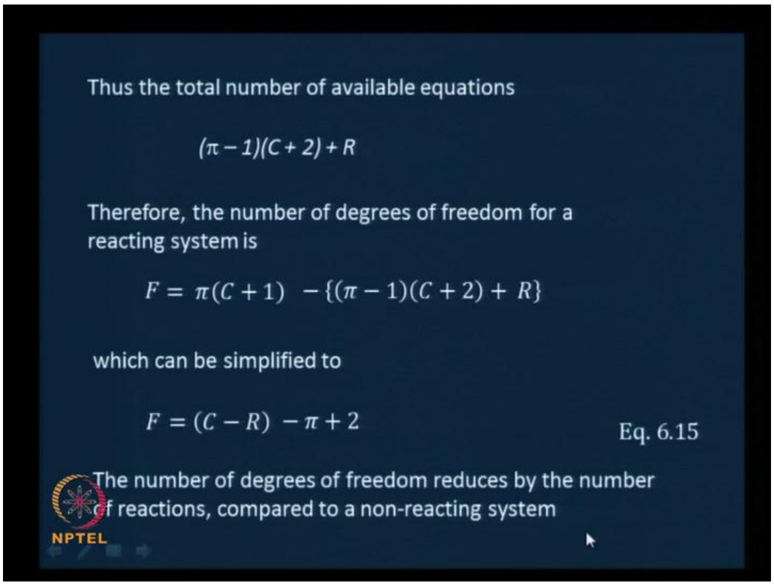

Thus the total number of available equations

$$(\pi - 1)(C + 2) + R$$

Therefore, the number of degrees of freedom for a reacting system is

$$F = \pi(C + 1) \ - \{(\pi - 1)(C + 2) + R\}$$

which can be simplified to

$$F = (C - R) \ - \pi + 2 \qquad \text{Eq. 6.15}$$

The number of degrees of freedom reduces by the number of reactions, compared to a non-reacting system

For the phase rule, we just saw that the phase rule for a non-reacting system just gets modified by a minus R for a reacting system. Number of degrees of freedom reduces by the number of independent equations in that system.

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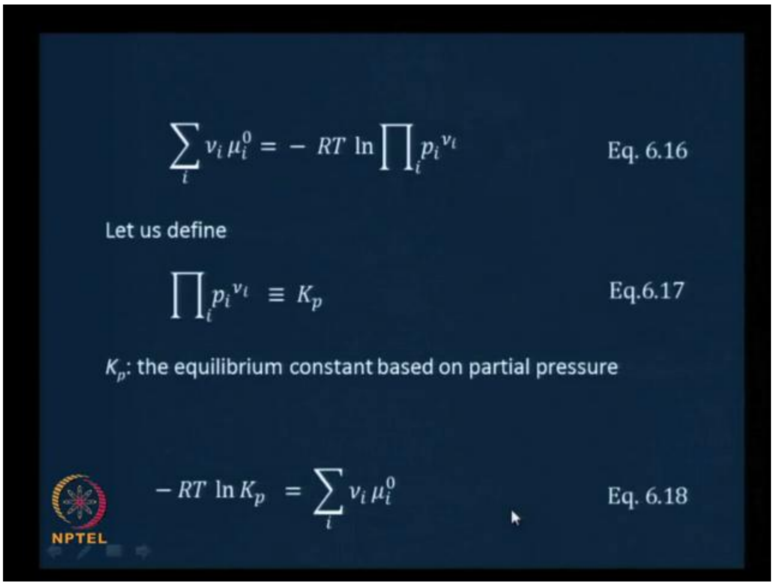

$$\sum_i \nu_i \mu_i^0 = -RT \ln \prod_i p_i^{\nu_i}$$ Eq. 6.16

Let us define

$$\prod_i p_i^{\nu_i} \equiv K_p$$ Eq.6.17

K_p: the equilibrium constant based on partial pressure

$$-RT \ln K_p = \sum_i \nu_i \mu_i^0$$ Eq. 6.18

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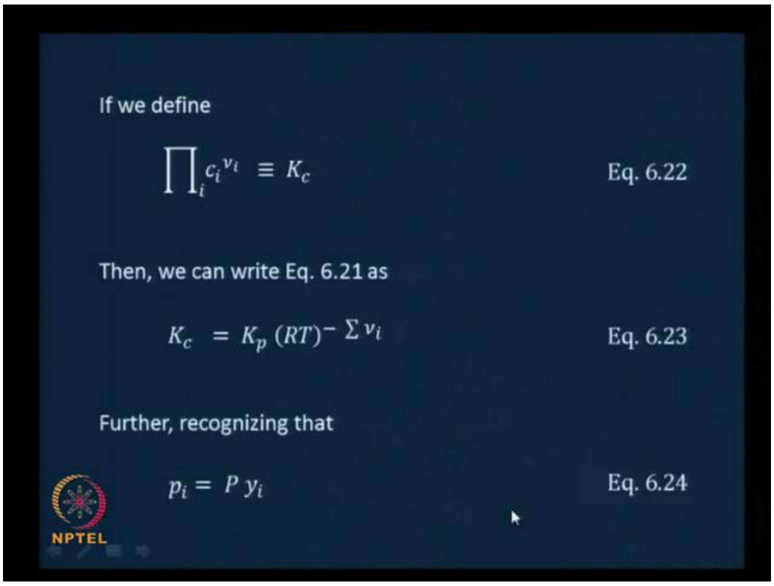

If we define

$$\prod_i c_i^{\nu_i} \equiv K_c$$ Eq. 6.22

Then, we can write Eq. 6.21 as

$$K_c = K_p (RT)^{-\sum \nu_i}$$ Eq. 6.23

Further, recognizing that

$$p_i = P y_i$$ Eq. 6.24

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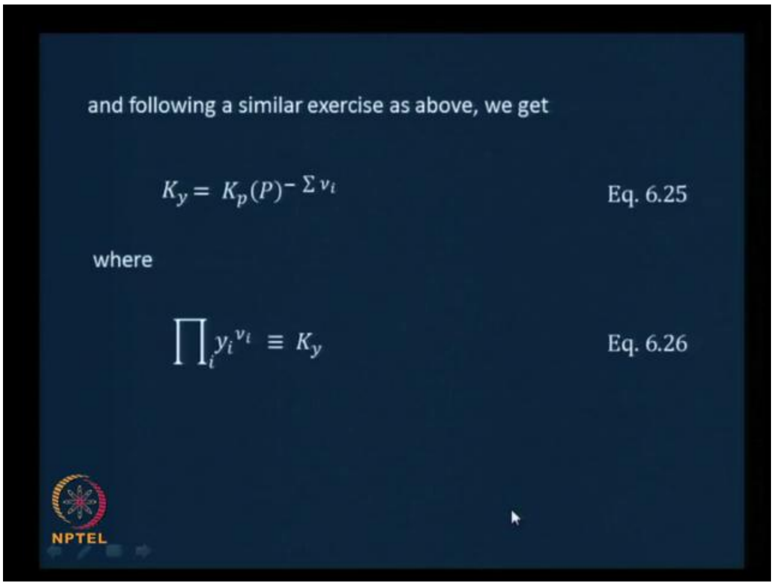

and following a similar exercise as above, we get

$$K_y = K_p (P)^{-\sum \nu_i} \qquad \text{Eq. 6.25}$$

where

$$\prod_i y_i^{\nu_i} \equiv K_y \qquad \text{Eq. 6.26}$$

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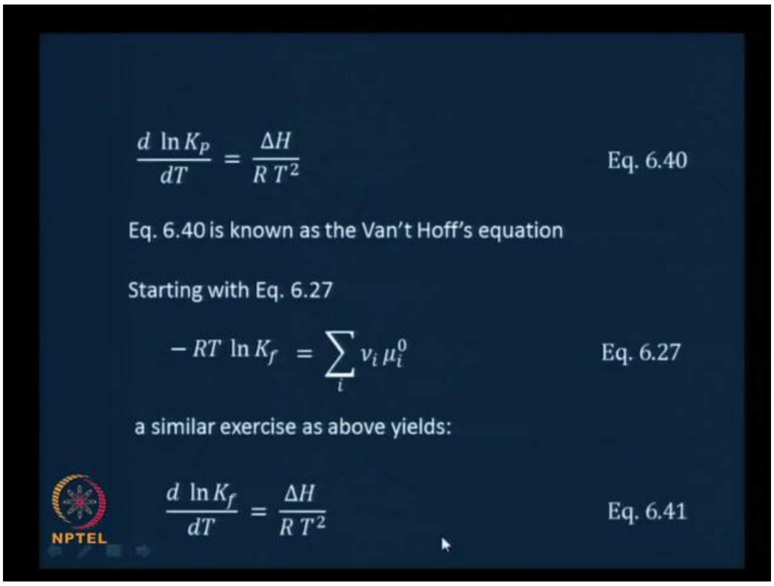

$$\frac{d \ln K_p}{dT} = \frac{\Delta H}{R\,T^2} \qquad \text{Eq. 6.40}$$

Eq. 6.40 is known as the Van't Hoff's equation

Starting with Eq. 6.27

$$-RT \ln K_f = \sum_i \nu_i\, \mu_i^0 \qquad \text{Eq. 6.27}$$

a similar exercise as above yields:

$$\frac{d \ln K_f}{dT} = \frac{\Delta H}{R\,T^2} \qquad \text{Eq. 6.41}$$

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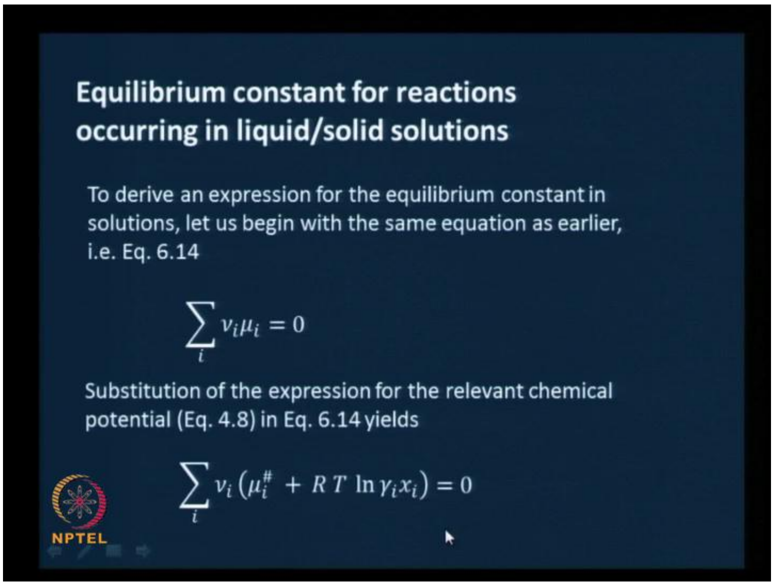

Equilibrium constant for reactions occurring in liquid/solid solutions

To derive an expression for the equilibrium constant in solutions, let us begin with the same equation as earlier, i.e. Eq. 6.14

$$\sum_i \nu_i \mu_i = 0$$

Substitution of the expression for the relevant chemical potential (Eq. 4.8) in Eq. 6.14 yields

$$\sum_i \nu_i \left(\mu_i^{\#} + R\,T\,\ln \gamma_i x_i\right) = 0$$

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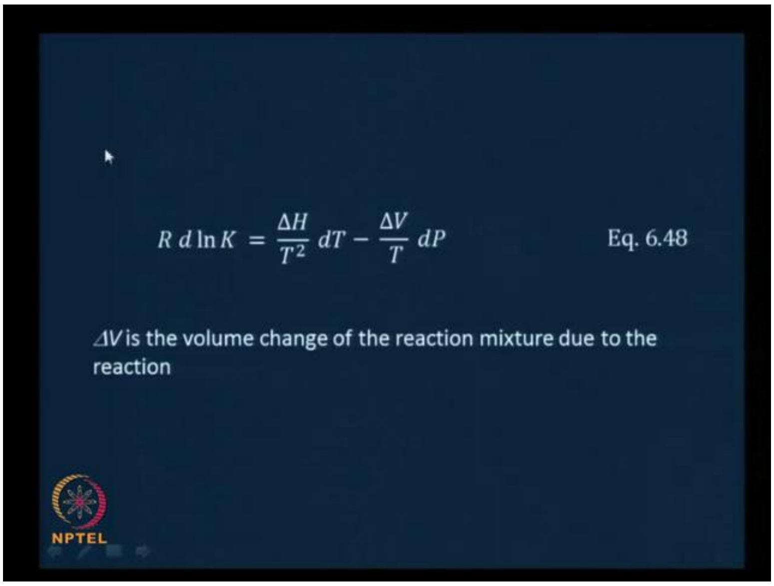

$$R\,d\ln K = \frac{\Delta H}{T^2}\,dT - \frac{\Delta V}{T}\,dP \qquad \text{Eq. 6.48}$$

ΔV is the volume change of the reaction mixture due to the reaction

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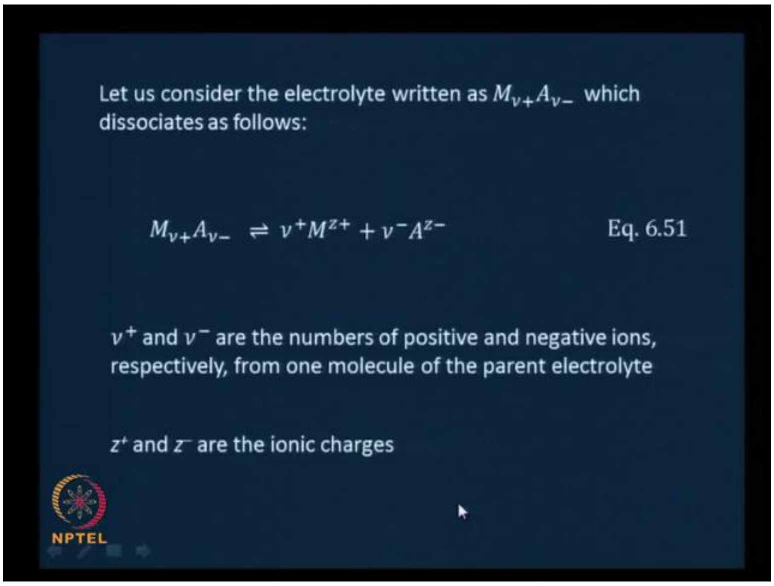

Let us consider the electrolyte written as $M_{\nu+}A_{\nu-}$ which dissociates as follows:

$$M_{\nu+}A_{\nu-} \rightleftharpoons \nu^+M^{z+} + \nu^-A^{z-} \qquad \text{Eq. 6.51}$$

ν^+ and ν^- are the numbers of positive and negative ions, respectively, from one molecule of the parent electrolyte

z^+ and z^- are the ionic charges

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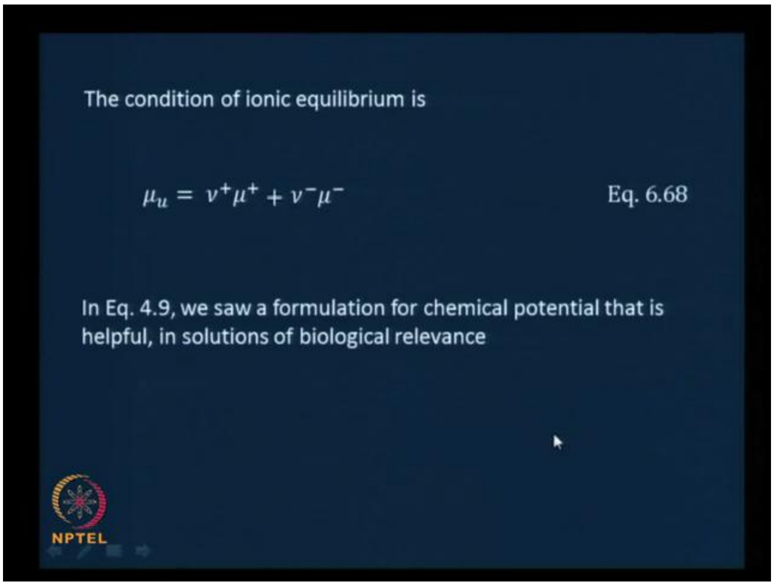

The condition of ionic equilibrium is

$$\mu_u = \nu^+\mu^+ + \nu^-\mu^- \qquad \text{Eq. 6.68}$$

In Eq. 4.9, we saw a formulation for chemical potential that is helpful, in solutions of biological relevance

Then, we defined the various equilibrium constants. I would like to you see that on your own K P, K c and K y. We also wrote the relationships between the various variables. And, this was the temperature dependence of K P – as delta H by R T squared; it was the Van't Hoff equation. We could also do that for K f, which is the equilibrium constant in terms of fugacities.

Then, we saw the equilibrium constant for reactions occurring in liquid and solid solutions too as this. And finally, some formulations for electrolytes we have seen, which is … I will just give you the condition for ionic equilibrium and I will stop there. We also looked at some temperature dependences. But, the condition of ionic equilibrium was mu u equals nu plus mu plus, the stoichiometric coefficient of the positively charged species, times mu plus, plus nu minus mu minus.

Let us stop … the review here. I hope that the course was useful, and you can always write back to me if you have any queries. See you then.