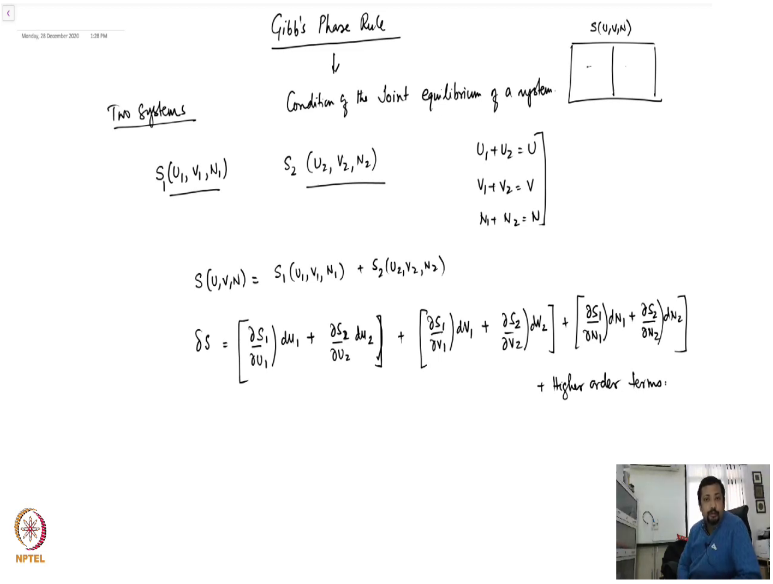
Statistical Mechanics
Prof. Dipanjan Chakraborty
Department of Physical Sciences
Indian Institute of Science Education and Research, Mohali

Lecture – 16
Conditions of Equilibrium and Gibbs Phase Rule

(Refer Slide Time: 00:21)



Monday, 28 December 2020 1:28 PM

Gibb's Phase Rule

↓

Condition of the Joint equilibrium of a system.

$S(U,V,N)$

Two Systems

$S_1(U_1, V_1, N_1)$ $S_2(U_2, V_2, N_2)$

$$\left.\begin{array}{l} U_1 + U_2 = U \\ V_1 + V_2 = V \\ N_1 + N_2 = N \end{array}\right]$$

$$S(U,V,N) = S_1(U_1,V_1,N_1) + S_2(U_2,V_2,N_2)$$

$$\delta S = \left[\left(\frac{\partial S_1}{\partial U_1}\right) dU_1 + \frac{\partial S_2}{\partial U_2} dU_2\right] + \left[\left(\frac{\partial S_1}{\partial V_1}\right) dV_1 + \left(\frac{\partial S_2}{\partial V_2}\right) dV_2\right] + \left[\left(\frac{\partial S_1}{\partial N_1}\right) dN_1 + \left(\frac{\partial S_2}{\partial N_2}\right) dN_2\right]$$

+ Higher order terms.

Welcome back. So, in this lecture, so we are going to study what is known as the Gibbs phase rule. We will see that this Gibbs phase rule, it follows from the condition of the joint equilibrium of a system, of a system right. Now, we have already seen the stability criteria for entropy and internal energy.

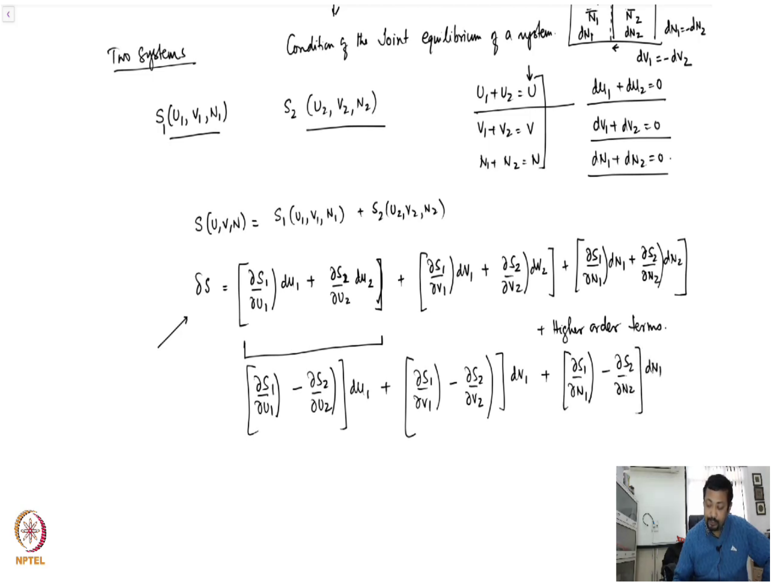
Here let us consider two systems with entropy U 1, V 1, and N 1; and S 2 as U 2, V 2 and N 2 and let us bring these two systems. So, two systems let us be for, but first we note that U 1 plus U 2 must be your total energy; V 1 plus V 2 must be your volume; N 1 plus N 2 is going to be your total particle number. U, V, N are being held fixed.

So, bring them together, so that they come into a joint equilibrium alternatively. You can imagine that I have a system let us say gas which has U, V, and N, is described by this fundamental relation. I can partition them into two sub systems such that they have entropies S 1 and S 2 as we have written now. So, once they come to a joint equilibrium, we will write down the total entropy as U, V, N, which is going to be S 1 U 1, V 1, N 1 plus S 2 U 2, V 2, and N 2.

Now, any change in this entropy near this joint equilibrium, let us calculate that, it is going to be del S 1 del U 1 d U 1 plus del S 2 del U 2 d U 2 plus del S 1 del V 1 d V 1 plus del S 2 del V 2 d V 2. And similarly, you have for the particle number which is going to be del S 1 del N 1 d N 1 plus del S 2 del N 2 d of N 2.

And then you have higher order terms which you ignore because you are let us say you are very, very infinitesimally close to the equilibrium point – the joint equilibrium point. Now, clearly at the joint equilibrium point, the delta S is 0 that is the stability criteria if it is a stable equilibrium point.

(Refer Slide Time: 03:36)



Two Systems

Condition of the Joint equilibrium of a system.

N_1 dN_1 | N_2 dN_2

$dN_1 = -dN_2$

$dV_1 = -dV_2$

$S_1(U_1, V_1, N_1)$ $S_2(U_2, V_2, N_2)$

$U_1 + U_2 = U$ $dU_1 + dU_2 = 0$

$V_1 + V_2 = V$ $dV_1 + dV_2 = 0$

$N_1 + N_2 = N$ $dN_1 + dN_2 = 0$.

$$S(U,V,N) = S_1(U_1,V_1,N_1) + S_2(U_2,V_2,N_2)$$

$$\delta S = \left[\left(\frac{\partial S_1}{\partial U_1}\right) dU_1 + \frac{\partial S_2}{\partial U_2} dU_2\right] + \left[\left(\frac{\partial S_1}{\partial V_1}\right) dV_1 + \left(\frac{\partial S_2}{\partial V_2}\right) dV_2\right] + \left[\left(\frac{\partial S_1}{\partial N_1}\right) dN_1 + \left(\frac{\partial S_2}{\partial N_2}\right) dN_2\right]$$

+ Higher order terms.

$$\left[\left(\frac{\partial S_1}{\partial U_1}\right) - \left(\frac{\partial S_2}{\partial U_2}\right)\right] dU_1 + \left[\left(\frac{\partial S_1}{\partial V_1}\right) - \left(\frac{\partial S_2}{\partial V_2}\right)\right] dV_1 + \left[\left(\frac{\partial S_1}{\partial N_1}\right) - \frac{\partial S_2}{\partial N_2}\right] dN_1$$

So, this means the left hand side is 0. Now, let us look at this term. From here, if I see since U is fixed it means that d U 1 plus d U 2 is going to be 0. Now, d V 1 plus d V 2 is going to be 0, and d N 1 plus d N 2 is also going to be 0. Which means you can imagine that if I move this partition infinitesimally to the left hand side some of this, so this was N 2, this was N 2.

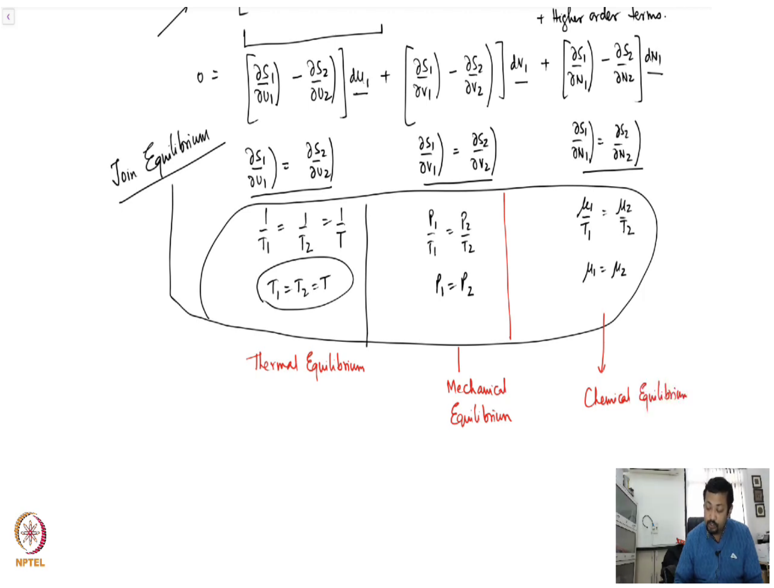
And this is N this was one N 1, this was one N 2, this one was V 1, this one was V 2. And you can see that a part of this volume goes if you just move the partition a little, little, little to the left, this is an imaginary partition by the way.

You are, you are not really putting a partition, but you are imagining that you have broken the system into two sub systems using an imaginary partition. And this partition if you move to the left a little bit or to the right, you see V 1 and V 2 are going to change.

So, any change in d V 1 will be compensated by a change in d V 2 that is exactly what your this relation tells you. Any change in particle number d N 1 in this is going to be compensated by particle number d N 2. So, the d N 1 is going to be minus of d N 2. If you move, for example, I have moved it to the left which means N 2 has increased, and there is a change in N 2 which we will denote as d N 2.

Since, it is the same system where the number of particles fixed, therefore, N 1 number of particles N 1 should decrease. So, we have these three relations. Let us substitute over here then you see that this term is del S del U 1 minus del S 2 del U 2 times d U 1 plus del S 1 del V 1 minus del S 2 del V 2 d V 1 plus del S 1 del N 1 minus del S 2 del N 2 times d of N 1.

(Refer Slide Time: 05:52)



+ Higher order terms.

$$0 = \left[\left.\frac{\partial S_1}{\partial U_1}\right) - \left.\frac{\partial S_2}{\partial U_2}\right)\right] \underline{dU_1} + \left[\left.\frac{\partial S_1}{\partial V_1}\right) - \left.\frac{\partial S_2}{\partial V_2}\right)\right] \underline{dV_1} + \left[\left.\frac{\partial S_1}{\partial N_1}\right) - \left.\frac{\partial S_2}{\partial N_2}\right]\underline{dN_1}$$

Join Equilibrium

$$\underline{\left.\frac{\partial S_1}{\partial U_1}\right) = \left.\frac{\partial S_2}{\partial U_2}\right)} \qquad \underline{\left.\frac{\partial S_1}{\partial V_1}\right) = \left.\frac{\partial S_2}{\partial V_2}\right)} \qquad \underline{\left.\frac{\partial S_1}{\partial N_1}\right) = \left.\frac{\partial S_2}{\partial N_2}\right)}$$

$$\frac{1}{T_1} = \frac{1}{T_2} = \frac{1}{T} \qquad \frac{P_1}{T_1} = \frac{P_2}{T_2} \qquad \frac{\mu_1}{T_1} = \frac{\mu_2}{T_2}$$

$$\boxed{T_1 = T_2 = T} \qquad P_1 = P_2 \qquad \mu_1 = \mu_2$$

Thermal Equilibrium

Mechanical Equilibrium

Chemical Equilibrium

Since the left hand side is identically 0, and this is valid for any arbitrary variation in U 1, V 1 and N 1. It follows that del S 1 del U 1 is going to be del S 2 del U 2. I have suppressed that factors variables which are held constant, you can easily figure them out. This means del S 1 del V 1 is going to be del S 2 del V 2.

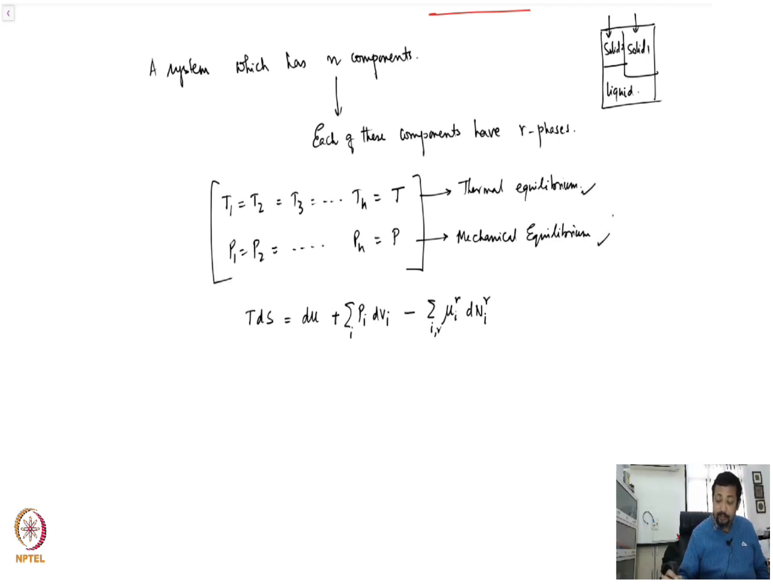
And this essentially means del S 1 del N 1 is going to be del S 2 del N 2 right. Provided the state you are looking at final state is an equilibrium state. If it is an unstable equilibrium the system might spontaneously go to a new equilibrium state. And in that case, delta S is not going to be 0 and we cannot argue in this manner.

But this thermodynamic relations all of you know this means 1 over T 1 is going to be 1 over T 2 is going to be 1 over T, so that I have T 1, T 2 is equal to T in the joint equilibrium state. This means P 1 by T 1 is going to be P 2 by T 2. And since T 1 is equal to T 2, I have P 1 is equal to P 2. And similarly this would mean that mu 1 over T 1 is going to be mu 2 over T 2. Once again since T 1 is equal to T 2, this is going to be mu 1 over mu 2.

Therefore, you see a joint equilibrium what does a joint equilibrium means? A joint equilibrium essentially has these three conditions. This is for a hydrostatic system we are looking at. This condition is what is called a thermal equilibrium. This condition is what is called a mechanical equilibrium and this is what is called a chemical equilibrium.

So, in general, in general, for any arbitrary thermodynamic system, an equilibrium state essentially means that you have a thermal equilibrium – temperature is uniform; you have a mechanical equilibrium which is means the balance of the external force is that describes the thermodynamic state of the system; and the chemical equilibrium again that essentially means that the chemical potentials must be same.

(Refer Slide Time: 08:40)



A system which has n components.

Each of these components have r-phases.

$$\left[\begin{array}{l} T_1 = T_2 = T_3 = \cdots T_n = T \\ P_1 = P_2 = \cdots\cdots P_n = P \end{array}\right] \begin{array}{l} \rightarrow \text{Thermal equilibrium} \checkmark \\ \rightarrow \text{Mechanical Equilibrium} \checkmark \end{array}$$

$$TdS = du + \sum_i P_i \, dV_i - \sum_{i,r} \mu_i^r \, dN_i^r$$

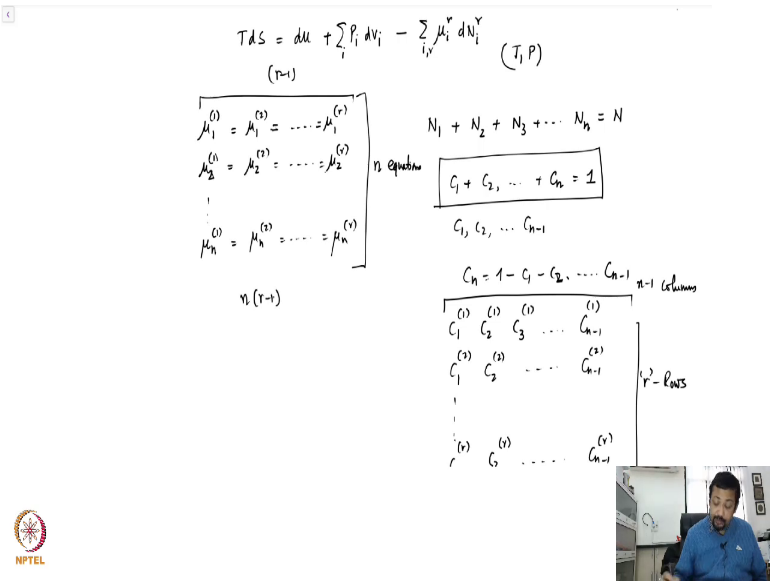
Now, suppose I have a system. So, here whatever we have considered, we have considered a single component one type. For example, the our system was made up of one type of gas particles. But now let us complicate things a little bit more. We take a system which has n components, but that is not the whole story. Now each of these components have r-phases.

So, essentially you are looking at an equilibrium a joint equilibrium between these n components and each of these components can exist in r-phases. For example, I can expect that there is a solid 1, solid 2. So, if one of the two components, one of them can be in a phase solid 1 and the other phase solid 2, and the other component can be in a liquid phase. So, this is the joint equilibrium that we are talking about.

Now, we have clearly seen what does the joint equilibrium means. So, joint let us write down. So, the temperatures must be equal T n must be equal to the temperature. We will take the case of a hydrostatic system, and therefore, we will write down the pressure must be all equal for this. These are the trivial things the there is a balance of mechanical force which is the mechanical equilibrium, this is the mechanical equilibrium, and this is the thermal equilibrium.

Now, if you recall your first law is T d S is d U plus P i d V i minus sum over i sum over mu i r d N i r. So, please understand that you have to be very very careful with this. But these two are done, the thermal equilibrium is done, the mechanical equilibrium is done. The point comes in for the chemical equilibrium. The chemical equilibrium essentially tells me that I have mu 1 is equal to mu 2 for a single component system.

(Refer Slide Time: 11:33)



$$TdS = du + \sum_i P_i dV_i - \sum_{i,r} \mu_i^r dN_i^r \qquad (T, P)$$

$(r-1)$

$$\left.\begin{array}{l} \mu_1^{(1)} = \mu_1^{(2)} = \cdots = \mu_1^{(r)} \\ \mu_2^{(1)} = \mu_2^{(2)} = \cdots = \mu_2^{(r)} \\ \vdots \\ \mu_n^{(1)} = \mu_n^{(2)} = \cdots = \mu_n^{(r)} \end{array}\right] n \text{ equations}$$

$n(r-1)$

$$N_1 + N_2 + N_3 + \cdots N_n = N$$

$$\boxed{C_1 + C_2, \ldots + C_n = 1}$$

$$C_1, C_2, \ldots C_{n-1}$$

$$C_n = 1 - C_1 - C_2, \ldots C_{n-1}$$

$$\overbrace{\begin{array}{cccc} C_1^{(1)} & C_2^{(1)} & C_3^{(1)} \cdots & C_{n-1}^{(1)} \\ C_1^{(2)} & C_2^{(2)} & \cdots & C_{n-1}^{(2)} \\ \vdots & & & \\ C^{(r)} & C_2^{(r)} & \cdots & C_{n-1}^{(r)} \end{array}}^{n-1 \text{ columns}} \Bigg] \text{'r'-Rows}$$

But now one has to be careful that mu 1 of 1 phase 1, the superscript denotes the phase must be equal to mu 1 of 2 is equal to mu 1 of r; that is what that chemical equilibrium would mean. One should then look at write down for mu 2 it is going to be mu 2 2 is going to be mu 2 of r. So, this is a chemical equilibrium between the phases. And one has mu n of 1 is going to be mu n of 2 all the way up to mu n of r.

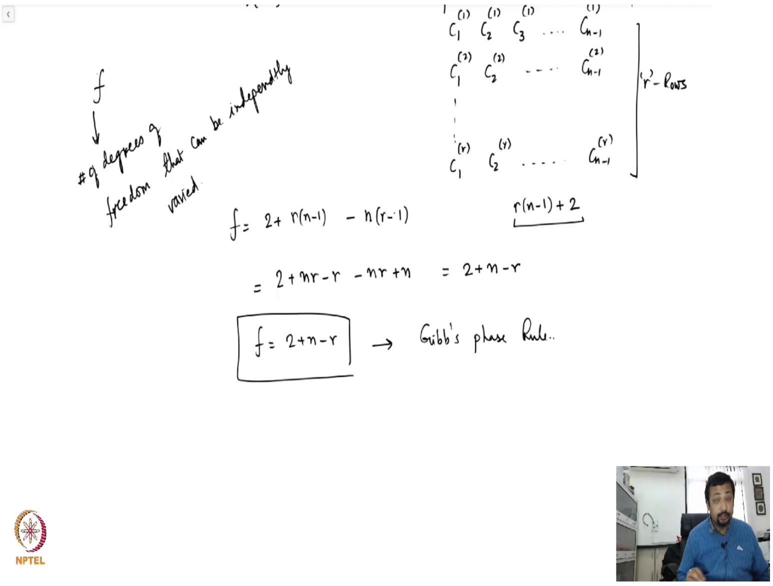
So, now, for this joint equilibrium, I want to now figure out how many possible coordinates thermodynamic coordinates I can vary independently. So, which means that this joint system how many thermodynamic coordinates describe that, and that is essentially the degrees of freedom of the system. Of course, two of them are known which is T and P, the temperature and the pressure right.

Now, note that, I have N components which means the number of particles in component 1 plus number of particles of component 2 so on and so forth all the way up to N n is going to be capital N total number of particles and that is fixed, so which means C 1 plus C 2 and all the way up to C n is going to be 1. Now, this condition itself tells you since total particle number is fixed that if I know C 1, C 2 and all the way up to C n minus 1, I actually know C n which is 1 minus C 1 minus C 2 going up to C n minus 1.

Therefore, how many coordinates you have? You have C 1 1, C 2 1, C 3 1 going up to C n minus 1 of 1 for phase is 1. Then you have C 1 of 2, C 2 of 2 for phase 2 going all the way up to C n minus 1 of 2. And you continue down to come to C n sorry the phase rth phase which is C 1 of r, C 2 of r going up to C n minus 1 of r, so that you see here that there are r rows and n minus 1 columns. And therefore, you have r times n minus 1 coordinates over here.

So, that the total number of coordinates is r times n minus 1 plus 2, but not all of them can be independently varied because I have this restriction that restricts the chemical potential. This is a equilibrium. This is a equilibrium condition for the this chemical equilibrium between the different components and the phases. And here you clearly see that I have n equations and r minus 1. So, your constraints are n times r minus 1.

(Refer Slide Time: 15:06)



f $\downarrow$ # of degrees of freedom that can be independently varied

$$\left.\begin{matrix} C_1^{(1)} & C_2^{(1)} & C_3^{(1)} & \cdots & C_{n-1}^{(1)} \\ C_1^{(2)} & C_2^{(2)} & & \cdots & C_{n-1}^{(2)} \\ \vdots & & & & \\ C_1^{(r)} & C_2^{(r)} & & \cdots & C_{n-1}^{(r)} \end{matrix}\right] \text{'r'- Rows}$$

$$\underline{r(n-1)+2}$$

$$f = 2 + r(n-1) - n(r-1)$$

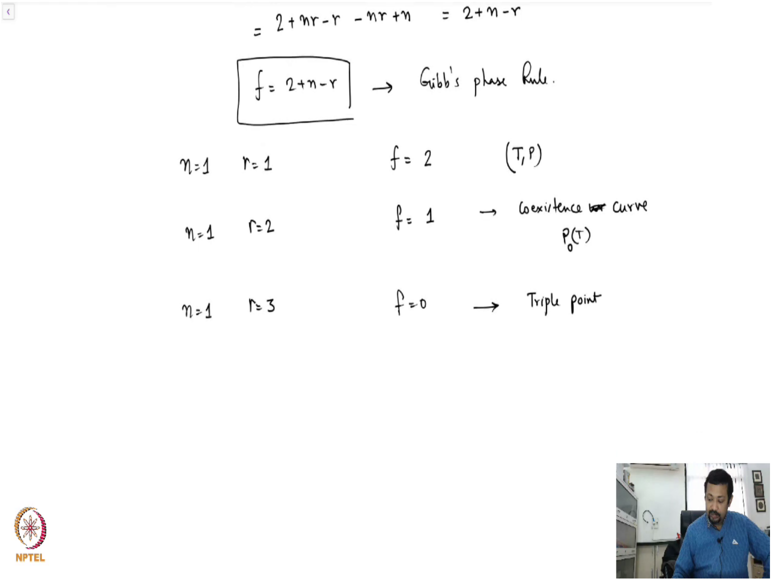
$$= 2 + nr - r - nr + n = 2 + n - r$$

$$\boxed{f = 2 + n - r} \rightarrow \text{Gibb's phase Rule..}$$

And if you denote f as the number of degrees of freedom which you can independently vary. So, let this be the number of degrees of freedom that can be independently varied f is the total number of degree of freedom which you have which is 2 plus n times r minus 1 minus n times.

No this has to be, sorry, this is 2 plus r times n minus 1 minus n minus r minus 1. And if you do that, then this is 2 plus n r minus r minus n r plus n which is 2 plus n minus r. So, you come up with this relation which is 2 plus n minus r. And this is what is called a Gibbs phase rule.

(Refer Slide Time: 16:35)



$= 2 + nr - r - nr + n \quad = 2 + n - r$

$\boxed{f = 2 + n - r}$ → Gibb's phase Rule.

$n = 1 \quad r = 1 \qquad f = 2 \qquad (T, P)$

$n = 1 \quad r = 2 \qquad f = 1$ → Coexistence curve $P_0(T)$

$n = 1 \quad r = 3 \qquad f = 0$ → Triple point

Say I have n equal to 1 – a single component; and r is equal to 1, it can exist in only one phase which means your degree of freedom f is going to be 2. And the variables you can vary are T and P, which is typically for a liquid. If n is equal to 1 and r is equal to 2, then you see the number of degrees of freedom, you have is 1.

So, this means that, for example, if you have a liquid vapor coexistence, this is the case which is the coexistence curve P as a function of T let us say P naught as a function of T. This gives you the coexistence curve because a single component a liquid let us a water which can now coexist between water and water vapor, and then you have this coexistence curve that essentially you can vary only one of them to move along the curve.

If you have n equal to 1 and r is equal to 3, a single component which can exist in three phases, for example – solid, liquid and gas, then you see f is equal to 0; you have no freedom in the phase in the P T phase in the thermodynamic phase diagram. And essentially this represents a point which is the triple point for a hydrostatic system right. So, with this, we conclude this lecture.