

# Thermodynamics And Kinetics Of Materials

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## Lecture 16

### Thermodynamic Equilibrium in Statistical Thermodynamics

In the last lecture I talked about computational entropy and how is it connected to the atomistic description of matter and we derived this formula  $S$  equals to minus  $R$ . So, we derived this formula  $S$  equals to minus  $R \sum x_i \ln x_i$  and  $x_i$  and if you have different species for example, A, B, C, D, E then you have equiatomic computation we have found that the configuration the configuration entropy configuration increases it becomes  $R \ln 5$  and  $n$  pi. So, as you can see here when it is equiatomic we find that the most probable macro state it is like the most probable macro state and with a large number of micro states and we get this we establish this formula this is the most important it is a very important formula that you will see by connecting the atomistic description with the thermodynamic description right by using Boltzmann's hypothesis  $S$  equals to  $k_B \ln \Omega$ . So, this is one very important hypothesis remember that  $S$  equals to  $k_B \ln \Omega$  where  $\Omega$  is basically the number of configurations or number of arrangements that is then basically it is basically the number of accessible micro states right for a given what the most probable macro state right. As I told you that  $\Omega$  is equal to  $\Omega_{max}$  is the one that will be realized by the system and that is what will maximize the entropy and that is exactly what in the next few slides I will show you or in the next few slides I will show you how this can be used this idea can be used to derive other useful quantities like energy and Helmholtz free energy heat capacity and so on. Okay and we will show you how this  $S$  equals to  $k_B \ln \Omega$  basically gives you back this constraint that the thermodynamic equilibrium right the idea of thermodynamic equilibrium can also be realized.

$\ln 2 = 0.693147$   
 $\ln 3 = 1.098612$   
 $\ln 4 = 1.386294$   
 $\ln 5 = 1.609437$   
 $\ln 10 = 2.302585$

High Entropy  
 Alloy  
 $k = 2 \dots 10$   
 $k = A, B, C, D, E, \dots$   
 $x_A = x_B = x_C = x_D = x_E = \dots = 0.2$

For  $n$ -Component  
 $S^{conf} = R \ln \Omega$   
 $S = -R \sum_{i=1}^n x_i \ln x_i$   
 $= -R \left( \frac{1}{5} \ln \frac{1}{5} \right) \times 5$   
 $= -R \ln \frac{1}{5} = R \ln 5$

$x_i$  - mole fraction of species  $i$

$$S = -k_B \ln \sum_{j=1}^n n_j \ln \left( \frac{n_j}{N} \right) \quad \text{where } n_1 + n_2 + n_3 + \dots + n_n = N$$

$$R = k_B N \quad X_j = \frac{n_j}{N}$$

$$S = -R \sum_j X_j \ln X_j = -k_B N \sum_j X_j \ln X_j$$

$$dS = -k_B d \left[ \sum_{j=1}^n n_j \ln \left( \frac{n_j}{N} \right) \right] = -k_B N \sum_j X_j \ln X_j$$

$$= -k_B \sum_{j=1}^n d \left[ n_j \ln n_j - n_j \ln N \right]$$

$$= -k_B \sum_{j=1}^n \left[ \ln n_j dn_j + dn_j \right]$$

$$d \ln N = \frac{1}{N} dN = \ln N dn_j - \frac{n_j}{N} dN$$

So, as you saw S equals to so basically if it is per mole then you use R if it is per atom then you use k\_B k\_B is Boltzmann's constant and R equals to k\_B times n right that we have shown. Now you see x\_j is equals to n\_j by n right x\_j equals to n\_j by n. So, I can write it as write this as so you have x\_j so you have minus k\_B n\_j l n n\_j by n. So, now why how can I write this so let us look at that so we have done this minus k\_B n x a l n x a plus x b l n x b or it is like x i l n x i.

If I do this which equal to one to R n\_j l n n\_j by n. So, if you see this S equals to minus R summation of x\_j l n x\_j right which is equals to minus k\_B n see R into n right k\_B into n\_j x\_j. Now as you can see this is nothing but if I take minus k\_B here if I put this here is x\_j is nothing but n\_j by n and there is an n here as you can see and l n n\_j right. So, now this n and this n goes up and what you get is basically this expression this expression minus k\_B l n n\_j summation over j equal to one to R if you have R components or R species n\_j l n n\_j by n. Now if you have that then as you know if I if I have that and it is entropy is an exact differential so I can write this as dS equals to minus k\_B k\_B is a constant right so minus k\_B d of this entire term right of this entire summation.

The image shows two panels of handwritten mathematical work. The left panel shows the derivation of the differential of the entropy term for a single species:

$$d(n_j \ln n_j) = \ln n_j dn_j + n_j d \ln n_j$$

$$= \ln n_j dn_j + \frac{n_j}{n_j} dn_j = \ln n_j dn_j + dn_j$$

$$d \ln n_j = \frac{dn_j}{n_j}$$

$$\frac{d \ln n_j}{dn_j} = \frac{1}{n_j}$$

The right panel shows the derivation for the total entropy differential:

$$= -k_B \left[ \sum_{j=1}^R (\ln n_j - \ln N) dn_j + \sum_{j=1}^R dn_j - \sum_{j=1}^R \left( \frac{n_j}{N} \right) dN \right]$$

$$= -k_B \sum_{j=1}^R \ln \left( \frac{n_j}{N} \right) dn_j + dN - dN$$

$$= -k_B \sum_{j=1}^R \ln \left( \frac{n_j}{N} \right) dn_j$$

Below this, it defines  $N = n_1 + n_2 + \dots + n_R$  and  $dN = dn_1 + dn_2 + \dots + dn_R = \sum_{j=1}^R dn_j$ . It then shows the identity  $\sum_{j=1}^R \left( \frac{n_j}{N} \right) = 1$  (labeled "Why?") and  $\sum_{j=1}^R X_j = 1$  where  $\frac{n_j}{N} = X_j$ .

So, minus k\_B d of this entire term and as you know d of this summation I can take the d inside right because all these n\_j s are separate right all the n\_j s are like each represents j equal to one to R represents different species right. So basically I can take the d inside the summation so that is what I have done here if you see that here you have d of the summation of this term and now I have taken the summation out and I have put d here which is perfectly valid because you have n one n two n three and all of these make up for n so basically you have this relation why why can I why can I do that because n one plus n two plus n three plus dot dot dot means continue the sum up to R and that is what is going to be equal to right. So, as you can see here I have directly used d l n so now this n n\_j by n is n n\_j minus n n\_m so this becomes d n\_j l n n\_j minus n\_j l n n\_m right d n\_j l n n\_j minus n\_j l n n\_m. So, a little bit of algebraic manipulation again so you will see you can write this as d of n\_j l n n\_j is nothing but d n\_j so so basically this is so let me write that so d of d of d of d of n\_j l n n\_j is nothing but equals to c such as product rule so d so l n n\_j d n\_j plus n\_j d l n n\_j which is equals to d of n\_j plus d of n\_j plus d of n\_j plus d of n\_j d n\_j.

Now, remember  $d \ln n_j$  is nothing but  $d \ln n_j$  is equal to  $d n_j$  by  $n_j$  right  $d n_j$  by  $n_j$  because  $d \ln x = \frac{1}{x} dx$  since  $d \ln n_j$   $d n_j$  equals to  $1$  by  $n_j$ . So, this follows right so now you have  $\ln n_j$   $d n_j$  plus  $n_j$  by  $n_j$  which is equal to  $\ln n_j$   $d n_j$  plus  $d n_j$  right. So, if you see this so you have  $\ln n_j$   $d n_j$  plus  $d n_j$ . So, then you have  $\ln n_j$   $d n_j$  minus  $\ln n_j$   $d n_j$  and then again you have  $n_j$  by  $n_j$  right  $n_j$  by  $n_j$   $d n_j$  right because  $d n_j$  by  $n_j$  right and  $n_j$  is a constant here right. So, because  $n_j$  is here right it is a product. So, as you can see here I have written that so  $n_j$   $d n_j$ . So, one term is  $\ln n_j$   $d n_j$  the next term is  $n_j$  remains and  $\ln n_j$   $d n_j$  is nothing but  $d n_j$  by  $n_j$  right. So, that is what I have written. Now, if I write that then you can further simplify it and you will finally see that you get something like  $d \ln n_j$  minus  $d n_j$  that goes off and then you have this and you have only  $\ln n_j$  by  $n_j$   $d n_j$  ok. So, you will have  $\ln n_j$  by  $n_j$  which is nothing but  $\ln x$   $d x$   $d x$ . So, basically  $\ln x$   $d x$  is nothing but  $d x$  or minus  $k_B \ln n_j$  by  $n_j$   $d n_j$  is what you will get right. Now, remember  $n_j$  sum of  $n_j$  by  $n$  has to be 1 because this is because  $x_1$  plus  $x_2$ . So, write  $n_j$  by  $n$  is  $x_j$  that is all. So, basically  $n_j$  by  $n$  equal to mole fraction  $x_j$  and sum of  $x_j$  for over all components  $j$  equal to 1 to  $r$  equal to 1 to  $r$  equal to 1 right. So, that is that. So, now, what you get is.

$$dS = -k_B \sum_{j=1}^r \ln\left(\frac{n_j}{N}\right) dn_j$$

Assume an isolated system  
 - Total  $U$  and total  $N$  cannot change

$$U = \sum_{j=1}^r E_j n_j$$

$E_j \rightarrow$  Energy of level  $j$

$n_1$  atoms of type 1 in  $E_1$   
 $n_2$  atoms of type 2 in  $E_2$

$dU = \sum_j E_j dn_j = 0 \quad \therefore n_j dE_j = 0$   
 $dN = \sum_j dn_j = 0$

So, you have a minus  $k_B \ln n_j$  by  $n_j$   $d n_j$  that is what you got as  $dS$ . So,  $dS$  is that right. So,  $dS$  equal to. So, this is what we have established now  $dS$  equals to minus  $k_B \ln n_j$  by  $n_j$   $d n_j$ . Now, you assume an isolated system why because I am now going to basically look at how this extremization principle how the thermodynamic equilibrium principles right what right energy minimization or entropy maximization right  $dS$  equal to 0 basically gives you for an isolated system  $dS$  or for an isolated system  $dS$  equal to 0 gives you the extreme of that right and  $d^2S$  less than 0 basically tells that entropy is maximized and as we know that entropy maximum principle or energy minimum principle right entropy maximum principle is always valid when you are talking about total internal energy is fixed right it cannot change right that is what exactly I have written here total  $U$  and total  $N$  cannot change right  $U$  is basically if you have this different energy levels.

S of the isolated system at equilibrium

$$dS = 0 \quad \text{with constraints}$$

$$dU = 0$$

$$dN = 0$$

Use Lagrange Multiplier method

$$dS + \alpha dN + \beta dU = 0$$

$\alpha, \beta$  - Lagrange multipliers

So, if you have different energy levels like energy of level  $j$  is  $\epsilon_j$  then if you have like  $n_j$  atoms of type  $j$  in say energy level  $\epsilon_j$  similarly  $n_2$  atoms of type 2. So, each type is distinguishable from the other right of type 2 in  $\epsilon_2$  and so on then total  $U$  is nothing but  $\sum \epsilon_j n_j$  right where  $\epsilon_j$  is the energy of level  $j$  right. So, now if you have  $dU$  is basically  $\sum \epsilon_j dn_j$  right it is  $\sum \epsilon_j dn_j$  equal to 0 since  $\sum \epsilon_j dn_j = 0$  why  $\epsilon_j$  is fixed right the energy of  $j$ th level is fixed energy of  $\epsilon_j$  which is energy of  $j$ th level that cannot change right for each level the energy is fixed this is fixed or constant. Now if this is fixed then  $\sum \epsilon_j dn_j$  has to be equal to 0 right now you have then you have  $dU$  equals to  $\sum \epsilon_j dn_j$  which is equal to summation of  $\epsilon_j dn_j$  which is equal to 0 and  $dN$  equals to 0 so  $dN$  which is equals to 0 because  $dN$  is  $\sum dn_j$  is basically  $\sum dn_j$  so  $dN$  is nothing but some  $dn_j$  which is again equal to some  $dn_j$  has to be equal to 0 why because  $n_j$  is constant total  $n$  cannot change and total  $U$  cannot change so this is also equal to 0 so now let us understand the so as we know from our thermodynamic macroscopic or phenomenological thermodynamics that for  $S$  of an isolated system at equilibrium  $dS$  has to be equal to 0 apart there are constraints here  $dS = 0$  for fixed energy fixed energy means now I can write fixed energy as if I think of fixed energy fixed energy means  $dU = 0$  is the constraint and also fixed mole number right mole number of the species right how many let  $r$  species be there but the total mole number is constant that cannot change so because it is an isolated system so you are telling  $dN = 0$  and  $dU = 0$  are the constraints and  $dS$  has to be also equal to 0 for the systematic equilibrium for the isolated systematic equilibrium  $dS$  has to be equal to 0 that is the first condition right extreme on condition is the first condition so  $dS$  has to be equal to 0 but these constraints are also there that  $dU$  the total energy is fixed that means  $dU = 0$  and  $dN = 0$  now use a technique which is called a Lagrange multiplier technique so where you are telling that  $dS$  plus with these constraint that  $dN = 0$  so this we are replacing with an  $\alpha dN$  and  $\beta dU$  where  $\alpha$  and  $\beta$  are Lagrange multipliers and we will try to

find out quarter alpha and beta right so this is your equation if you use the Lagrange multiplier method you have d s plus this constraint equations are there right this is like Lagrange multiplier times the first one of the constraints like d n equal to 0 and another Lagrange multiplier times the another constraint that is d u equal to 0 now if you write that then basically you already know what is d s right you know already this so you are using this d s so as you know that is only so you have l n n j by n d n j right that is what the minus k b l n n j by n d n j so this is nothing but your d s and this is nothing but your d n and this is nothing but your d u right so if you have that as you can see all of them have a summation of j right and j basically tells you the different species right

$$\begin{aligned}
 & -k_B \sum_j \ln\left(\frac{n_j}{N}\right) dn_j + \alpha \sum_j dn_j + \beta \sum_j \epsilon_j dn_j = 0 \\
 \Rightarrow & \sum_j \left[ -k_B \ln\left(\frac{n_j}{N}\right) + \alpha + \beta \epsilon_j \right] dn_j = 0
 \end{aligned}$$

What does this mean?

$$\begin{aligned}
 & -k_B \ln\left(\frac{n_j}{N}\right) + \alpha + \beta \epsilon_j = 0 \\
 & \quad j = 1, 2, \dots, r \\
 \therefore & k_B \ln\left(\frac{n_j}{N}\right) = \alpha + \beta \epsilon_j \\
 \ln\left(\frac{n_j}{N}\right) &= \frac{\alpha}{k_B} + \frac{\beta}{k_B} \epsilon_j \\
 \frac{n_j}{N} &= e^{\left\{ \frac{\alpha}{k_B} + \frac{\beta}{k_B} \epsilon_j \right\}}
 \end{aligned}$$

$$\begin{aligned}
 e^A e^B &= e^{A+B} \\
 \frac{n_j}{N} &= e^{\alpha/k_B} e^{\beta \epsilon_j / k_B} \\
 \text{Note } \sum_j \frac{n_j}{N} &= x_1 + x_2 + \dots + x_r \\
 &= 1 \\
 \sum_j e^{\alpha/k_B} e^{\beta \epsilon_j / k_B} &= 1 \\
 \text{or } e^{\alpha/k_B} &= \frac{1}{\sum_j \left( e^{\beta \epsilon_j / k_B} \right)}
 \end{aligned}$$

so the entire term all these terms I can club together with this d n j because it can be like d n 1 is independent d n 2 is independent like that only one dependent component right d n 3 is independent and such that the sum of all these different species add up to the sum of mole numbers of all these different species add up to n so if I have this I can write it separately like some j and inside some I am writing minus k b l n so as you can see minus k b l n n j by n right that is for each j this expression works right minus k b l n n j by n plus alpha plus beta x n j d n j equal to 0 so now if it is yeah so this means that means for each j for each species this equation holds right minus k b this equation holds for each species right so whether j is 1 j is 2 j is r right these are different species right so if that is so then k b l n n j by n equals to alpha plus beta x n j right alpha plus beta so because this is minus so I am taking it on the other side then it becomes and I rewrite so I get k b l n n j by n equals to alpha plus beta x n j so now if I write so we can now rearrange I can take k b this side and if I say take k b this side it becomes alpha by k b and beta by k b of sin j so n j by n if I tell n j by n n j is the number of mole number of species j and the ratio of mole number of species j to the total mole number or total number of atoms right total mole

number is  $n$  so  $n_j$  by  $n$  is nothing but  $x_j$  right which is equals to  $e$  to the power  $\alpha$  by  $k_B$  plus  $\beta \epsilon_j$  but still I don't know what is  $\alpha$  what is  $\beta$  right now as you know that  $e$  to the power  $a$  times  $e$  to the power  $b$  is nothing but  $e$  to the power  $a + b$  right and since you know that you can write this as  $n_j$  by  $n$  equals  $2$  so what I am doing is this summation I am separating it out I get  $e$  to the power  $\alpha$  by  $k_B$  there is one term  $e$  to the power  $\beta \epsilon_j$  by  $k_B$  that is something now you see as you can see that summation  $n_j$  by  $n$  is equal to  $1$  right so that means if I do summation of  $n_j$  by  $n$  is equal to  $1$  so similarly here the summation so I have written  $i$  but if you whether I write  $i$  or  $j$  as the initial index it does not really matter right so I can write  $x_n$  and I can put  $j$  if you want if you insist I can do that but you can also use  $i$  right whether I am using  $i$  or  $j$  it does not matter because it is an index so  $x_n$  and  $e$  to the power  $j$  equal to  $1$  right to be consistent I have used the same index this index notation  $j$  right so if I use the same index  $j$  what I get is  $e$  to the power  $\alpha$  by  $k_B$  times  $e$  to the power  $\beta \epsilon_j$  by  $k_B$  equal to  $1$  when it is summed over all the  $j$  species right or we can write  $e$  to the power  $\alpha$  by  $k_B$  see it is independent of  $j$  right it has no  $j$  so  $e$  to the power  $\alpha$  by  $k_B$  I can take it out of the summation sign which is basically nothing but  $1$  by summation again I can just for consistency so that you do not get confused I can use  $j$  here and write  $j$  here right so this is what is established right  $e$  to the power  $\alpha$

Define partition function  $p$  (static 'p')

$$p = \sum_i e^{\frac{\beta \epsilon_i}{k_B}}$$

$$e^{\alpha/k_B} = \frac{1}{p}$$

$$\frac{n_j}{N} = e^{\alpha/k_B} e^{\frac{\beta \epsilon_j}{k_B}}$$

$$= \frac{1}{p} e^{\frac{\beta \epsilon_j}{k_B}}$$

$$dS = -k_B \sum_i \ln \left( \frac{n_i}{N} \right) dn_i \quad \ln e^x = x$$

$$= -k_B \sum_i \ln \left( \frac{1}{p} e^{\frac{\beta \epsilon_i}{k_B}} \right) dn_i$$

$$= -k_B \sum_i \left( \frac{\beta \epsilon_i}{k_B} - \ln p \right) dn_i$$

$$= -\beta \sum_i \epsilon_i dn_i + k_B \ln p \sum_i dn_i$$

$$= \underline{-\beta dU} + \underline{k_B \ln p dN}$$

but still I do not know what is  $\beta$  what is  $\alpha$  but now comes here so we define some partition function ok we define some partition function which is number of you will let us see that is basically again the number of the probability of finding an accessible microstate so this  $p$  and this is sum over all  $i$  as you can see or all species right so basically again I am using  $i$  here so I have been using so  $j$  or  $i$  does not really matter right so I have used  $i$  here so summation over  $i$  equals to  $1$  to  $e$  to the power  $\beta \epsilon_i$  by  $k_B$  right so that is the thing so if you see this is if you got  $\alpha$  by  $k_B$  which is  $1$  by  $p$  right so  $n_j$  by  $n$  because if you got  $\alpha$  by  $k_B$  into  $e$  to the power  $\beta \epsilon_i$  by  $k_B$  which is basically  $1$  by  $p$  because if you got  $\alpha$  by  $k_B$  is  $1$  by  $p$  right according to this relation this relation so  $1$  by  $p$   $e$  to the power  $\beta \epsilon_i$  by  $k_B$  or  $\beta \epsilon_j$  by  $k_B$  so if it is  $n_j$  by  $n$  so so I am using  $n_j$  by  $n$  so we have to be consistent left hand side and right hand side the index the notation the index that we use should be the same right if I use  $j$  on left hand side it

should be  $j$  on the right hand side but still I do not know  $\beta$  now now comes the interesting part so I am using here instead of  $z$  I will use this partition function I am using a rotation which is basically like italicized  $d$  right that is your partition function and I have defined partition function so it is just a function of these different states of energy right these are all the accessible energy states  $\epsilon_i$  are the accessible all the energy states  $i$  equals to 1 to  $r$  you have  $r$  energy states that are available so you have  $r$  energy states that are available right so this is something that we have to understand here so when I tell  $\epsilon_j$   $\epsilon_j$  is the energy of this different levels of energy right you have say  $r$  levels you can have any number of levels and you have this many levels of energy right so if you have this partition function okay if you have this partition function which is basically  $e^{-\beta \epsilon_i}$  to the power  $\epsilon_i$  by  $k_B$  you just think of this as if you think of this here so you have this equation this equation yeah this equation so this is the equation that I was talking about so you have this equation where  $\ln Z$  equals to  $-\beta$  times  $\sum_{i=1}^r \epsilon_i e^{-\beta \epsilon_i}$  and I am defining  $Z$  to be  $\sum_{i=1}^r e^{-\beta \epsilon_i}$  as my partition function right as my partition function I will give the significance of partition function you will see soon see later the physical significance of that so now if you see that you have  $dS$  equals to  $-k_B$  means I am just rewriting it  $\ln \frac{1}{p}$   $e^{-\beta \epsilon_i}$  by  $k_B$   $d$  and  $i$  now be very careful here yeah so now basically you can write this as  $-k_B \beta \epsilon_i$  because this is a  $\ln$  of  $1/p$  so  $\ln$  of  $1/p$  is  $-\ln p$  right and because  $\ln$  of 1 is 0 and  $\ln$  of  $e^{-\beta \epsilon_i}$  to the power  $\epsilon_i$  by  $k_B$  is  $-\beta \epsilon_i$  itself right logarithm of if I take the natural logarithm of  $e^{-\beta \epsilon_i}$  is basically  $-\beta \epsilon_i$  right so basically that's what I have written so  $\beta \epsilon_i$  by  $k_B$  and this is  $d_i$  now

So you can see here if I rearrange a little bit you will see the  $k_B$   $k_B$  cancels so you have you have and there is a  $d_i$  here are you seeing that so here there is a  $d_i$  here so the  $dS$  right  $dS$  was expressed in terms of  $d_i$  so I am using that  $dS$  is expressed as in terms of  $d_i$  so if I do this little manipulation what I will see is this this is  $k_B$  and this is  $k_B$  so this goes on so basically  $k_B$  so this becomes  $-\beta \epsilon_i d_i$  and then  $k_B \ln p$  right there is an  $\ln p$   $\mu$  so why because there is a minus sign here is minus sign so plus  $k_B \ln p$  summation  $d_i$  so which is basically equals to  $\sum \epsilon_i d_i$  is nothing but  $du$  right you remember so it is basically  $du$  and summation  $d_i$  is nothing but  $dn$  so you see you can write this as  $dS$  equals to  $-\beta du$  plus  $k_B \ln p$   $d$  that  $p$  is the partition function and partition function is defined as  $\sum e^{-\beta \epsilon_i}$  so basically it is a summation right this is a summation over all the energy levels  $\beta \epsilon_i$  by  $k_B \ln$ .

Microscopic (particle-based)

$$dS = -\beta dU + k_B \ln p dN \quad \text{--- (micro)}$$

Macroscopic

$$S = S(U, V, N) \quad + \quad dU = T dS - p dV + \mu dN$$

$$dS = \left( \frac{\partial S}{\partial U} \right)_{V, N} dU + \left( \frac{\partial S}{\partial V} \right)_{U, N} dV + \left( \frac{\partial S}{\partial N} \right)_{S, V} dN$$

$$= \frac{1}{T} dU + \frac{p}{T} dV - \frac{\mu}{T} dN \quad \text{--- (macro)}$$

Compare:

$$\beta = -\frac{1}{T} \quad -\frac{\mu}{T} = k_B \ln p$$

$$\mu = -k_B T \ln p$$

Now so you got a equation a fundamental equation in terms of particles right distribution of particles in terms of distribution of particles in the fundamentals levels we have got now a microscopic description of change in entropy right in terms of partition function so instead of using z I will use p here okay so  $\ln p$   $k_B \ln p$   $dN$  and  $ds$  equals to so note that here I am using a p I will tell you why I am not using z in fact you can use z some people use z in books but when we use z as the partition function there is some other concept called ensemble that I will come to okay so here I haven't yet given the concept of ensemble but only thing that I have given is there are discrete energy levels which are occupied by particles of different kinds right so particles can occupy different energy levels and the different energy levels have different discrete energies like  $\epsilon_0$   $\epsilon_1$   $\epsilon_2$  and based on that I have defined the partition function right so instead of using a ensemble averaged energy so I will come to what is an ensemble microscopic ensemble I am basically giving you this idea but it is actually equivalent these are all equivalent the definitions are all equivalent is what you will see so this what I have established now just by doing a little bit of algebra is that there is a microscopic fundamental equation where  $ds$  is expressed in terms of  $s$  is so where  $ds$  again is an exact differential and it is written in terms of  $du$  and  $dn$  right so  $s$  is a function of  $u$  remember we haven't used  $v$  here because so this is a first approximation so we haven't used any term that represents  $dv$  so but all said and done if we just use this so this basically tells you that  $s$  is a function of  $u$  as well as  $n$  right and it's also has a coefficient of minus beta and in this case it is  $k_B \ln p$  now macroscopically we know that  $ds$  equals to  $1/T du$  right we have done this several times you can also from the combined statement of first and second laws you can also derive it right and you will see that  $\partial s / \partial u$  is nothing but  $\partial u / \partial s$  is  $T$  so  $\partial u / \partial s$  is  $T$  but  $\partial s / \partial u$  is  $1/T$  and then  $\partial s / \partial v$  is  $p/T$  and  $\partial s / \partial n$  is  $-\mu/T$  right we have we can also derive it from here so that is coming from the macroscopic description of phenomenological thermodynamic description now if you compare the

microscopic and the macroscopic description of the macroscopic form of the fundamental equation in the microscopic form right of these two equations where this is also ds this is also ds the same ds is what we are talking about for an isolemic system now if you can see beta basically becomes as you can see minus beta is 1 by T or beta equal to minus 1 by T and minus mu by T is k\_B ln partition function right k\_B ln physically size p so k\_B logarithm of the partition function and mu is nothing but minus k\_B T minus k\_B T ln right if minus mu by T is this so mu becomes minus k\_B T ln p right so p is now basically becoming as you can

The image shows a handwritten derivation on a blackboard. At the top, it defines the partition function  $\mathcal{p} = \sum_i e^{-\frac{\epsilon_i}{k_B T}}$  and identifies  $\beta = \frac{1}{T}$ . Below this, it gives the expression for the number of particles in state  $i$ ,  $\frac{n_i}{N} = \frac{1}{\mathcal{p}} e^{-\epsilon_i/k_B T}$ . The entropy  $S$  is then calculated using the Boltzmann formula  $S = -k_B \sum_i n_i \ln \left( \frac{n_i}{N} \right)$ , which is simplified to  $S = -k_B \sum_i n_i \ln \left[ \frac{1}{\mathcal{p}} e^{-\frac{\epsilon_i}{k_B T}} \right]$ . A note  $\sum_i n_i = N$  is written to the left. The entropy is further simplified to  $S = \frac{U}{T} + k_B N \ln \mathcal{p}$ . Finally, the partition function is expressed as  $\mathcal{p} = \sum_i e^{-\epsilon_i/k_B T} = \frac{1}{T} U + k_B \ln \mathcal{p} \sum_i n_i$ , which is then rearranged to  $\mathcal{p} = \frac{U}{T} + k_B N \ln \mathcal{p}$ .

see here is the the partition function the partition function that we define is now now instead of beta I am putting minus 1 by T so this becomes minus epsilon i by k\_B T right minus epsilon by k\_B T so n\_i by n that is the number of species the mu is the number of species that is the number of species i related to the total number because 1 by p right this p is partition function e to the power minus epsilon i by k\_B T right now since I know beta I can also find out we know alpha right we also know the partition function in terms of the energy levels right in terms of the in terms of the discrete energy levels or discrete energies that this particular particles can occupy right it can occupy different types of energy levels like like epsilon 0 epsilon 1 epsilon 2 and so on and so forth right these are discrete energy levels that a particle that the system of particles can occupy right it so I will show you how it is connected to the ensemble definition in statistical mechanics so now all of these things have been established so S is minus k\_B n\_i ln n\_i by n which is basically coming to B so here which is basically coming to B k\_B n\_i ln n\_i by n so minus k\_B n\_i ln 1 by p so this would be 1 by p it would be 1 minus epsilon i by k\_B T so if you if you if you just follow this if you follow that derivation you will see you have n\_i and then there is epsilon i by k\_B T and ln p and if you look at this if you you will see k\_B times n\_i ln i epsilon i epsilon n\_i epsilon i is u so you have 1 by T u and k\_B k\_B cancels so 1 by T u plus k\_B ln partition function summation of i n\_i which is basically now summation again over all different kinds of species this is equal to T so this becomes S equals to again I am writing u by T plus k\_B N and see if n is Avogadro number then k\_B n is nothing but R ln this is right this is and p is basically sum of e to the power minus epsilon i by k\_B well epsilon i is an energy that is

accessible by the particles right it is a and it is summed over all i's that are possible right these i's are the different discrete energy levels that the particles in the system can operate now as you know that the particles in the system you know S as a function of u by T and all so basically F as you know is Helmholtz free energy right this is Helmholtz free energy F equals to u minus T right it is u minus T so then S is this right S is this this is what I have we just proved right now

The image shows two panels of handwritten mathematical derivations on a dark background.

**Left Panel:**

- Top line: Helmholtz free energy  $F = U - TS$
- Second line:  $S = \frac{U}{T} + k_B N \ln p$
- Third line:  $\therefore F = U - T \left[ \frac{U}{T} + k_B N \ln p \right]$
- Fourth line:  $= -N k_B T \ln p$
- Fifth line:  $dF = -S dT - P dV + \mu dN$
- Sixth line:  $S = - \left( \frac{\partial F}{\partial T} \right)_{V, N}$

**Right Panel:**

- Top line:  $S = - \left[ \frac{\partial}{\partial T} (-N k_B T \ln p) \right]$
- Second line:  $= N k_B \ln p + N k_B T \left( \frac{\partial \ln p}{\partial T} \right)_{V, N}$
- Third line:  $U = F + TS$
- Fourth line:  $= -N k_B T \ln p + T \left[ N k_B \ln p + N k_B T \left( \frac{\partial \ln p}{\partial T} \right)_{V, N} \right]$
- Fifth line:  $= N k_B T^2 \left( \frac{\partial \ln p}{\partial T} \right)_{V, N}$

you can just express F right you can express F so it is minus u minus T and this is the S definition so this becomes minus n k B T and p and again this p this partition function is very important because partition function is basically giving you the number of accessible the sum the number of all the accessible microstates right for a given for the most probable macrostate so as a result p in some so this basically gives you this partition function is now giving you the connection between see physically n k B n k B is R right which is gas constant and when n is our number T is temperature F is Helmholtz free energy these are all phenomenological F is phenomenological n is phenomenological T is also but p p is coming from the distribution of particles right distribution of particles in the across different energy levels right so it is like probability of finding a microstate so it is like you can think of this as a probability of finding a given microstate right so I will come to that it is not exactly the probability it is basically the sum of all the accessible microstates. So now you have d F which is minus is T minus p dV plus mu dn right we have done it we got it from previously right we have derived it we have also shown that F equal to minus T S and F is basically using the conjugate variable T right S instead of S we are using the conjugate variable T and we have also established that for there we can write d F is this right and therefore S is nothing but minus del F del T V n right V n n. So first of all F I got a connection now F which is a permanent potential defined phenomenologically right we placed on mu minus T S now we got a relation with the partition function. Similarly I got S and S again can be written as n K B ln p right again this p don't confuse this p so plus n K B T del ln p del T. Okay so and then from here we can basically write so u equals to F plus T S right from the definition so we can write in you will get that it is n K B T

squared how because you have F plus T S you know the F right you know F and that is what I have written and then you have T S right and that we have also written and see all of all process p or partition function right which basically gives you the microscopic description of particles arranged in different energy levels.

$$c_v = \left( \frac{\partial U}{\partial T} \right)_{V,N}$$

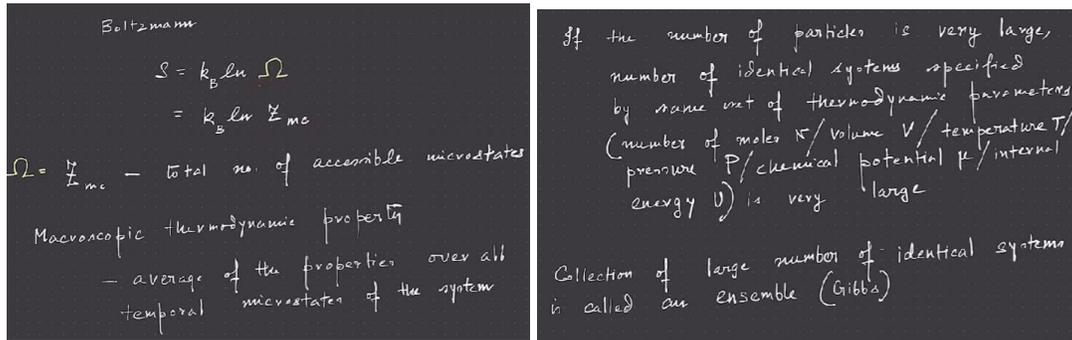
$$= 2 N k_B T \left( \frac{\partial \ln p}{\partial T} \right)_{V,N} + N k_B T^2 \left( \frac{\partial^2 \ln p}{\partial T^2} \right)_{V,N}$$

In all these derivations, we are using discrete energy levels  $\epsilon_i$  that are accessible by particles

So similarly I can get  $\Delta C_V$  which is  $\Delta u / \Delta T$  which again I get from here so once I know the partition function of a microscopic system right which contains a large number of particles we basically get all the phenomenological or macroscopic thermodynamic quantities based on this partition function. So now it becomes very very useful that to now it becomes very evident that these are all connected so in all derivations we are using discrete energy levels  $\epsilon_i$  that are accessible the particles right and that is where partition function comes it is the sum of  $e^{-\epsilon_i / k_B T}$  to the power minus so it basically gives you some sort of a distribution a probability distribution of finding this different accessible microstates ok which are occupying this discrete energy levels. Now as you know our distribution so this is something that we have to understand and we have established every time so this is like you have a distribution of  $n_1$  atoms of type 1  $n_2$  atoms of type 2 and  $n_r$  atoms of type 3 right so there are such say total  $n$  particles and you have  $n_1$  particles of type 1  $n_2$  particles of type 2 and  $n_r$  particles of type  $r$  and all of these particles are occupying discrete energy levels  $\epsilon_i$  right and with the fixed so remember when I am talking about this distribution of particles we are telling that we have to describe that ok so this is one microstate so basically I am telling  $n_1$  so I am telling for example  $n_1 n_2 n_r$  they are occupying this  $\epsilon_1 \epsilon_2$  and so on so it can be  $\epsilon_i$  whatever how many energy levels are there say there are 100 energy levels so these cannot apply so such that the total  $u$  does not change so this basically gives you this basically gives you this distribution that this many balls in this box and this many balls in this box defines a state or a macrostate right so this  $c$  is a macrostate for a



will have the greatest number of microstates so there can be different states of a system that is defining the macrostate so for each macrostate there will be some number of microstates now that macrostate which has the maximum number of microstates is the one which will determine the entropy of the system that macrostate that will have the maximum number of microstates is the one or is that which will determine the entropy of the system and that is Boltzmann's Hypothesis right



so that's why he wrote that  $S$  equals to  $k_B \ln \Omega$  right so this  $\Omega$  now you see some here it is written as  $\Omega$  and some books also write it as  $Z$  where  $Z$  is called a micro canonical  $Z$  corresponds to micro canonical ensemble now you will see what does this mean right so I will come to that so it is only thing this  $\Omega$  or  $Z$  that you have this is the partition function for a micro canonical ensemble the physical meaning is that the  $\Omega$  or  $Z$  whatever name you give it is basically giving you the total number of accessible microstates because  $\Omega$  corresponds to  $\Omega_{max}$  right that is the one which is most likely now this  $Z$  or  $\Omega$  right so this is the same  $Z$  is same as  $\Omega$  and that basically gives the total number of accessible microstates why I am using these two notations because there have been because if you look at a statistical mechanics book then most of the times they will use this notation of  $Z$  okay instead of  $\Omega$  okay so as a result I just to to to to to give parity I am telling that whatever different notations are used I am using both and I am just telling that this is the same right but here this  $Z$  stands for micro canonical ensemble what does this mean I will just come to that so what is macroscopic thermodynamic property this is also we have to understand there is average of properties over all temporal microstates of the system for a given macrostate so macrostate and state are the same right we have talked about that so average of the property so you have but one macrostate corresponds to a many number huge number of microstates right and each of these microstates can appear at some instant of time right so this this if I take this temporal distribution of all the microstates and for each microstate I have a property and I take an average of that of that property and that average is going to give me the value of the macroscopic thermodynamic property right that's the idea so see this is another thing when we look at the statistical thermodynamics we are talking about number of particles that is very very large right very large so so if the number of particles is very large number of identical systems with the same set of thermodynamic parameters which

can be number of moles or volume or temperature or pressure or some chemical or fixed chemical potential or internal energy that also will be very large so basically if the number of particles is large number of identical systems basically identical in terms of the macroscopic thermodynamic properties so identical system or identical system simple state so if the number of particles is very large then the identical systems or identical systems that will have the same set of thermodynamic properties will be very large and this collection of large number of identical systems is called an ensemble right so it is basically given by Gibbs the definitions came by Gibbs so collection of a large number of identical systems which are the same thermodynamics same set of thermodynamic parameters this is like the same set of thermodynamic parameters this collection of large number of identical particle systems is called an ensemble. So one of the ensembles that we have talked about and the easiest ensembles that we talked about means easiest to understand is the one which is micro canonical ensemble where micro canonical right so this is the MC that we talked about right so we will find something called ZMC which is nothing but.

Different types of thermodynamic systems based on specified thermodynamic conditions

1. Microcanonical Ensemble: Isolated simple systems with constant internal energy  $U$ , constant volume  $V$  and constant number of particles  $N$

$T, P, \mu$  can fluctuate in each system as well as from system to system

$$\Omega_{mc} = \Omega$$

Canonical Ensemble: A collection of closed simple systems bounded by a thermal reservoir at constant temperature  $T$ , constant volume  $V$  and constant number of particles  $N$

$U, P, \mu$  can vary in each system and from system to system

Grand canonical ensemble: Open simple systems bounded by a thermal reservoir and a chemical reservoir

fixed parameters:  $T, V, \mu$

Variable parameters:  $U, P, N$

Microcanonical ensemble:

Partition function  $\Omega_{mc}$  is the total no. of accessible microstates having same energy  $U$ , same volume  $V$  and same no. of particles  $N$

$$\Omega_{mc} = \Omega \text{ (total no. of accessible microstates)}$$

Probability of accessing  $i^{\text{th}}$  microstate

$$P_i = \frac{1}{\Omega_{mc}}$$

So this micro canonical ensemble tells you what it tells you isolated so it is basically an isolated simple system with constant internal energy  $U$  and constant volume  $V$  and constant number of particles  $N$ . So it is so a micro canonical ensemble points to an isolated simple system with a constant internal energy  $U$  constant volume  $V$  and constant mole number a constant number of particles  $N$  right so what can fluctuate  $U$  you cannot  $U$  is fixed  $V$  is fixed and  $N$  is fixed so this  $T$  can fluctuate pressure can fluctuate chemical potential can fluctuate in each system as well as from system to system right from one system to the

other chemical potential can fluctuate pressure can fluctuate temperature can fluctuate right so this micro chemical ensemble is characterized by the partition function  $ZMC$  which is nothing but  $\Omega$  in Boltzmann hypothesis right KBLN  $\Omega$ . Now canonical ensemble canonical ensemble is where we fix the temperature so our collection of closed simple systems remember here it was a collection it is an isolated system right cannot exchange energy or matter with the surroundings right energy exchange is also not permitted but here we are talking about fixing the temperature then immediately we are talking about a reservoir right so there is a reservoir so what we are doing is canonical ensemble is the one in which a collection of closed simple systems bounded by a thermal reservoir at constant temperature  $T$  right it is bounded it has to be bounded by a thermal reservoir at constant pressure  $P$  constant volume  $V$  and constant mole number of particles  $N$  but you see here the internal energy the pressure or chemical potential they can vary in each system from system to system so  $\mu$  can vary  $P$  can vary  $U$  can vary but  $T$  cannot because  $T$  it is in the system is in contact it is a closed system in contact with the thermal reservoir right so this is what is called a canonical. And then you have the special type of ensembles which are used for determining many a times to determine phase diagrams so these are called grand canonical ensembles so grand canonical ensembles are one those are open system simple system that means mass transfer is permitted that means particles can come in the number of particles can increase or decrease right these are the variable parameters  $U$   $P$  as well as  $N$  but what is fixed is  $\mu$  see it is having a thermal reservoir as well as a chemical reservoir chemical reservoir means it will have the same chemical potential as the system right so fixed chemical potential fixed volume and fixed temperature but you can vary  $P$  can vary and  $N$  can vary and this becomes very very interesting and important when you have multi component system because I can fix the chemical potential and I see that how many particles are getting how the particles are getting distributed and based on the particle distribution of different species particles of different species how they are distributed we can basically arrive at phase diagrams ok or phase stability diagrams in multi component systems. So there is also this so as I told you so this each of these have a we define some partition function to characterize this ensembles right I am going very I am going to go very fast here because I do not want to spend a lot of time here what I have established here is that with this partition function known ok which basically gives you some sort of the total number of accessible microstates right so in the micro canonical ensemble it is the total number of accessible microstates with the same energy  $U$  same volume  $V$  and same number of particles  $N$  right so if I fix the energy if I fix the volume and fix the mole number then the number of accessible microstates is given by  $ZMC$  right that is partition function and as I told you once you define this partition function you can by the way the partition function that we defined that  $P$  is a partition you will soon see that this very similar to the partition function that is used for canonical ensembles right so  $ZMC$  is  $\Omega$  which is the micro-calculable which is total number of accessible microstates so  $\Omega$  or  $ZMC$  both give you the total

number of accessible microstates which have the same energy  $U$  same volume  $V$  and same number of particles  $N$  and probability of accessing this  $i$ th microstate is given by  $1/Z$  so it is a reciprocal of the partition function the probability is just the reciprocal of this partition function right so we can write  $S$  the same thing this is this is nothing but Boltzmann's hypothesis.

$$\begin{aligned}
 S &= k_B \ln Z_{mc} \quad (\text{Boltzmann Hypothesis}) \\
 Z_{mc} &= Z_{mc}(U, V, N) \\
 dS &= \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN \\
 \left( \frac{\partial S}{\partial U} \right)_{V, N} &= k_B \left( \frac{\partial \ln Z_{mc}}{\partial U} \right)_{V, N} \\
 - \frac{\mu}{T} &= \left( \frac{\partial S}{\partial N} \right)_{U, V} = k_B \left( \frac{\partial \ln Z_{mc}}{\partial N} \right)_{U, V}
 \end{aligned}$$

So as you can see here we can write you have this  $dS$  so the same  $S$  and  $dS$  is  $1/T$  by  $dU$ ,  $P/T$  by  $dV$  and we have already done that we have established this so basically now we can basically write everything in terms of the ZMC or partition function and that partition function gives you the connection between the particle or atomistic description of matter and the phenomenological description of matter which is basically given by the macroscopic thermodynamic parameters. Okay so similarly we can do this canonical ensemble so as you can see you talked about we just before that we talked about  $P$  right what we told is  $P$  is the particle or atomistic where  $\epsilon_i$  is the energy of the  $i$ th energy right here also we are talking about these are nothing but the energy of microstate right so this is like these are they are basically equivalent right they are basically equivalent only thing I just want to tell you that the same thing basically however this  $U_i$  is energy of microstate  $i$  okay that microstate contains has a collection of particles and these particles are so basically instead of talking about a single different energy levels what I am talking about is like you have  $U_i$  is energy of microstate  $i$  which can have say  $n_1$  particles in means which can have some particles in energy level  $\epsilon_1$  and energy level  $\epsilon_2$  some other particles so basically  $U_i$  and  $\epsilon_i$  are basically one and the same right they are basically one and the same and now if you have that then the probability of finding the  $i$ th microstate is basically given by this right which is  $e^{-\beta U_i} / Z$  right and you can basically write  $U$  as  $\sum_i U_i p_i = -k_B \ln Z$  right so and  $\beta$  is  $1/k_B$  so you can see that you can go through that I am not going to discuss all of these in detail but what I am trying

to say is that once you have this established you get back you can basically go from particular particle based description to the macroscopic description and come back from there so that is possible so we have this very special ensemble that is the grand canonical ensemble which is also based on this grand potential which we have not discussed previously so grand potential is the same it is one thermodynamic potential so we go into the macroscopic thermodynamics which is basically given by so for example G is H minus TS F is U minus TS or right so there are these different thermodynamic potentials that we can define right where we are replacing where we are doing the Lagrange transform that S equal to VN we are basically writing as F equals to some so we are trying to replace so U is VN say for example I have U S VN and from there I can go to G T P N right where S is replaced by the conjugate variable T and V is replaced by the conjugate variable T right so G is basically H minus TS or U plus PV at this energy minus P S. So this is the way we are going to do it. Now similarly I can write a grand potential where I am replacing N by its conjugate variable which is mu right so phi is U minus TS minus mu M which is also given by Landau free energy omega so this d phi is basically minus V d phi minus S d T minus N d mu so note that it is minus N d mu and where dA dU is dDS minus V dV plus mu VN so it in phi is a Lagrange transform of U where N is replaced by slope right where which is basically mu. Slope with respect to the so U del U del N right del U del N if we fix S and V so is basically mu.

Canonical ensemble:  $\rho = \sum_i e^{-E_i/k_B T}$

$$Z_c(T, V, N) = \sum_i e^{-\frac{U_i}{k_B T}} = \sum_i e^{-\beta U_i}$$

$U_i$  - Energy of microstate  $i$   $\beta = \frac{1}{k_B T}$

$$P_i = \frac{e^{-U_i/k_B T}}{Z_c(T, V, N)} = \frac{e^{-\beta U_i}}{Z_c}$$

$$U = \langle U_i \rangle = \sum_i P_i U_i = \frac{\sum_i e^{-\beta U_i} U_i}{\sum_i e^{-\beta U_i}} = \frac{\sum_i \frac{\partial}{\partial \beta} (e^{-\beta U_i})}{\sum_i e^{-\beta U_i}} = \frac{\frac{\partial}{\partial \beta} \sum_i e^{-\beta U_i}}{\sum_i e^{-\beta U_i}} = \frac{\partial \ln Z_c}{\partial \beta}$$

$$d \ln Z_c = \frac{\partial \ln Z_c}{\partial \beta} d\beta +$$

$$= -U d\beta$$

$$U d\beta = d(\beta U) - \beta dU$$

$$\therefore d(\ln Z_c) = -d(\beta U) + \beta dU$$

$$dU = \frac{1}{\beta} d(\ln Z_c) + \frac{1}{\beta} d(\beta U)$$

$$dU = T dS$$

So N goes to mu and S goes to T so this is the relation that I wanted to tell you so you have U as a function of S VN but here phi as a function of T V so S has been replaced by T right so here the Lagrange transform is replaced S is replaced by T and V remains V and N is replaced by mu right so minus S is now if I write in terms of grand potential so minus S is del phi grand potential del phi so this phi is special right we have this sign so the way we write the grand potential energy is this right so this is one notation we can use different other notation so minus N as you can see it is the derivative of the grand potential energy with respect to mu and that will give you N and that is why it becomes very very useful when it comes to understanding or evaluating or obtaining phase diagrams right. So when

we write  $\Xi$  or this  $\Xi$  is nothing but the grand potential partition function so grand can also be partition function  $\Xi$  is the partition function means it is called grand canonical

Grand canonical ensemble  $U(S, V, N) \rightarrow \Phi(T, \mu, N)$

System with fixed  $V$  in contact with both thermal (energy) and chemical (particle) reservoir

Grand potential (Landau potential)

$$\Phi = U - TS - \mu N = \Omega_{\text{Landau}}$$

$$d\Phi = -PdV - SdT - Nd\mu$$

$$\therefore dU = TdS - PdV + \mu dN$$

$$N \rightarrow \mu$$

$$S \rightarrow T$$

$$U = U(S, V, N) \quad \Phi(T, \mu, N)$$

$$T = \frac{\partial U}{\partial S} \quad -S = \frac{\partial \Phi}{\partial T}$$

$$\mu = \frac{\partial U}{\partial N} \quad -N = \frac{\partial \Phi}{\partial \mu}$$

$$\Phi = U - TS - \mu N \quad U = \Phi + TS + \mu N$$

Grand canonical partition function

$$\Xi_G = \sum_i e^{-\frac{\Phi_i}{k_B T}}$$

$$= \sum_i e^{-\frac{(U_i - \mu N)}{k_B T}}$$

$$p_i = \frac{1}{\Xi_G} e^{-\frac{U_i - \mu N}{k_B T}}$$

$$\Phi = -k_B T \ln \Xi_G$$

$p_i$  - probability of appearance of microstate  $i$

$$S = -R \sum x_i \ln x_i$$

$$S = -k_B \sum p_i \ln p_i$$

$$p_i (\text{isolated}) = \frac{1}{\sum_{\text{mc}} (U, V, N)}$$

$$p_i (\text{closed}) = \frac{e^{-U_i/k_B T}}{\Xi_G(T, V, N)}$$

you see that here there is minus phi i right instead of minus U i you have minus phi i by k B T right here so minus phi i by k B T and which is basically can be written as U i minus mu N by k B T right and where phi is phi can be written as again this grand potential phi can be written as minus k B T and then  $\Xi$  right so this is what I just want to talk about that so and as you can see probability of appearance of microstate i you can write S right we have already established this like S equals to minus R sum x i ln x i so similarly I can write minus k B pi ln pi where pi is the probability of appearance of microstate right and pi isolated is basically given by 1 by ZMC pi close is given by e to the power minus u i by k B T by Z C right we have we have established all of this so now you have say a two state system so this is some application so if you have two states like two two energy levels are there

Two-state system -  $N$  particles Two energy levels  $\epsilon_0$  and  $\epsilon_1$

$$p = \sum_i e^{-\epsilon_i/k_B T}$$

$$= e^{-\epsilon_0/k_B T} + e^{-\epsilon_1/k_B T}$$

$$\frac{n_1}{N} = \frac{e^{-\epsilon_0/k_B T}}{p} \quad n_1 \rightarrow \epsilon_0$$

$$\frac{n_2}{N} = \frac{e^{-\epsilon_1/k_B T}}{p} \quad n_2 \rightarrow \epsilon_1$$

$$F = -Nk_B T \ln p$$

Let  $\epsilon_0 = \epsilon$   
 $\epsilon_1 = 2\epsilon$

$$p = e^{-\epsilon/k_B T} \left[ 1 + e^{-\epsilon/k_B T} \right]$$

$$\ln p = -\frac{\epsilon}{k_B T} + \ln \left( 1 + e^{-\epsilon/k_B T} \right)$$

$$F = -Nk_B T \left\{ -\frac{\epsilon}{k_B T} + \ln \left( 1 + e^{-\epsilon/k_B T} \right) \right\}$$

$$= N\epsilon - Nk_B T \ln \left[ 1 + e^{-\epsilon/k_B T} \right]$$

so basically you have energy level epsilon 0 and epsilon 1 then P as you can see you have only two energy levels epsilon 0 and epsilon 1 right so N 1 by N so if you have N 1 that is coming to so N 1 by so total number of particles is N ok where N 1 particles are going to epsilon 0 right and N 2 particles go to say epsilon 0 epsilon 1 now the first of all the partition from summation will have only two terms right which corresponds to epsilon 0 and epsilon 1 right so this is for a two state system now if you have that you know how N 1 is related to the total number of particles and N 2 is related to the total number of particles if you know P right where P is given by this right which is basically the same as Z m's now once you know that you can use the so if once you know that you know the F F is minus N k B T N L P right and P is the partition function here grand chronicle particle function now if you take 7 0 is epsilon and epsilon 1 is 2 epsilon basically you can use that and you can get into very useful relations for example just by knowing the partition function knowing the energy level so knowing the particle based description we can basically get right see we just have a particle based description or atomistic description and just based on the next description because there are two energy levels we can easily get back the Helmholtz free energy internal energy entropy and C V and so on so for example this is something that you can prove right you can prove in this two particle system two state system not two particle remember particles is N but the energy levels there are only two energy levels that are available now if the energy levels are like one is epsilon the other is two epsilon then basically you can prove that C V equals 2 so basically epsilon 0 here epsilon 0 equal to epsilon and epsilon 1 there are two so it is again for a two state system for a two state two state system two state means it has two energy levels and one is epsilon and the other is two epsilon then you can basically prove that right so this is something you can think of doing by yourself and to understand exactly all the concepts. Monoatomic gas we know for example argandian so these are all monoatomic gases and they are all non-monoatomic gases and then you have for example for one particle state if you have to define for one particle then you have to give its mass right for one particle you have to give the mass and the positions the position coordinates and the velocity coordinates if you give mass and velocity coordinates basically you give the momentum

coordinates. So you have if  $m v_x$   $m v_y$   $m v_z$  are the three momentum coordinates along  $x$   $y$  and  $z$  and you have also this  $x$   $y$  and  $z$  right these are the position coordinates. Now once you have that you can basically write the energy for one particle is half  $m v$  square which is half  $m v_x$  square plus  $v_y$  square plus  $v_z$  square ok.

Prove that

$$C_V = \frac{N \epsilon^2}{k_B T^2} \frac{e^{-\epsilon/k_B T}}{(1 + e^{-\epsilon/k_B T})^2}$$

*for a two-state system*

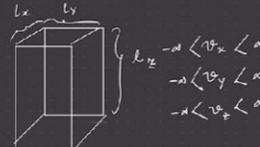
$$\epsilon_0 = \epsilon$$

$$\epsilon_1 = 2\epsilon$$

So this is for one particle. Now you can think of the gas as a container  $l_x$   $l_y$  and  $l_z$  is at the dimensions of the container but the velocity can go anywhere between minus infinity and plus infinity right.  $v_y$  also can go anywhere between minus infinity and plus infinity as long as it is finite and again  $v_z$  also is that. So then if I want to establish the partition function if you are canonical so this is the canonical partition function right  $Z$  and  $c$  or  $p$  then basically right this is a canonical partition function. So this is the canonical partition function if the power minus epsilon by  $k_B T$  right and but you have these integrals now you have  $d v_x$  plus there are six variables right  $d v_x d v_y d v_z d x d y d z$  right.

Monoatomic gas  
 Composed of identical single atoms  
 Example - Argon, Neon  
 One particle state -  $m, x, y, z, v_x, v_y, v_z$   

$$E = \frac{1}{2} m v^2 = \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2)$$

The gas is in a container  
  

$$Z_0 = \int_0^{l_x} \int_0^{l_y} \int_0^{l_z} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-E/k_B T} dv_x dv_y dv_z dx dy dz$$
  
 Canonical partition function

$$Z_0 = \int_0^{l_x} \int_0^{l_y} \int_0^{l_z} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{mv_x^2}{2k_B T} - \frac{mv_y^2}{2k_B T} - \frac{mv_z^2}{2k_B T}} dv_x dv_y dv_z dx dy dz$$

$$Z_0 = \int_0^{l_x} \int_0^{l_y} \int_0^{l_z} dx dy dz \int_{-\infty}^{\infty} e^{-\frac{mv_x^2}{2k_B T}} dv_x \int_{-\infty}^{\infty} e^{-\frac{mv_y^2}{2k_B T}} dv_y \int_{-\infty}^{\infty} e^{-\frac{mv_z^2}{2k_B T}} dv_z$$

$$V = \int_0^{l_x} \int_0^{l_y} \int_0^{l_z} dx dy dz$$

So now if I do this so you have say for example you have so the dimensions are  $l_x \times l_y \times l_z$  but the velocities can go from minus infinity to infinity minus infinity to infinity and minus infinity to infinity right but the dimensions are from 0 to  $l_x$  0 to  $l_y$  and 0 to  $l_z$  this is the partition function and here what are the energies we know for one particle one energy is minus  $m v_x^2$  square by  $2 k_B T$  and then minus  $m v_y^2$  so basically half  $m v_y^2$  square half right and you have epsilon by  $k_B T$  and epsilon as we know is half  $m v^2$  square which is this right. So again we are not considering any other interaction energy so we are just considering the so this is for a monoatomic and you can see we can think of this as a let us continue let us continue then we will see what is so basically you are looking at only the translation of kinetic energy right. So if I do this if I do this what I get is  $e$  to the power minus  $m v_x^2$  square by  $2 k_B T$   $dv_x$  and this is  $dv_x$  this is  $dv_y dv_z$  and this part of the integral is nothing but the volume right it is  $l_x$  times  $l_y$  times  $l_z$  right which is basically the volume of the container right in which the gas is enclosed. Now this part is the interesting integral where the integral goes from minus infinity to infinity is an infinite integral right with the limits at minus infinity and infinity to infinity. Now if you see if you if you if you write this is called a Gaussian integral right you have seen the Gaussian functions normal functions so you have like  $e$  to the power minus  $a x^2$  square  $dx$  the the minus infinity to infinity the answer is  $\sqrt{\pi/a}$  by a right  $a$  is the coefficient.

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\pi/a}$$

Gaussian Integral

$$a = \frac{m}{2k_B T}$$

$$\int_{-\infty}^{\infty} e^{-\frac{mv_x^2}{2k_B T}} dv_x = \sqrt{\frac{2\pi k_B T}{m}}$$

$$p = V \left( \frac{2\pi k_B T}{m} \right)^{3/2}$$

$$\ln p = \ln V + \frac{3}{2} \ln \left( \frac{2\pi k_B T}{m} \right) + \frac{3}{2} \ln T$$

$$U = N k_B T \left( \frac{\partial \ln p}{\partial T} \right)_V = N k_B T^2 \left( \frac{3}{2} \frac{1}{T} \right)$$

$$= \frac{3}{2} N k_B T$$

$$C_V = \frac{3}{2} N k_B$$

Now here the coefficient  $a$  is nothing but  $m$  by  $2 k_B T$  so minus  $e$  to the power minus  $m$   $v_x$  square by  $2 k_B T$   $dv_x$  is nothing but root over of  $2 \pi k_B T$  by  $m$ . So the partition function becomes  $V$  times  $2 \pi k_B T$  by  $m$  right root over and then again this is for the  $x$  component then for the  $y$  component as well as for the  $z$  component so you get  $2 \pi k_B T$  by  $m$  to the power  $3$  by  $2$  right  $2 \pi k_B T$   $m$  to the power  $3$  by  $2$ . So basically now if I have this expression I can take logarithm on both sides I get  $\ln p$  equals to  $\ln$  partition function equals to or logarithm of the partition function equals to logarithm of the volume plus  $3$  by  $2$   $\ln 2 \pi k_B$  by  $m$  plus  $3$  by  $2$   $\ln T$  right. So now we can basically write  $U$  which is basically  $N k_B T$  the  $\ln$  partition function  $\partial \ln p$  right we have proved this already so which is basically  $N k_B T$  square into  $3$  by  $2$   $1$  by  $T$  so it becomes  $3$  by  $2$   $N k_B T$  or  $3$  by  $2$  so or  $3$  by  $2$  you can write if  $N$  is Avogadro number  $3$  by  $2$   $r t$  right and this becomes I have write correct  $3$  by  $2$   $r t$   $U$  is you please check this I think what we have done is correct so  $3$  by  $2$   $r t$  so and  $C_V$  then is basically nothing but  $3$  by  $2$   $r$  right so I have  $U$   $V$   $n$   $t$  square and there is a  $t$  so  $t$  and  $t$  square cancels so it makes  $3$  by  $2$   $N k_B T$  so  $3$  by  $2$   $N k_B T$  or  $3$  by  $2$   $r t$  and  $C_V$  is  $3$  by  $2$   $r$  yeah. So you please have a look at this and so this is in graphs and it can be applied many in many places again for lag media and absorption isotherm when I discuss that I will again bring back this concepts of the statistical concepts and statistical thermodynamic concepts and we will use this concepts to for many for deriving many useful relations which describe the fundamental properties or thermodynamic properties of materials whether it is a polymer or whether it is a say for example particles getting absorbed or absorbed on a surface so all places you can basically use this connection and what we have established here and in a very simple terms and very rudimentary way is this is not a course on statistical mechanics but it at least gives you the idea how you can relate the macroscopic or phenomenological thermodynamic quantities with the particle based description and as you can see we derived this partition functions we understood what this partition functions are and we have used this and we have seen that this basically gives you the same results that you obtained in macroscopic components right.

So into that again the same thing you please pass on comments there may be some places where I have gone too fast so wherever there is some doubt you can basically give me this comments I can try to work on them and try to explain all this concepts. Thank you so much. Thanks.