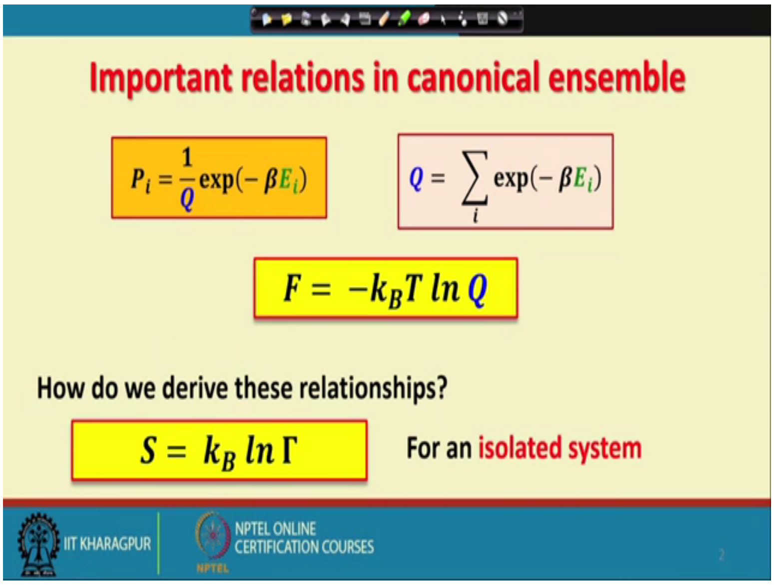
Introduction to Molecular Thermodynamics
Prof. Srabani Taraphder
Department of Chemistry
Indian Institute of Technology, Kharagpur

Lecture – 18
Canonical Ensemble part I (Contd.)

Welcome back. Let us continue on our discussion on the basic framework of canonical ensemble.

(Refer Slide Time: 00:28)



Important relations in canonical ensemble

$$P_i = \frac{1}{Q}\exp(-\beta E_i) \qquad Q = \sum_i \exp(-\beta E_i)$$

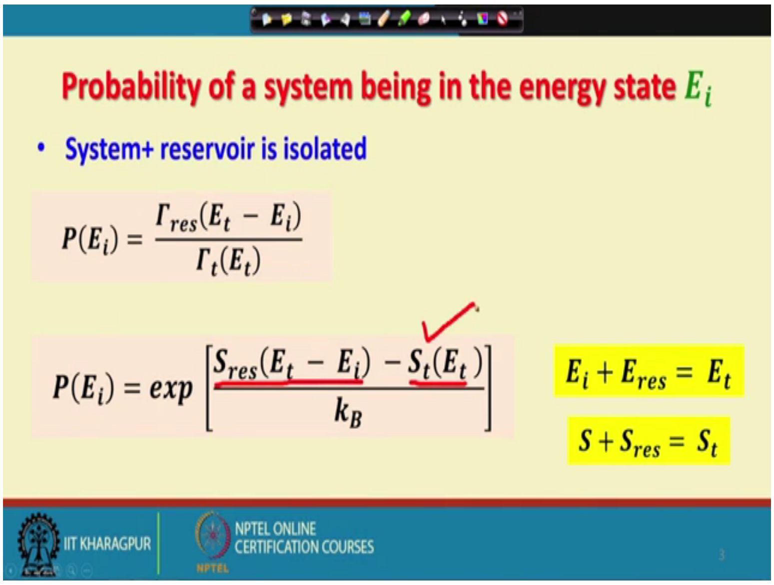
$$F = -k_B T \ln Q$$

How do we derive these relationships?

$$S = k_B \ln \Gamma$$ For an isolated system

And we are discussing here, the very important relationships that we have already shown and that is the probability of the system being in it is i-th microstate. How this probability is normalized in terms of the partition function, and the bridging relationship that connects the information gathered from the microscopic states to a thermodynamic function. And the question that we have posed here is how do we derive this relationships, and we have I have already told you that we are going to do so, starting from the Boltzmann hypothesis. And that is the connection between entropy of a system to the number natural logarithm of the number of microscopic states possible for an isolated system. So, let us try and get at the derivation in this lecture.

(Refer Slide Time: 01:31)



Probability of a system being in the energy state E_i

- System+ reservoir is isolated

$$P(E_i) = \frac{\Gamma_{res}(E_t - E_i)}{\Gamma_t(E_t)}$$

$$P(E_i) = exp\left[\frac{\underline{S_{res}(E_t - E_i)} - \overset{\checkmark}{\underline{S_t(E_t)}}}{k_B}\right]$$

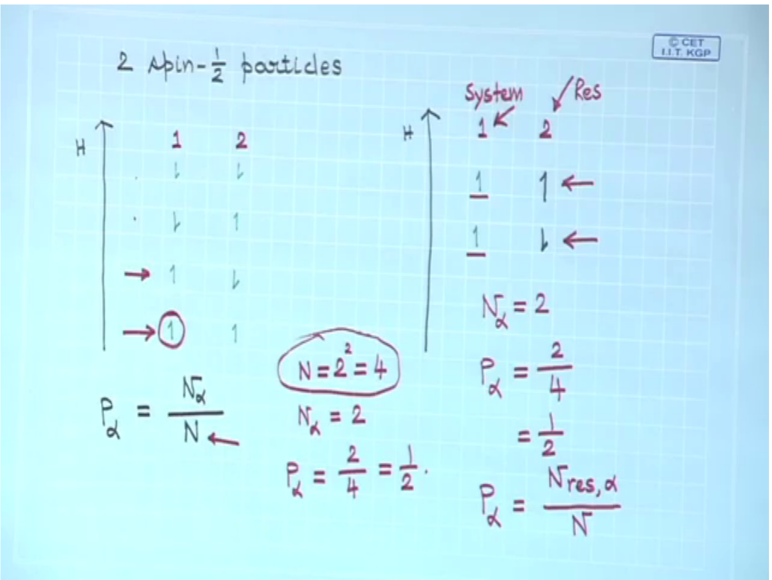
$$E_i + E_{res} = E_t$$

$$S + S_{res} = S_t$$

Now, when we talk about the probability of a system being in an energy state E i. So, basically we are assuming in a canonical ensemble, that if I take the system and the reservoir together, then this composite setup is isolated. So, under such condition it is possible to write down these 2 expressions, if the energy of the system is E i, and the energy of the reservoirs is E res both of them should sum up to a constant value E total that is the total energy of this isolated setup of system and reservoir.

Similarly at equilibrium if S is the entropy value associated with the system, and S res is the entropy of the reservoir, then both of them should add up to give a constant value S t for the system plus reservoir setup. So, under such condition it is possible to write down that the probability of observing the system in it is i-th energy state E i that is given by gamma res divided by gamma t. Now this might appear a little counterintuitive to you, but let us take an example where we allude back to a very simple model system that we have already seen.

(Refer Slide Time: 03:16)


2 spin-$\frac{1}{2}$ particles

H

1	2
↓	↓
↓	↑
→ ↑	↓
→ ↑	↑

$P_\alpha = \frac{N_\alpha}{N} \leftarrow$

$\boxed{N = 2^2 = 4}$

$N_\alpha = 2$

$P_\alpha = \frac{2}{4} = \frac{1}{2}.$

H

System ↙ ↙ Res

1	2
↑	↑ ←
↑	↓ ←

$N_\alpha = 2$

$P_\alpha = \frac{2}{4} = \frac{1}{2}$

$P_\alpha = \frac{N_{res,\alpha}}{N}$

So, I am choosing a system of 2 spin half particles that are non interacting and that are distinguishable, and they are present in a constant volume container where there is an embedded magnetic field H. Now I have 2 positions here position 1, and position 2 right. So, do I know what are the different possible microscopic states of the system we have done this before so, i find that this is a spin up in a position 1, spin up in position 2, spin up in position 1, spin down in position 2, spin down in position 1, and spin up in position 2, and then both are down.

Now, this is a complete collection of microscopic states possible for this particular system, and then I am asking this very specific question what is the probability that my spin 1 that is the spin half particle in position 1 will be oriented parallel to the direction of the field. So, in this case I know that the probability of observing the event alpha is given by n alpha divided by N. Now what is n alpha n alpha is the number of times you encounter the alphath event. And what is N alpha? N alpha is the total number of possible outcomes.

So, in this particular example what is N capital, N is equal to 2 square that is equal to 4. Now what is N alpha, in my case N alpha let me see this microscopic state has at position 1 a spin half particle oriented parallel to the direction of the field the same here, but not here and here. So, what is my N alpha, N alpha is equal to 2. So, what is P alpha? P alpha is equal to 2 divided by 4 which is half. Now the question is here if I think of a little bit differently let us say that this first spin is my system of course, this is a very very simplified idealized kind of situation, that I am talking about for the sake of simplicity. So, my spin 1 is my system and I am asking the question that if I fix my spin 1 in the position 1, with an orientation parallel to the direction of the applied field. So, in the position 1 the spin can only be a spin up a configuration right.

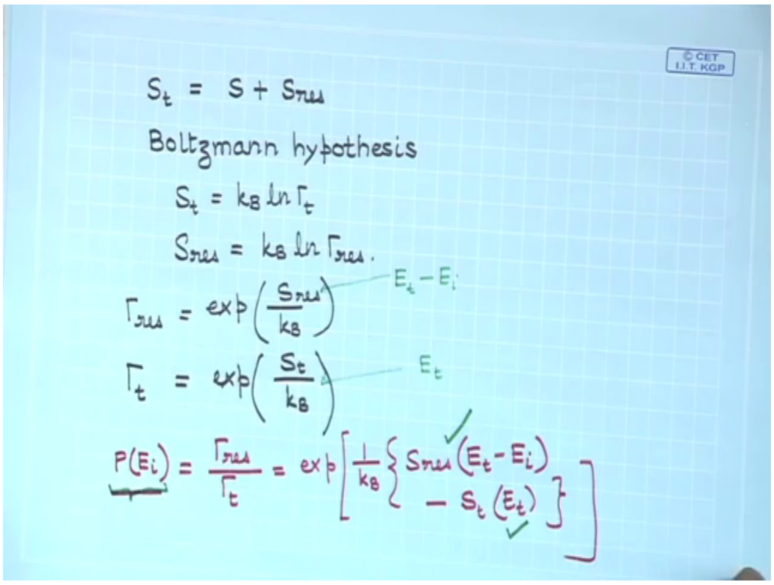
And then I am asking this question, then what is the probability of observing any such configuration. So, then what we do once again is we say let me find out what is the direction of the field, and what are the positions that I am talking about, yes I have once again position 1, and position 2. Now the microstates that I am interested in are where the position 1 is occupied by a spin up spin up orientation. Now this is 1 possible thing. So, this is my system which is fixed in this configuration.

So, what can be the rest of the system the rest of the system there is only 1 position that is position 2 and it can have 2 different orientations, 1 is spin up and fixing the system at spin up, the rest of the system which in my case is a highly simplified representation of the reservoir, it can take up 2 different orientations or configurations therefore, I understand that in this particular case still capital N is 4, even if capital N is 4 the I do not have to count all the microstates to be able to know what is N alpha. I have fixed the orientation in position 1 that I call the system.

And position 2 is now corresponding to my reservoir. So, what are the different ways a different microscopic states possible for the reservoir, this is 1 possible microstate that is another possible microstate. So, what is N alpha? N alpha equal to 2. So, what is P alpha? So, once again p alpha is given by 2 by 4 that is equal to half. So, essentially what I have done here is that, I am writing down P alpha is as the number of microstates available to the reservoir when this event alpha happens divided by the total number of microstates possible.

Now this is applicable for an isolated system and therefore, if I call this my system and I call this my reservoir, then system plus reservoir must be isolated. Now look back at what I have written down here. So, what I have written down here, is as follows I have written down that P of E i, I have fixed my system at the energy state E I, if that is so, then what is the energy of the reservoir E t minus E i by the constancy condition that I have already shown here, and then this E t minus E i this value will decide the number of microscopic states possible for the reservoir. So, that I represent here as gamma res. So, res means the reservoir, and in our case it is a thermal reservoir. Now i divide it by gamma t which is a function of E t. So, what is gamma t gamma t is the total number of microscopic states available to this totals isolated system comprised of the system as well as the reservoir. Now if that happens then I can very quickly write this down, now do you know where this relationship came from of course, this relationship came from the fact that the property of entropy of the system is such that.

(Refer Slide Time: 10:48)



$S_t = S + S_{res}$

Boltzmann hypothesis

$S_t = k_B \ln \Gamma_t$

$S_{res} = k_B \ln \Gamma_{res}$.

$\Gamma_{res} = \exp\left(\frac{S_{res}}{k_B}\right)$ — $E_t - E_i$

$\Gamma_t = \exp\left(\frac{S_t}{k_B}\right)$ — E_t

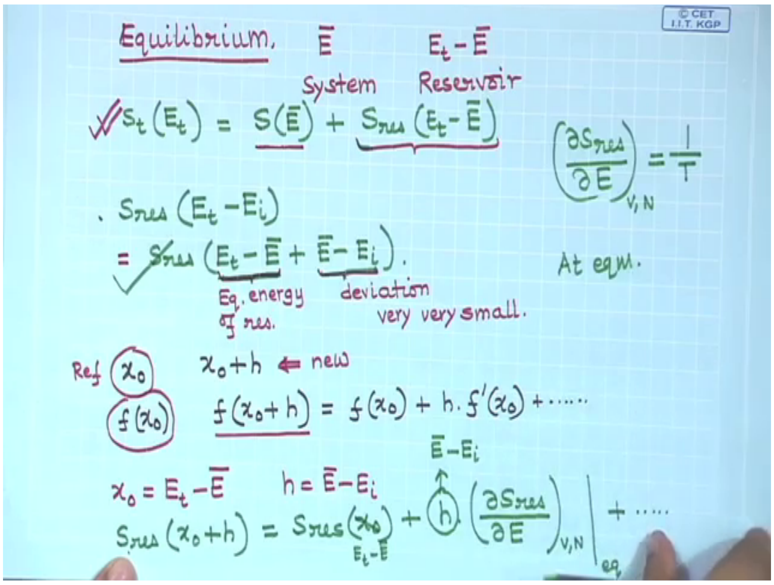
$$\underline{P(E_i)} = \frac{\Gamma_{res}}{\Gamma_t} = \exp\left[\frac{1}{k_B}\left\{S_{res}\overset{\checkmark}{(E_t-E_i)} - S_t\underset{\checkmark}{(E_t)}\right\}\right]$$

The total entropy of the system, for such a composite setup fed system plus reservoir is isolated at equilibrium always you can write down that S t is S plus S reservoir. Now using Boltzmann hypothesis, I can very easily write that S t must be equal to k B ln gamma t and S res that must be equal to k B ln gamma res and therefore, very easily i can say that gamma res is equal to exponential S by k B, S res by k B, and similarly gamma t is equal to exponential of S t by k B.

Now please remember that this S res is a function of E t minus E i which is the reservoir energy. And this S total this 1 is a function of the total energy. Now the next thing that we do is we do a little bit of algebra we write down P of E i which is equal to gamma res by gamma t this can now be written as exponential of 1 by k B into, S res which is a function of E t minus E i minus S t which is a function of E t clear.

So, I have been able to go from the first equation that I have written about P E i to here, simply by the application of the Boltzmann hypothesis Now in order to find out what then P E i is I need to understand what this S res minus S t is in order to do that, there is something I would like to mention over here, and that is as follows first of all.

(Refer Slide Time: 13:26)



Equilibrium. $\bar{E}$ $E_t - \bar{E}$

System Reservoir

✓ $S_t(E_t) = \underline{S(\bar{E})} + \underbrace{S_{res}(E_t - \bar{E})}$

$\left(\frac{\partial S_{res}}{\partial E}\right)_{V,N} = \frac{1}{T}$

At eqm.

$S_{res}(E_t - E_i)$

$= S_{res}(\underbrace{E_t - \bar{E}}_{\text{Eq. energy of res.}} + \underbrace{\bar{E} - E_i}_{\text{deviation}})$. ✓

very very small.

Ref x_0 $f(x_0)$ $x_0 + h \Leftarrow$ new

$\underline{f(x_0 + h)} = f(x_0) + h.f'(x_0) + \cdots\cdots$

$x_0 = E_t - \bar{E}$ $h = \bar{E} - E_i$

$S_{res}(x_0 + h) = S_{res}(\underset{E_t - \bar{E}}{x_0}) + \overset{\bar{E} - E_i}{h} \left(\frac{\partial S_{res}}{\partial E}\right)_{V,N}\Bigg|_{eq} + \cdots\cdots$

If the system has attained equilibrium in that case let us say that the energy total energy of the system, now is E bar that is the internal energy of the system. If the system energy is E bar in that case what is the energy of the reservoir E t minus E bar. So, this is the energy of the reservoir, and I can very easily write that S t which is a function of E t that is equal to S as a function of E bar plus S res as a function of E t minus E bar.

Now, this is one relationship that I am going to use later to find out the difference that I am looking for. Now please have a look at this particular quantity, S res E t minus E bar. Now before I go into the evaluation of this term let me go back, and have a look at the kind of let me remind you of the kind of system that we are looking at, thermal equilibrium between the system, and the reservoir the average value of energy E bar is a constant of time. And a magnitude of E bar minus E i is very small when the number of particles and available energy both are very very large. I am going to use these 2 results in the next step of my derivation. And this is what I say? I am going to find out S reservoir E t minus E i because that is exactly what you require in your calculation please have a look back over here. So, I require to evaluate S res which is E t minus E i as a function of E t minus E I, and it is difference with the total entropy of the system plus reservoir which is a function of the constant total energy E t.

Now, I have this second term written down in terms of the equilibrium value of energy E bar. So, this is the system entropy, and this is a reservoir entropy at equilibrium. So, what is the other quantity that I need to find out? I need to find out this particular quantity in the numerator of the exponential term, then I need to understand what E t minus E i is and I need to understand S res as a function of this difference.

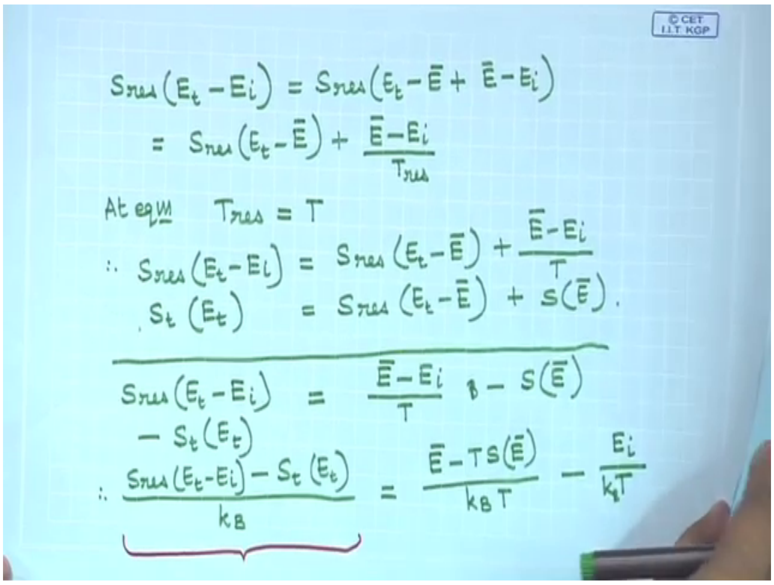
Now, in order to understand this behaviour let me rewrite this S res term like this, S res is equal to E t minus E bar plus E bar minus E i. So, all I have done is here, I have carried out a change in variable. So, that now I have this as a reference point, and this as a variation over the reference point by the property of my system, this is the equilibrium energy value of the reservoir. And what is this? This quantity is the deviation from the equilibrium value.

Now since the equilibrium is being maintained between the system and the reservoir, you understand that this deviation must be very very small.Now let me remind you that if you have know a function at a given point x naught say, and you want to know what that function is at a nearby point x naught plus h where h is a very small number, then the corresponding function you know the function f at x naught, and you would like to find out what f x naught plus h is how do you do that, 1 can use a Taylor expansion.

If I do it, then I can write it as f x naught plus h into f prime x naught and so on and so forth. So, here try to understand that I am doing the same thing, I have written down as so, x naught is my reference point, and this is my new point. So, this is the value of the function at the reference point, and this is how I evaluate the value of the function at the new point. Now look at the task that I have in hand let me designate as x naught E t minus E bar. And let me designate as h E bar minus E i therefore, I have set myself the task of finding S res x naught plus h, that is this quantity. So, what is x naught? x naught is this equilibrium energy value and of the reservoirs, and this is the deviation from the equilibrium energy value of the reservoir, which is very very small and therefore, I can use the Taylor expansion once again to evaluate this quantity. So, what is this going to be that is going to be S res at x naught plus h into del S res of course, here the derivative is in terms of E keeping volume, and number of particles constant, and evaluated at equilibrium where x is equal to x naught and so on and so forth.

Of course, I am going to replace this x naught value instead of this, I am going to write E t minus E bar. Now what is h? h I am going to replace, and I am going to write it as E bar minus E i. Now what is del S res del E of course, we know from our thermodynamics that del S res del E evaluated at constant volume, and number of particles that is equal to 1 by t. So, at equilibrium condition what is this t this is the temperature of the reservoir.

(Refer Slide Time: 21:22)



$$S_{res}(E_t - E_i) = S_{res}(E_t - \bar{E} + \bar{E} - E_i)$$

$$= S_{res}(E_t - \bar{E}) + \frac{\bar{E} - E_i}{T_{res}}$$

At $\underline{eq^m}$ $T_{res} = T$

$$\therefore S_{res}(E_t - E_i) = S_{res}(E_t - \bar{E}) + \frac{\bar{E} - E_i}{T}$$

$$S_t(E_t) = S_{res}(E_t - \bar{E}) + s(\bar{E}).$$

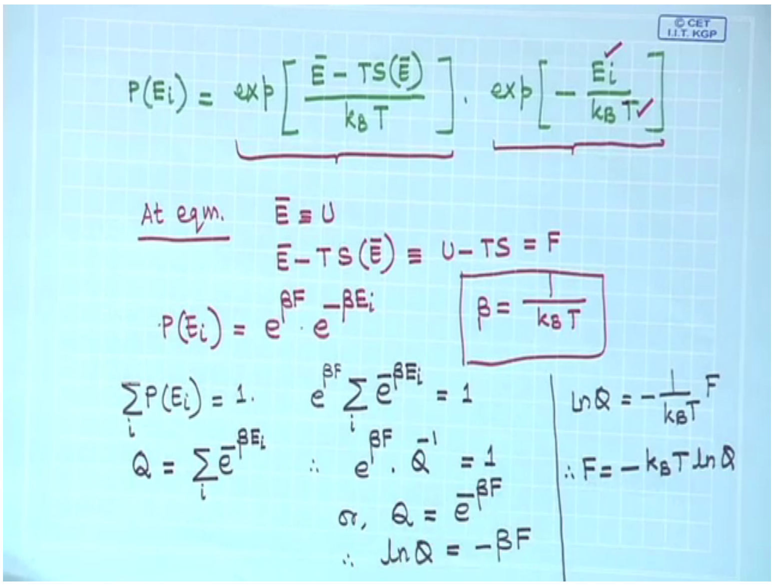
$$S_{res}(E_t - E_i) - S_t(E_t) = \frac{\bar{E} - E_i}{T} - s(\bar{E})$$

$$\therefore \underbrace{\frac{S_{res}(E_t - E_i) - S_t(E_t)}{k_B}} = \frac{\bar{E} - Ts(\bar{E})}{k_B T} - \frac{E_i}{k_B T}$$

And therefore, we can now write down the following expression for S res E t minus E i. So, this is equal to S res E t minus E bar plus E bar minus E i, that is equal to S res E t minus E bar plus E bar minus E i divided by T, now please look back . So, now I know S res in terms of the equilibrium value of entropy of the reservoir plus some small incremental term involving the temperature of the reservoir right. Now I know that at equilibrium T res is equal to T the temperature of the system therefore, I am now writing this expression as S res E t minus E i that is equal to S res E t minus E bar plus E bar minus E i divided by T. Now I already have the expression for the total entropy of the system which is like this, plus entropy of the system characterized by the average energy at equilibrium. If I now subtract the second equation from the first, what do I get, I get S res E t minus E i minus S t E t that is equal to of course, these 2 terms cancel out, and I am getting E bar minus E i by t minus S E bar.

Now, as you see that I can divide both sides by the Boltzmann constant therefore, I will be having S res E t minus E i minus S t E t divided by k B, that is equal to I am going to write it in a little different fashion E bar minus T of S E bar divided by k B T minus E i divided by k B T. Now why did I try to find out this particular term, because this is the term which appears in the expression for a probability, let us go back and have a look at it look at it again. So, I require this term by k B exponentiated to find out P of E 1 and here, that is exactly what I have got here, and therefore I can now very easily write what is P of E 1.

(Refer Slide Time: 25:03)



© CET I.I.T. KGP

$$P(E_i) = \underbrace{\exp\left[\frac{\bar{E} - TS(\bar{E})}{k_B T}\right]} \cdot \underbrace{\exp\left[-\frac{E_i}{k_B T}\right]}$$

At eqm. $\bar{E} \equiv U$

$\bar{E} - TS(\bar{E}) \equiv U - TS = F$

$P(E_i) = e^{\beta F} \cdot e^{-\beta E_i}$

$$\boxed{\beta = \frac{1}{k_B T}}$$

$\sum_i P(E_i) = 1.$ $e^{\beta F} \sum_i e^{-\beta E_i} = 1$

$Q = \sum_i e^{-\beta E_i}$ $\therefore e^{\beta F} \cdot Q^{-1} = 1$

or, $Q = e^{-\beta F}$

$\therefore \ln Q = -\beta F$

$\ln Q = -\frac{1}{k_B T} F$

$\therefore F = -k_B T \ln Q$

So, P of E i that is equal to exponential of E bar minus T S of E bar divided by k B T, then exponential minus E i divided by k B T right. Now please note that I have written down 2 types of terms in this expression for probability. So, the first term does it depend on E i no, the second term yes, it depends on E i and also it depends on the temperature at which the system has attained equilibrium with the thermal reservoir.

Now, let us have a look very closely at what we have got here, at equilibrium when the system is at equilibrium with the thermal reservoir E bar is nothing, but the internal energy. So, what is E bar minus temperature into S of E bar that is nothing, but u minus TS which is the Helmholtz free energy? So, I have here P of E i that is equal to E to the power of beta F into E to the power of minus beta E i, where I have represented as beta 1 by k B t clear.

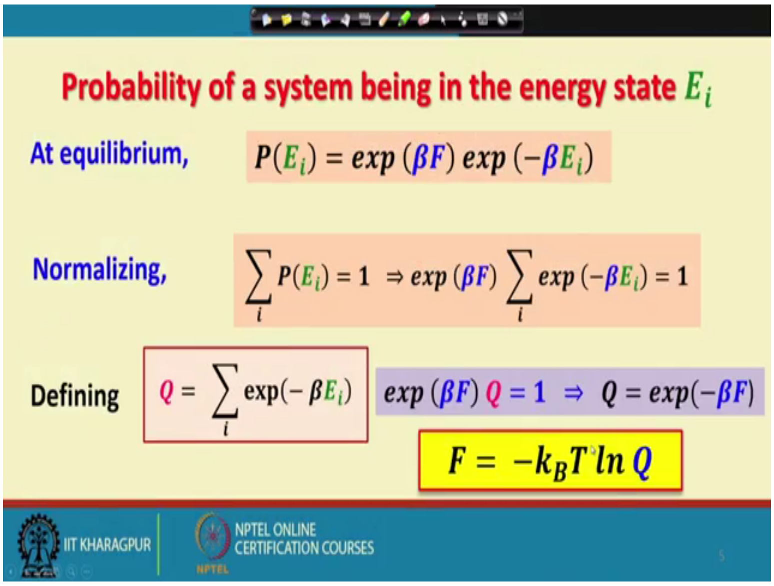
Now if that happens then I would say that I have achieved a lot, I mean I have been able to obtain an expression for the probability of the system being in it is i-th microscopic state, but do I know if this probability is normalized of course, if it has to be normalized in that case I must be having summation over i P of E i that is equal to 1 and therefore, I must be having this relationship valid, that e to the power of beta F into summation over i E to the power of minus beta E i that is equal to 1.

Now in our previous description we denoted as a normalization constant capital Q which is nothing, but e to the power of minus beta i beta E i summed over i and therefore, i can write e to the power of beta F into Q inverse is equal to 1 or q is equal to e to the power of minus beta F. So, this is exactly what we have shown here in the slides as well.

So, when we decide that E bar minus E i is a very small number, E bar is a constant of time and so, is E t minus E bar then we have been able to show, that P of E i is exponential beta F into e to the power of minus beta E i, and upon normalization i come across this expression that Q is equal to exponential of minus beta F.

Now, can I just rewrite everything therefore, what is ln Q, ln Q is equal to minus beta fF. Now I put back the expression for beta. So, ln Q is equal to minus 1 by k B T into F or in other words F is equal to minus k B T, ln Q and this is a relationship that we were looking for.

(Refer Slide Time: 29:11)



Probability of a system being in the energy state E_i

At equilibrium, $P(E_i) = exp\,(\beta F)\; exp\,(-\beta E_i)$

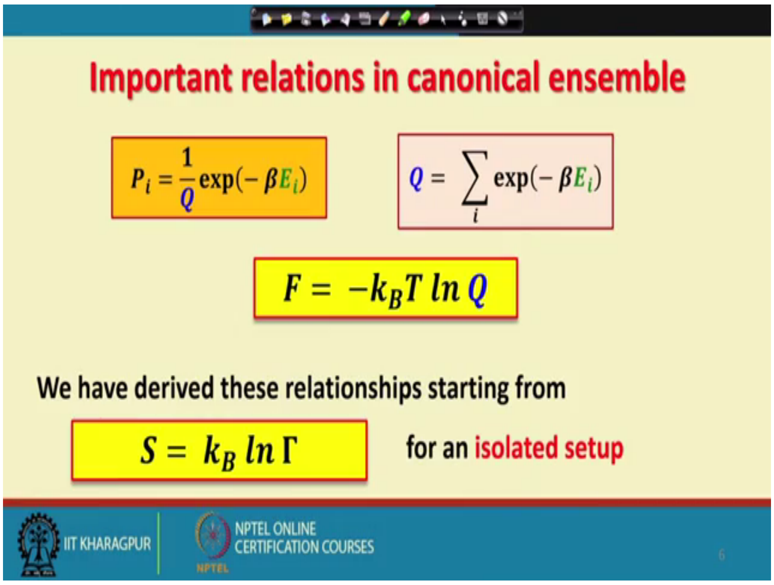
Normalizing, $\sum_i P(E_i) = 1 \Rightarrow exp\,(\beta F) \sum_i exp\,(-\beta E_i) = 1$

Defining $Q = \sum_i \exp(-\beta E_i)$ $exp\,(\beta F)\, Q = 1 \Rightarrow Q = exp(-\beta F)$

$$F = -k_B T \ln Q$$

This is the bridging relationship between the microscopic state of the system, and the thermodynamic property as manifested through the free energy Helmholtz; free energy which is nothing, but the thermodynamic potential of the system maintained at a constant temperature volume and number of particles.

(Refer Slide Time: 29:37)



Important relations in canonical ensemble

$$P_i = \frac{1}{Q}\exp(-\beta E_i)$$

$$Q = \sum_i \exp(-\beta E_i)$$

$$F = -k_B T \ln Q$$

We have derived these relationships starting from

$$S = k_B \ln \Gamma$$

for an isolated setup

So, in conclusion in this lecture we have been able to use a very general treatment to arrive at 3 most important relationships, in the description for canonical ensemble. And we have been able to derive these relations starting from the Boltzmann hypothesis applied to an isolated setup, where the system plus reservoir are can be treated as an isolated a set up.

So, in the next lecture we are going to see, how we are going to use these kind of relationships to find out useful thermodynamic properties starting from a model of the microscopic model of the system.

Thank you.