Fundamentals of Statistical Thermodynamics

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Lecture – 21

Recovering molecular partition function q from canonical partition function Q

Welcome back to the next lecture of Statistical Thermodynamics. So far, we have talked in terms of molecular partition function and then we talked in terms of canonical partition function. We developed some expression for canonical partition function, basically that was based upon similar considerations that we used for deriving an expression for molecular partition function. Now the next question is can we recover the molecular partition function from the more general canonical partition function? Remember that we talked about different types of ensembles, we talked about micro canonical ensemble, we talked about canonical ensemble and we also talked about grand canonical ensemble, but we chose canonical ensemble for further discussion for further developing equations. And the canonical ensemble is NVT common and we allowed the molecules even to interact with it with each other, so that the energy can be exchanged and the energy of the system may not be constant. After such a discussion, then we came up with an expression for canonical partition function which was given a symbol of capital Q.

So, that is what the title is given here, recovering molecular partition function small q from canonical partition function capital Q. So, what we will do is in this discussion we will discuss the methodology that will allow us in recovering the molecular partition function from the more general canonical partition function when the molecules are independent. Let us take a look at the next comment. The total energy of a collection of n independent molecules is the sum of the energies of the molecules.

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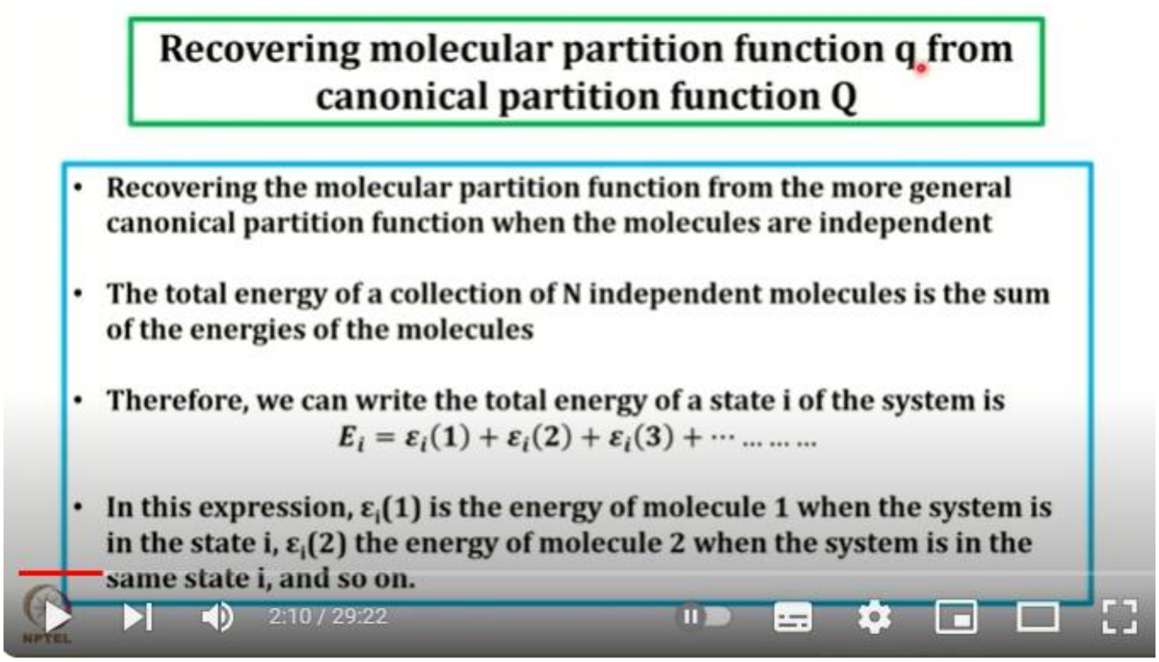

Recovering molecular partition function q from canonical partition function Q

- **Recovering the molecular partition function from the more general canonical partition function when the molecules are independent**
- **The total energy of a collection of N independent molecules is the sum of the energies of the molecules**
- **Therefore, we can write the total energy of a state i of the system is**

$$E_i = \varepsilon_i(1) + \varepsilon_i(2) + \varepsilon_i(3) + \cdots \ldots\ldots\ldots$$

- **In this expression, $\varepsilon_i(1)$ is the energy of molecule 1 when the system is in the state i, $\varepsilon_i(2)$ the energy of molecule 2 when the system is in the same state i, and so on.**

Yes. So therefore, what we can write that the total energy of a state i of a system can be written as E_i is equal to E_i (1) plus E_i (2) plus E_i (3) and so on. In this expression, this E_{i1} is the energy of the molecule when the system is in state i, E_i (2) is the energy of the molecule when the system is in the same state i, similarly E_{i3} is the energy of molecule 3 when the system is in the same state I. That is why we can write E_i is equal to E_i (1) plus E_i (2) plus E_i (3) and so on. So, what we have now? The total energy of a state I of the system is let us say if there are n molecules then E_i is equal to E_i (1) plus E_i (2) plus E_i (3) plus so on so on up to E_i (N).

Let us write the expression for canonical partition function. Q is equal to summation I exponential minus βE_i, where E_i we are talking about the energy of i^{th} state. So let us now from this expression we substitute for E_i exponential minus β in place of E_i, I will write E E_i (1) plus E_i (2) plus so on plus E_i, I write up to n. Remember that 1, 2, 3 or n are just representing the molecules. So therefore, now I can allow this summation or on individual states.

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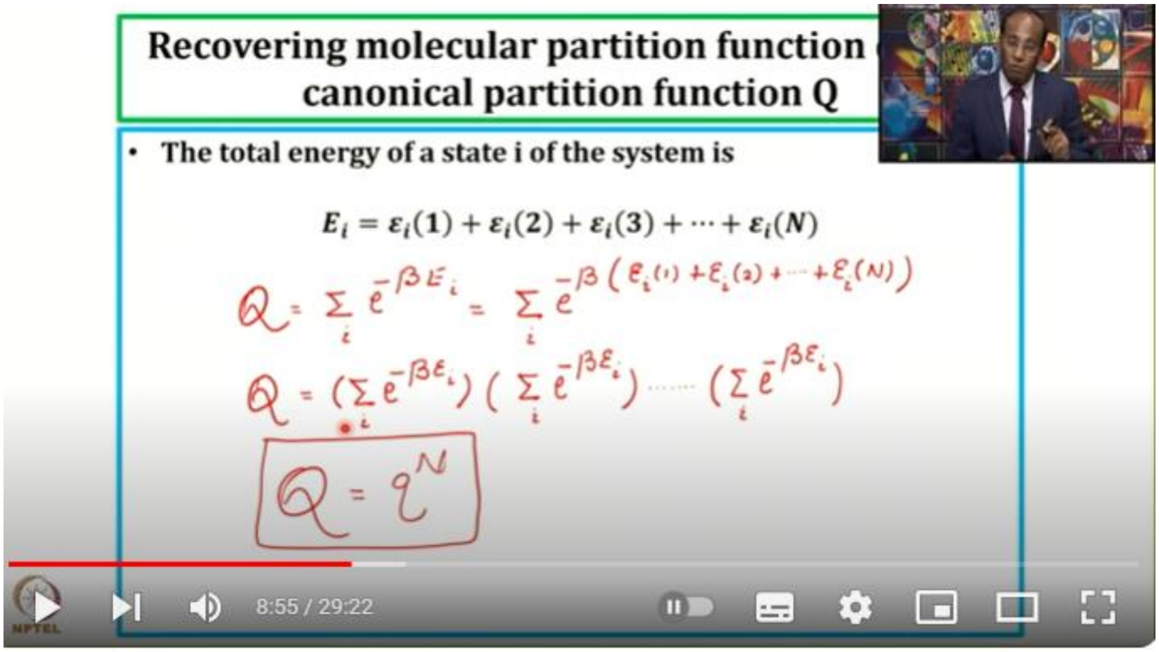

Recovering molecular partition function
canonical partition function Q

- The total energy of a state i of the system is

$$E_i = \varepsilon_i(1) + \varepsilon_i(2) + \varepsilon_i(3) + \cdots + \varepsilon_i(N)$$

$$Q = \sum_i e^{-\beta E_i} = \sum_i e^{-\beta(\varepsilon_i(1) + \varepsilon_i(2) + \cdots + \varepsilon_i(N))}$$

$$Q = \left(\sum_i e^{-\beta\varepsilon_i}\right)\left(\sum_i e^{-\beta\varepsilon_i}\right)\cdots\cdots\left(\sum_i e^{-\beta\varepsilon_i}\right)$$

$$\boxed{Q = q^N}$$

So mathematically it is allowed now to write this as summation I exponential minus βE_I into summation I exponential minus βE_i. I am not writing 1, 2, 3 etcetera now because that was just for the sake of understanding and this will continue up to n times and again, I will write summation i exponential minus βE_i. Now it is over the individual molecular states and each one, this each bracketed term is molecular partition function. So therefore, this each term in this overall product is repeated n times for n molecules. Remember we are having n molecules in one member of the n sample.

So therefore, now I can write Q is equal to q raise to the power n. By this expression you see we have connected canonical partition function with molecular partition function. Capital Q is canonical partition function, small q or in the lowercase written q is the molecular partition function. So, we have recovered molecular partition function Q from canonical partition function and we have derived some thermodynamic equations which relate S with canonical partition function, which relate U with canonical partition function. So therefore, now this connection of capital Q canonical partition function with the molecular partition function allows us to now recover the equations which were connected with molecular partition function into now we can express as those expression in terms of molecular partition function.

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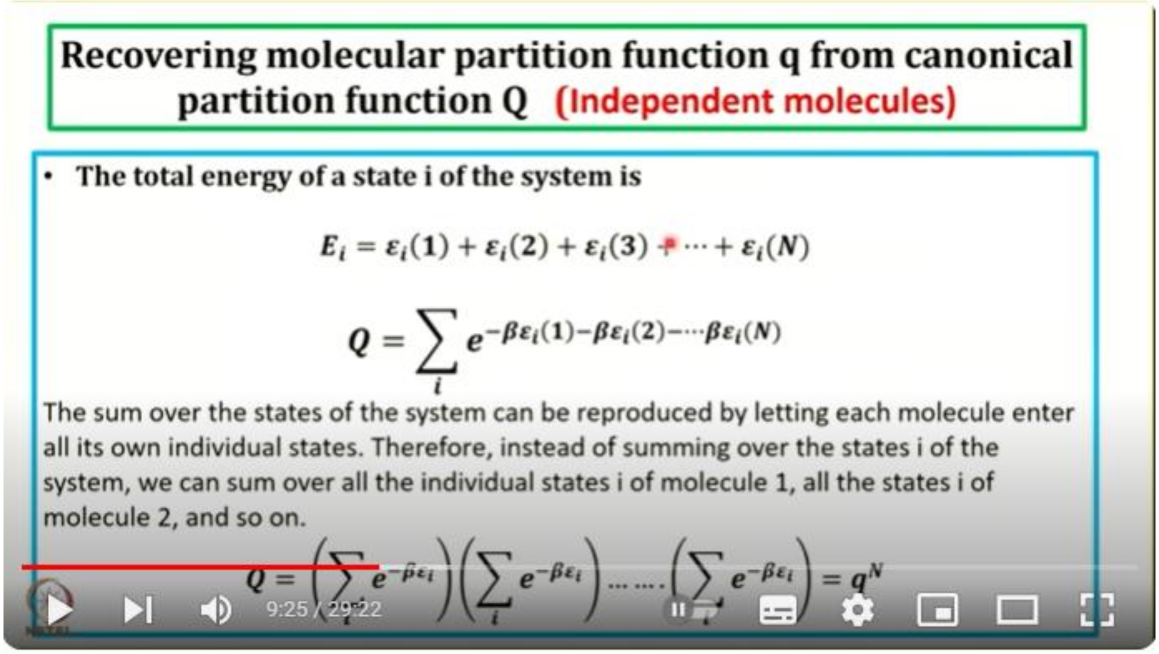

Recovering molecular partition function q from canonical partition function Q (Independent molecules)

- The total energy of a state i of the system is

$$E_i = \varepsilon_i(1) + \varepsilon_i(2) + \varepsilon_i(3) + \cdots + \varepsilon_i(N)$$

$$Q = \sum_i e^{-\beta\varepsilon_i(1) - \beta\varepsilon_i(2) - \cdots \beta\varepsilon_i(N)}$$

The sum over the states of the system can be reproduced by letting each molecule enter all its own individual states. Therefore, instead of summing over the states i of the system, we can sum over all the individual states i of molecule 1, all the states i of molecule 2, and so on.

$$Q = \left(\sum_i e^{-\beta\varepsilon_i}\right)\left(\sum_i e^{-\beta\varepsilon_i}\right) \dots \dots \left(\sum_i e^{-\beta\varepsilon_i}\right) = q^N$$

But now the question is that is this expression is this expression always valid? We may have molecules which are indistinguishable, we have molecules which are distinguishable. So therefore, we must ensure that we do not over count the number of states. I repeat the molecules can be distinguishable, the molecules can be indistinguishable. Therefore, we need to make sure that we do not over count the number of states. In this treatment we have considered the molecules as distinguishable.

Now let us see if the molecules are indistinguishable, then what form it will take. Just before discussing that it is a recap of what we have just done. What we did was we expressed the total energy of a state I as the sum of the individual molecular energies, individual particles energy in ith state and then we put that expression of E_I into an expression for canonical partition function and then we were able to express this as product of individual molecular partition function. So, we got an expression Q is equal to q raise to the power N. Now let us switch over to distinguishable and indistinguishable molecules discussion.

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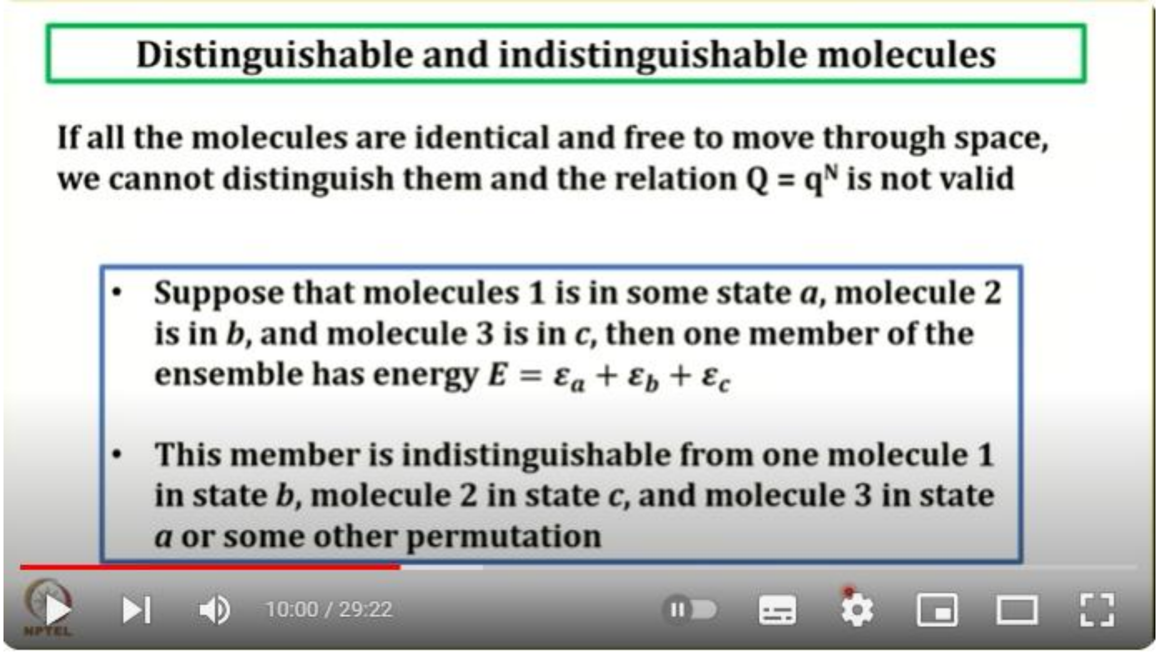

Distinguishable and indistinguishable molecules

If all the molecules are identical and free to move through space, we cannot distinguish them and the relation $Q = q^N$ is not valid

- **Suppose that molecules 1 is in some state *a*, molecule 2 is in *b*, and molecule 3 is in *c*, then one member of the ensemble has energy $E = \varepsilon_a + \varepsilon_b + \varepsilon_c$**
- **This member is indistinguishable from one molecule 1 in state *b*, molecule 2 in state *c*, and molecule 3 in state *a* or some other permutation**

You consider a gas, helium gas, argons gas, nitrogen gas, we cannot distinguish between molecules right. The molecules are indistinguishable from each other. Therefore, if all the molecules are identical and free to move through space, we cannot distinguish between them and in that case Q equal to q raise to the power N is not valid. Why it is not valid? Let us have some discussion on it. Look at the comment.

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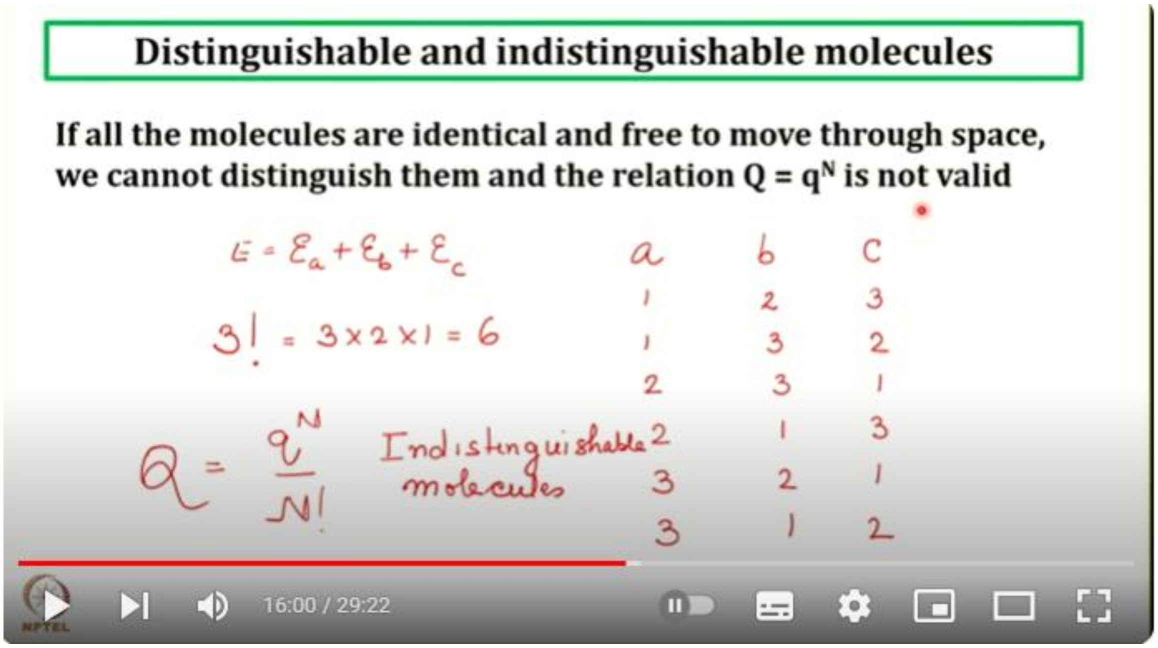

Distinguishable and indistinguishable molecules

If all the molecules are identical and free to move through space, we cannot distinguish them and the relation $Q = q^N$ is not valid

$E = \varepsilon_a + \varepsilon_b + \varepsilon_c$

$3! = 3 \times 2 \times 1 = 6$

$Q = \frac{q^N}{N!}$ Indistinguishable molecules

a	b	c
1	2	3
1	3	2
2	3	1
2	1	3
3	2	1
3	1	2

Suppose that molecule 1 is in some state a, molecule 2 is in state b molecule 3 is in state c, then one member of the ensemble will have an energy E_a plus E_b plus E_c because one of the molecules is in state a, 2 is in b, 3 is in c. We are not fixing the energy of a system in canonical ensemble. The member does not have a fixed energy. Therefore, it allows different molecules to be in states of different energy. That means that one member of the ensemble will have an energy E_a plus E_b plus E_c.

Now you let us consider a different scenario in which molecular 1 is in state b, molecule 2 is in state c and molecule 3 is in state a. Still the total energy is going to be E_a plus E_b plus E_C. So, we cannot distinguish between these different kind of arrangements. Now let us see how many different combinations are possible. We are talking about energies of states a, b, c. Let us say molecule 1 is in this for a member 2, 3. The total energy for this is total energy is equal to E_a plus E_b plus E_c. I can put one two three. Then let us say one three two, two three one, two one three, three two one, three one two, one two three, four five six. There are six combinations, right, one two three four five six permutations are there.

The molecules are not distinguishable. In each case the energy is going to be E_a plus E_b plus E_c. You can put one two three, one three two, different permutations combinations are possible. We talked about here three molecules. For three molecules it was three factorial possible ways that you will achieve the same energy and three factorial is equal to three times two times one is equal to six ways.

Therefore, what we are doing is we may be over counting the number of states because the different arrangements are leading to the same energy and we cannot distinguish between you know this kind of arrangements leading to same energies. So, we are over counting the number of states. If we apply this formula Q is equal to q raise to the power N. Therefore, a correction factor is required. What is that correction factor? The detail arguments, detail discussions are elaborate.

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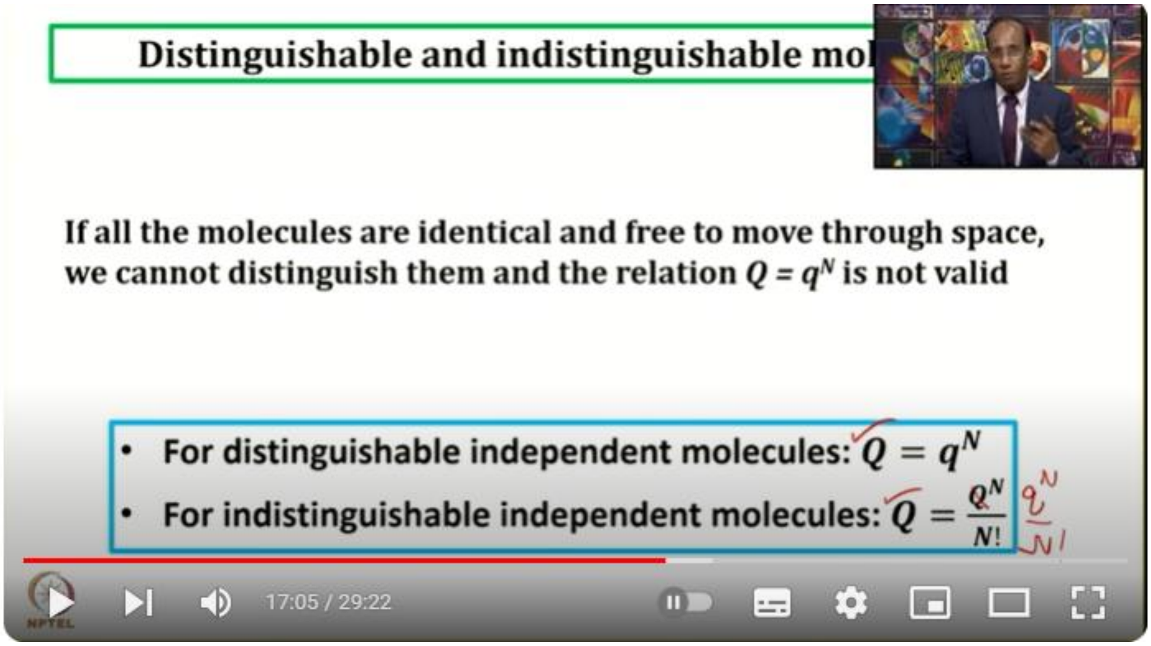

Distinguishable and indistinguishable mol

If all the molecules are identical and free to move through space, we cannot distinguish them and the relation $Q = q^N$ is not valid

- For distinguishable independent molecules: $Q = q^N$
- For indistinguishable independent molecules: $Q = \frac{Q^N}{N!}$

$\frac{q^N}{N!}$

We will not go into that mathematical elaboration, but it turns out that the correction factor required is one by N factorial. Q raise to the power N by N factorial, this is for indistinguishable molecules, molecules because you do not want to over count the number of states. That is why this F factor of N factorial is required in the denominator when you connect canonical partition function with the molecular partition function. That is why you read the comment again if all the molecules are identical and free to move through space, then we cannot distinguish between them, then Q is equal to q raise to the power N is not valid. Therefore, let us conclude.

For distinguishable independent molecules, if it is distinguishable, remember this keyword distinguishable Q canonical partition function is equal to molecular partition function raise to the power N. For indistinguishable independent molecules Q canonical partition function is equal to, let me correct this, this is q raise to the power N over N factorial. So therefore, depending upon the given system, you have to make a choice whether you need to use this definition or you need to use this definition and you should be able to make this choice whether the molecules are distinguishable or the molecules are indistinguishable. Let us have a little further discussion on this. For molecules to be indistinguishable, they must be of the same kind.

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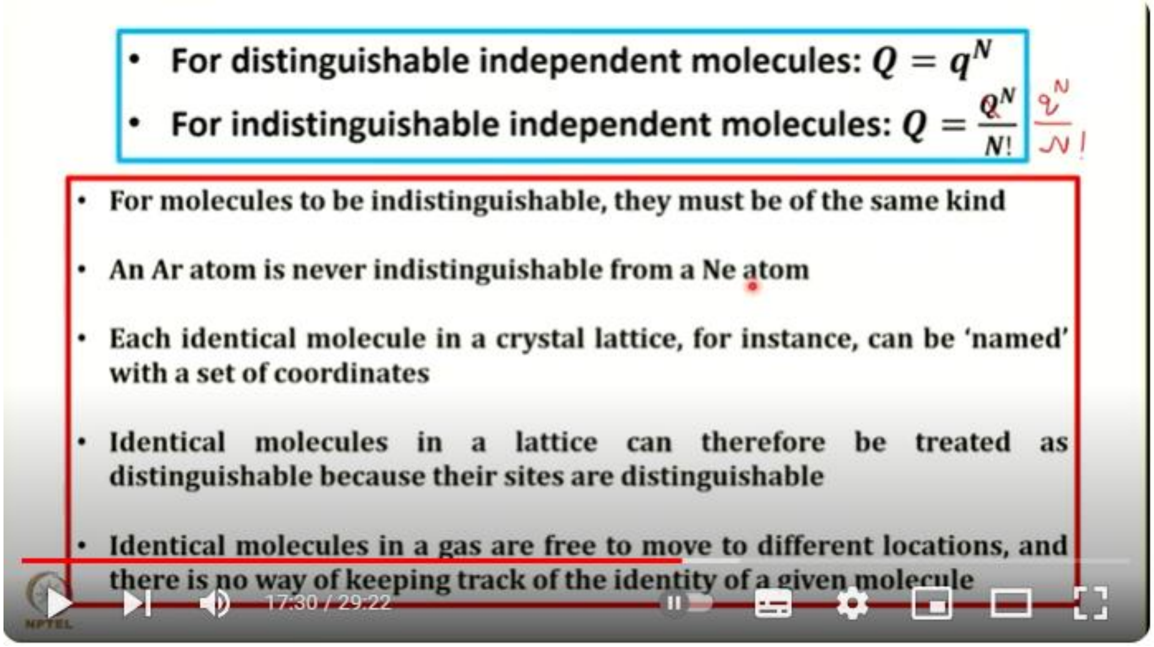

- **For distinguishable independent molecules: $Q = q^N$**
- **For indistinguishable independent molecules: $Q = \frac{Q^N}{N!}$** $\frac{q^N}{N!}$

- **For molecules to be indistinguishable, they must be of the same kind**
- **An Ar atom is never indistinguishable from a Ne atom**
- **Each identical molecule in a crystal lattice, for instance, can be 'named' with a set of coordinates**
- **Identical molecules in a lattice can therefore be treated as distinguishable because their sites are distinguishable**
- **Identical molecules in a gas are free to move to different locations, and there is no way of keeping track of the identity of a given molecule**

Example is gas. Like an argon atom is never indistinguishable from a neon atom. You take a gas in which you have argon also, you have neon also. You cannot distinguish between them. So, then the system becomes molecules which are indistinguishable. So, when you can distinguish between the molecules, under what circumstances, under what conditions? Take an example of a crystal lattice.

When you have a crystal lattice, you have studied solid state. When you consider a lattice, when you consider a unit cell, the coordinates are defined. X Y Z positions are defined. So therefore, if you are considering a crystal lattice, then each identical molecule in a crystal lattice, you can name them because you can provide them a set of coordinates. You know at what value of X Y Z or other, you know, if you want to use other notations, you can give the name to each identical molecule in the form of set of coordinates and there the molecules become distinguishable.

Therefore, identical molecules in a lattice can therefore be treated as distinguishable because their sides are distinguishable because you are providing a set of coordinates. Identical molecules in a gas are free to move to different locations and there is no way of keeping track of the identity of a given molecule. In that case, the molecules become indistinguishable. So, I am sure that by now it is clear when to use q equal to small q raised to the power n or q equal to small q raised to the power n over n factorial. While when I say small q, I am talking about molecular partition function.

When I talk about capital Q, I am talking about canonical partition function. Let us try to understand with some example. Identify systems for which it is essential to include a factor of 1 by n factorial on going from canonical partition function to molecular partition function. What it means is we have just discussed two expressions q raised to the power n and we have discussed q is equal to q raised to the power n over n factorial. This is for distinguishable molecules.

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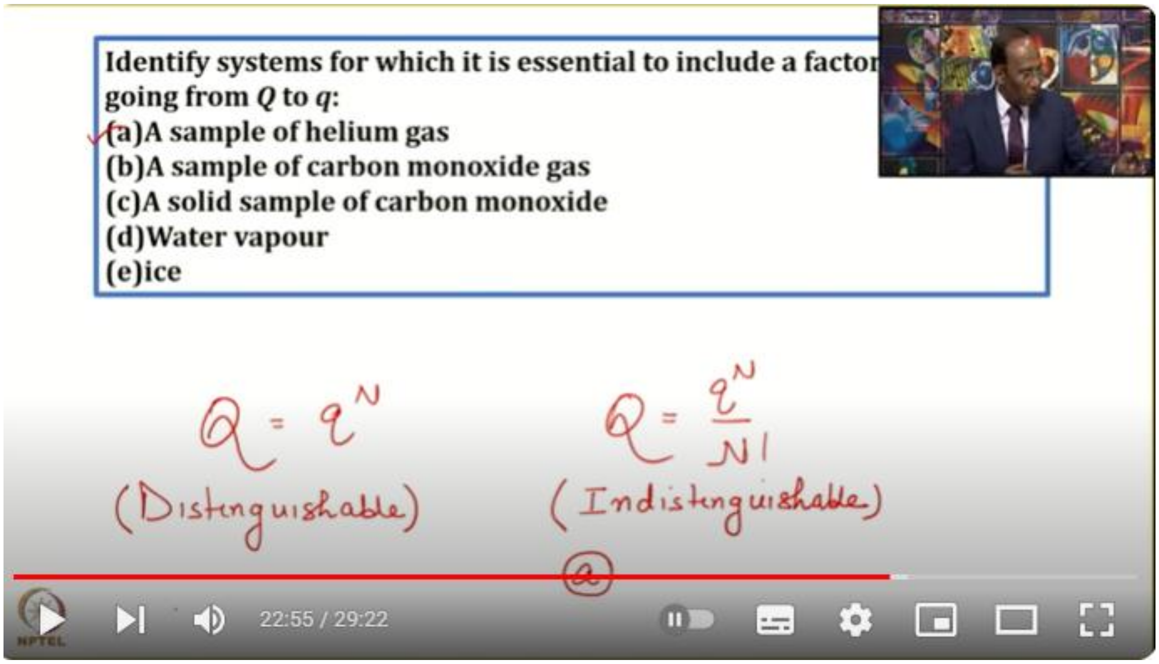

Identify systems for which it is essential to include a factor going from Q to q:

✓(a)A sample of helium gas

(b)A sample of carbon monoxide gas

(c)A solid sample of carbon monoxide

(d)Water vapour

(e)ice

$Q = q^N$

(Distinguishable)

$Q = \frac{q^N}{N!}$

(Indistinguishable)

ⓐ

So this Q canonical partition function is equal to small q which is molecular partition function raised to the power n for distinguishable molecules and this formula is for indistinguishable molecules. Now let us go one by one and see in which case which formula to use. A sample of helium gas. It is helium gas. You consider a gas enclosed in a cylinder.

There are helium atoms. We cannot distinguish one atom from another. Therefore, which formula to use? The formula which is applicable for indistinguishable molecules or atoms. So that means A, a sample of helium gas will fall under this category indistinguishable. So, you require a factor of 1 by n factorial. Now A we have done. Now let us talk about a sample of carbon monoxide gas. There are two atoms in this carbon and oxygen but it is a one molecule carbon monoxide gas. Again, in a gas there are several carbon monoxide molecules. You cannot distinguish one carbon monoxide from the other carbon monoxide. So therefore, once again here it is indistinguishable and you require a factor of 1 by n factorial in this.

So therefore B also will fall into this category. Now comes third one. A solid sample of carbon monoxide that is you lower the temperature, let carbon monoxide freeze the solid sample. We have just discussed that if there is a solid, in the solid state you can assign coordinates because the molecules will be occupying some fixed position. So therefore, you can name them, you can identify them by providing coordinates.

Therefore C which is a solid sample of carbon monoxide will fall in the case of distinguishable. Next one is water vapor H_2O. Two hydrogens, one oxygen, three atoms in one molecule but it is a vapor, one molecule. Vapor form, consider steam, water vapors you cannot distinguish from one vapor or one water molecules to from another water molecule in the vapor form. Therefore, these molecules are indistinguishable.

Therefore D will fall in this category where 1 over n factorial is required. Now consider the last one, ice, solid, same arguments you can assign coordinates. Therefore, there is no need to apply 1 over n factorial because molecules are distinguishable. So, E will fall in this category. Therefore, when you recover the molecular partition function from canonical partition function, we need to be very careful whether we need 1 over n factorial or not because this can change your result.

So if we choose the wrong representation this can bring inaccuracy in your calculations. We have discussed that the internal energy in terms of the canonical partition function is given by U (0) minus 1 over q del q by del β at constant volume.

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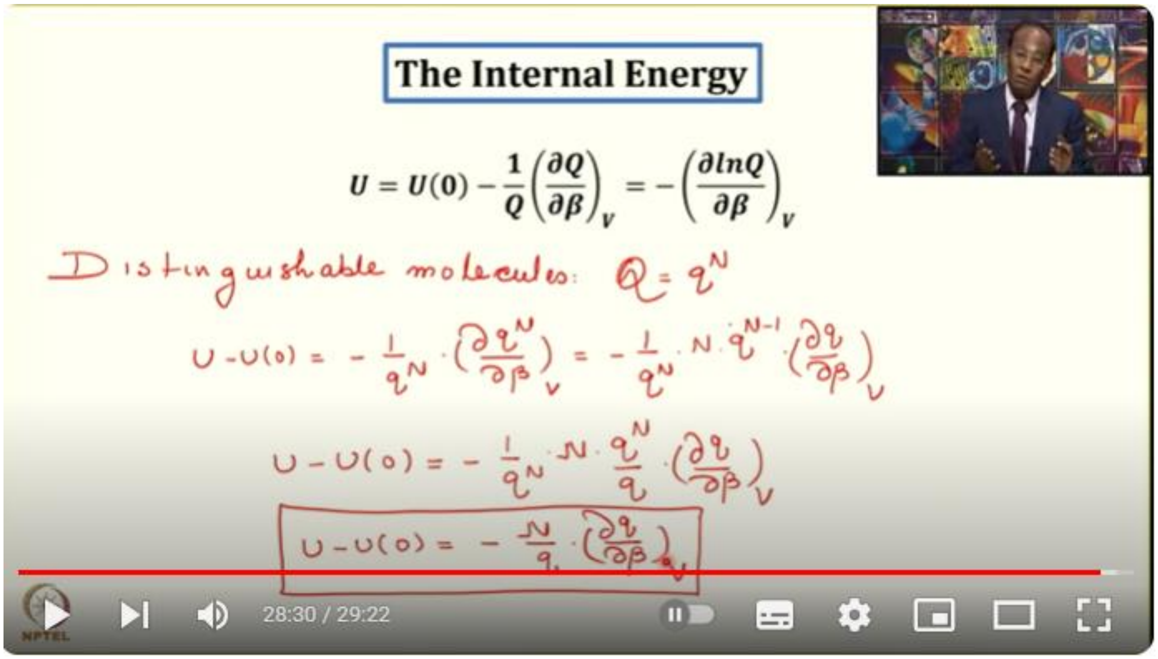

The Internal Energy

$$U = U(0) - \frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)_V = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_V$$

Distinguishable molecules: $Q = q^N$

$$U - U(0) = -\frac{1}{q^N}\cdot\left(\frac{\partial q^N}{\partial \beta}\right)_v = -\frac{1}{q^N}\cdot N\cdot q^{N-1}\left(\frac{\partial q}{\partial \beta}\right)_v$$

$$U - U(0) = -\frac{1}{q^N}\cdot N\cdot\frac{q^N}{q}\cdot\left(\frac{\partial q}{\partial \beta}\right)_v$$

$$\boxed{U - U(0) = -\frac{N}{q}\cdot\left(\frac{\partial q}{\partial \beta}\right)_v}$$

Let me see what form it takes for let us say I talk first about distinguishable molecules. Distinctable molecules means q is equal to q raise to the power n.

This is the formula that we need to use. Let us apply U – U (0) is equal to minus 1 over q, q raises to the power n. I am using this for distinguishable molecules into del Q raise to the power n over del β at constant volume. What we get here is minus 1 over q raise to the power n into now derivative of Q raise to the power n into q raise to the power n minus 1 into del q del β at constant volume. What I have now U – U (0) is equal to minus 1 over Q raise to the power n into n into q raise to the power n over q that is what is q raise to the power n minus 1 del q del β at constant volume. So, U - U(0) is equal to minus n by q del q del β at constant volume.

This is the expression for distinguishable molecules. Carefully examine what we have done. We started with the expression for internal energy in terms of canonical partition function and then we applied this expression for the canonical partition function connecting with molecular partition function for distinguishable molecules and we came up with an expression U – U(0) is equal to minus n by q del q by del β at constant volume. You remember that this is the same expression which we derived for internal energy when we were talking only in terms of molecular partition function. Next, we need to see that for indistinguishable molecules do we get a different formula that we will discuss in the next lecture. Thank you.