Indian Institute of Technology Madras

NPTEL

National Programme on Technology Enhanced Learning

Chemical Engineering Thermodynamics

by

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Lecture 35

Molecular basis of Thermodynamics II

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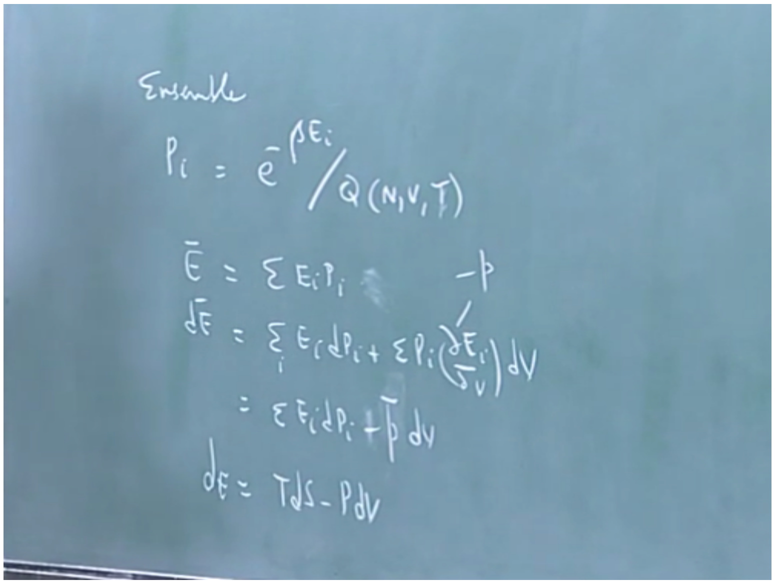

Ensemble

$$P_i = e^{-\beta E_i} / Q(N,V,T)$$

$$\bar{E} = \sum E_i P_i \qquad -p$$

$$d\bar{E} = \sum_i E_i dP_i + \sum P_i \left(\frac{\partial E_i}{\partial V}\right) dV$$

$$= \sum E_i dP_i + \bar{p}\, dV$$

$$dE = TdS - PdV$$

Let me start we were discussing the ensemble we were discussing the probability of a state P I we showed this was $e^{-\beta ei}$/Q remember Q is a function of N,V,T and we said E bar is equal to sum over ei, pi I this is first of all layer and de bar is equal to sum over I dei which we said partial of AI with respect to Dv.

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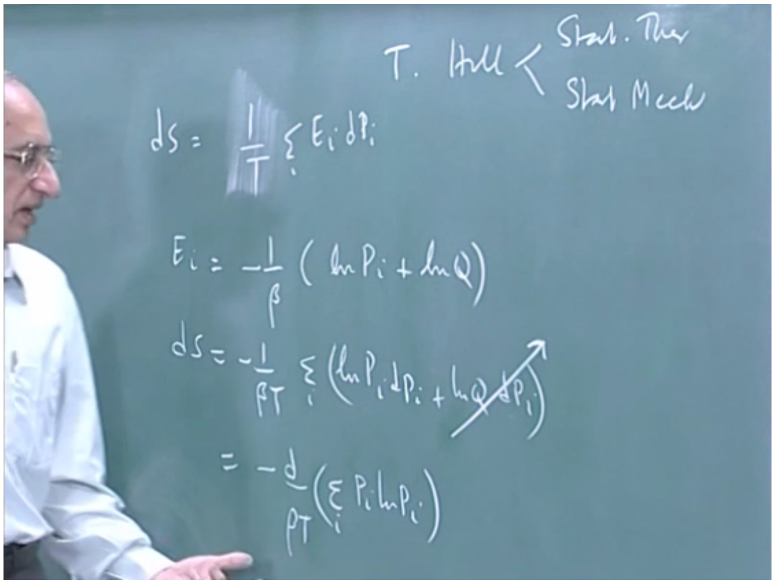

This is equal to sum over a Ei, Pi - p bar dV because this was -p you small p for pressure when we said this corresponds to de in classical thermodynamics which is TDS -PDV so we said ds was equal to is equal to 1 /βT so I have to do this ei de sorry 1 /T times sum over I of Eid p I we say di was after all - 1 /β you take it from here take the log of all this into log of PI+ log Q you so you had ds=-1/β T sum over I of Ln pi di dpi +ln Q * Dpi.

We said sum over P I is one there for some our DPI is 0 so this term is 0 and we rewrote this exactly for the same reason as - 1 / β T some are I, I put the d outside p i log P I because D of log p ID p I is log P I DPI which I have here plus P I times D log here Pi will cancel some over DP I 0 now if you take two independent systems I am going to give this argument very quickly which is a rather important argument.

If I have two systems A and B at the same temperature and in equilibrium with one another you know that the entropy of the combined system is simply the sum of SI plus SP the corresponding probabilities of two systems are independent you know that the probabilities of independent systems are products of the probabilities so if you take the product term you will find SI+SB being the same requires that βT is a constant and give you references the book.

That I have the only book I have read covered the cover is hill, hill has two books one he wrote he was actually at Oregon University it was actually originally a deal with on saga code and all those big people then you move to Oregon and he wrote a book called statistical mechanics in

1950's when people said it is too difficult to read so they called it big hill they said you have to write a small hill and so he wrote another book which is actually fatter than the first book.

But simpler to read it is called statistical thermodynamics and both of them are really classics federal hill something else I forgotten this middle initial thing is called introduction I think one is called statistical thermodynamics maybe it is called introduction to statistical thermodynamics the other is called statistical mechanics and please look at this essentially what that he tell you is if the entropy is to be an extensive property which if you have two systems in the entropy is additive and the probabilities are automatically if they are independent systems.

You know the probability of an event that is the probability of finding your system a in state P I and system be in state PJ is simply P I times PJ p I of a times PJ of B so if that is true then the logarithms will become additive and you will get the same result that plus s B is equal to the sum of the two entropy and for that to happen β that to be an absolute constant so we will simply say here βT is equal to an absolute constant.

And then by proceeding further and deriving the properties of an ideal gas you can verify that this constant surprise is actually the Planck's constant it is surprising that there are so few universal constants this Planck's constant comes up again and again and again so this is this was not necessary for statistical mechanical theory it is exactly like your absolute temperature and the ideal gas temperature being proportional to one another with proportionality constant of one so all I need in the theory is that this should be constant but management by measurement by comparison ideally has properties.

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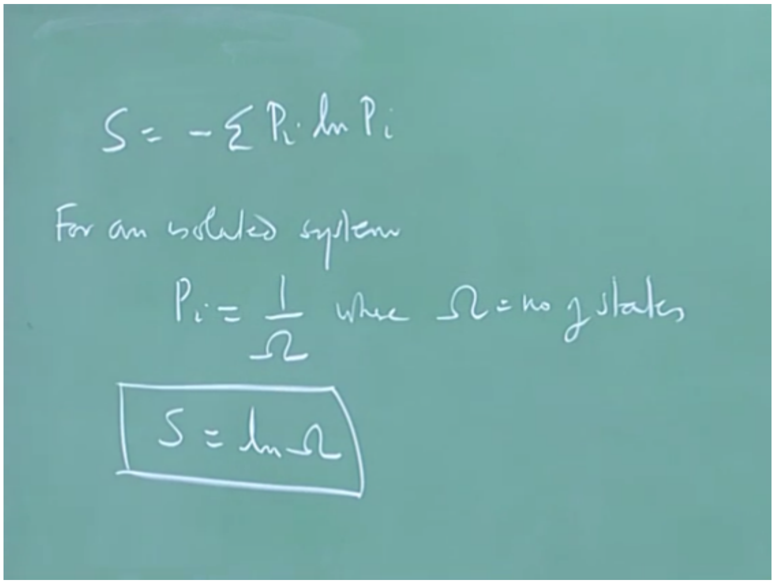

$$S = -\sum P_i \cdot \ln P_i$$

For an isolated system

$$P_i = \frac{1}{\Omega} \text{ where } \Omega = \text{no of states}$$

$$\boxed{S = \ln \Omega}$$

You can show that it is actually k now let me get back here so therefore equal to minus sum over P I log VA for an isolated system we have to looking at a closed system right now but if you isolate the system then all the probabilities are equal p I is simply equal to 1 by Ω all where Ω is the number of states so if you put pi equal to 1 by Ω will simply get s =log Ω incidentally this is inscribed on the dome of on the burial stone of volts MA Boltzmann's burial stone carries this inscription s = log Ω in some senses.

It is the most profound result in statistical physics simply tells you that the number of possible states in which an isolated system the logarithm of that gives you the entropy so entropy is about choice if you have a larger number of such possible states then the entropy increases and the famous statement has to be said in German to sound very perform at the entropy developed Zimmer I forgotten always increases but in the word for increases in German anyway the entropy of the world always increases of the universe always increases that is the famous statement.

The idea is that you get more and more choices but there is nothing to prevent the system from going back to the original choices but it never does that is what gives you the reversibility that is if you have for example this is the most classical example that is always given I have the same gas a hydrogen gas on either side I have an impermeable partition at t = 0 I break this partition let us say I have hydrogen gas here and vacuum here.

Initially this is gas this is vacuum I cut this membrane at t= 0 there is nothing that tells the hydrogen atoms they cannot stay on this side but they will not simply very large number on an average you know with time they will spread out evenly the number of states if these two partitions are equal sized the number of states available to the system has doubled because you got twice the volume if it is double then the entropy will changes in log 2 times the original entropy.

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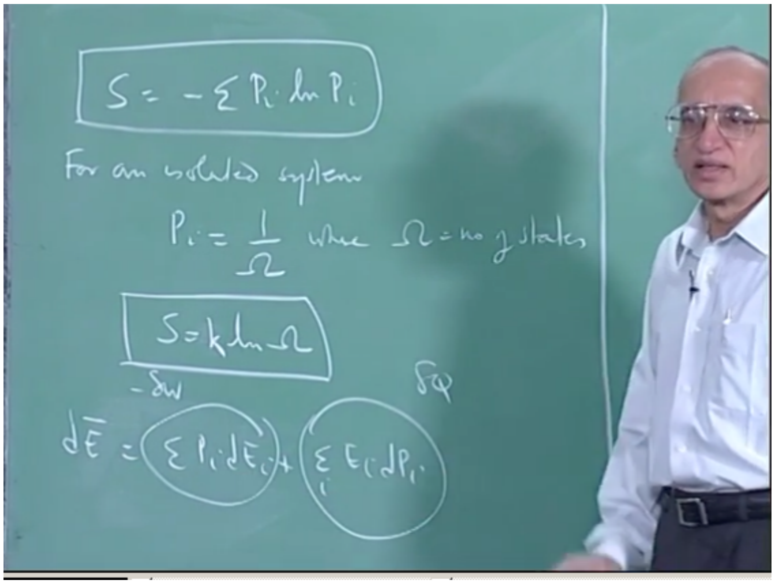

$$\boxed{S = -\sum P_i \ln P_i}$$

For an isolated system

$$P_i = \frac{1}{\Omega} \quad \text{where } \Omega = \text{no of states}$$

$$\boxed{S = k \ln \Omega}$$

$$d\bar{E} = \underbrace{\sum P_i \, dE_i}_{-\delta W} + \underbrace{\sum_i E_i \, dP_i}_{\delta Q}$$

This is this is the entropy 10 ∂s is equal to our log 2 is the classical if you do this for v1 and v2 you will get ds is equal to if you do it at constant temperature ds - CV dT see let us let us do this okay we will write it in cv dt by t plus partial of s with respect to V s with respect to T then s with respect to V is partial of P with respect to T right s increases with me and this is for an ideal gas this is P by T this is r by b.

So as s will integrate our log v2 by v1 right the entropy change for an ideal gas at constant temperature is our log v2 by v1so if you double the volume the entropy increase will be r log 2 and this tells you that the number of states has doubled so the entropy will go as I should not say Ln should say K but remember this is molecular entropy if you do it for one mole you will multiply by Avogadro number.

So you will get r log Ω and this is done per molecule but you have to actually calculate per mole because your practical chemical engineering measure of sizes in terms of moles not in terms of molecules so you simply x we address number this is the result that you use because this is by definition for an isolated system and you cannot verify it directly for an isolated system because the minute you make measurements on a system it is no longer isolated.

So you get into this problem of relating to an isolated system so you can only about isolated systems you can say anything you want trouble is logic will lead you to conclusions about a closed system for which you can make measurements and you will be exposed at that time and if you are expressed nobody will read your theory afterwards so this is the final result this is the most important result that you have from statistical thermodynamics.

The other result is this, this is an important result too I should write this if I write this as dei and we go back say this Ve bar is equal to some or P I be i plus some are I eid this says the energy of a system can change only in two ways one is because the energy levels themselves changed the other is because the probabilities of occupation of those energy levels changed right and this turns out to be work where the energy levels change if the volume changes ei e changes because quantum mechanics tells you I is a function of N and B as you change V the energy levels change and as the energy levels change you do work on the system whereas the energy levels remain the same.

But the occupation changes the number of systems in that state changes then this energy changes because of heat so this has the interpretation of ∂Q this has the interpretation of -∂W depends on the - sign only comes because of convention II with respect to V is -P then you will get otherwise you can say work done on the system is positive and then become plus in terms of measurable variables of course the equations are always the same.

But this is formally work this is heat so this is something that falls out of molecular theory naturally but this is what took joule thousands of experiments to prove to the royal society long after they were convinced he had to continue convincing them because he was not convinced anyway after so the biggest achievement in thermodynamics is to find that there is a perfect differential which is the algebraic sum of two quantities heat and work.

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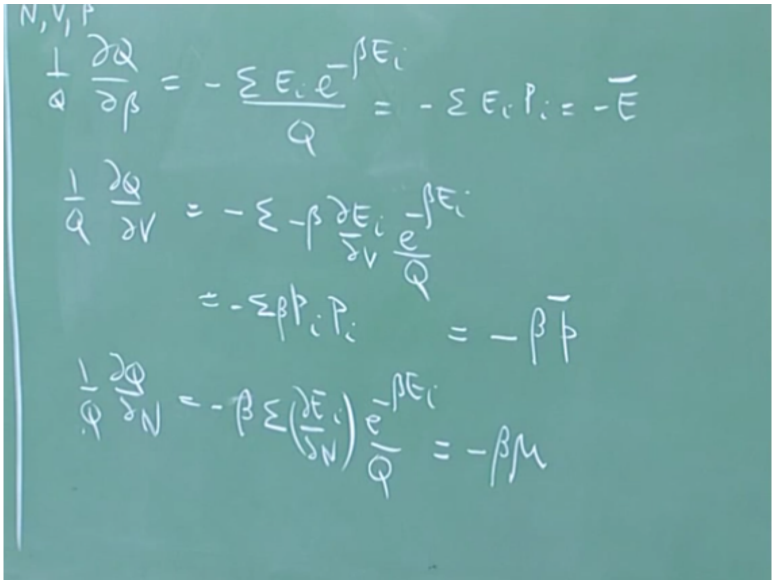

N, V, β

$$\frac{1}{Q}\frac{\partial Q}{\partial \beta} = -\frac{\sum E_i e^{-\beta E_i}}{Q} = -\sum E_i P_i = -\bar{E}$$

$$\frac{1}{Q}\frac{\partial Q}{\partial V} = -\sum -\beta \frac{\partial E_i}{\partial V}\frac{e^{-\beta E_i}}{Q}$$

$$= -\sum \beta p_i P_i \qquad = -\beta \bar{p}$$

$$\frac{1}{Q}\frac{\partial Q}{\partial N} = -\beta \sum \left(\frac{\partial E_i}{\partial N}\right)\frac{e^{-\beta E_i}}{Q} = -\beta \mu$$

And there are only two quantities that you have to worry about heat and work that we have said but in a circle thermodynamics you get expressions for them the way to derive thermodynamic properties finally to make life easier you go back to lnQ you go back to Q this is true of I have done this for the canonical partition canonical system that means the closed system q is simply sum over $a^{-\beta e}$ I so let us look at s is Q with respect to β this Q is a function of Ken V and β is1 by K T it is not I am writing β instead of T β remember is 1 by K Tit is the more natural variable in statistical mechanics.

So if I take partial of Q with respect to β I get minus some over ei a $^{-\beta}$ if I divide this by Q in divide this by cube this becomes minus sum over ei pi which is minus e bar the second result it is a function only three variables so let us differentiate with respect to all three variables partial of Q with respect to V is minus sum over I am differentiating this I am going to minus but I am going to get –β ∂ eI by ∂v e $^{-\beta\ ei.}$
Now you know the dome divided by Q/Q on both sides this ∂ e i/∂ V is, is it - P so this is equal to minus pressure in the ith state there is a β of course times capital ph which is the probability so this is equal to -β P bar and then ∂ Q /∂ n let me divide by Q in anticipation would be –β again some our partial of ei with respect to power minus β.

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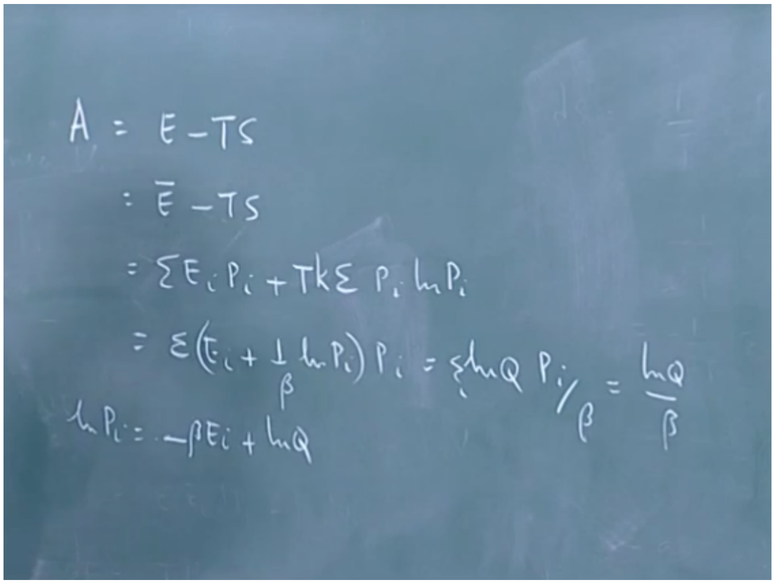

$$A = E - TS$$

$$= \bar{E} - TS$$

$$= \sum E_i P_i + Tk\Sigma\, P_i \ln P_i$$

$$= \Sigma\left(E_i + \frac{1}{\beta}\ln P_i\right) P_i = \sum_i \ln Q\, P_i/\beta = \frac{\ln Q}{\beta}$$

$$\ln P_i = -\beta E_i + \ln Q$$

Because they have divided both sides by q is also a queue there at the moment I am going to write this as -βμ and tell you why in a minute or actually I will go to an easier proposition then we will get this result okay let me do this let us look at a, a is a - TS so this will be e bar minus TS incidentally we do not put an S bar or an A bar you write only E bar I told you the averages can be calculated only for mechanical quantities, quantities that are defined in the individual state which will be pressure energy entropy arises.

Because of the existence of multiple states so it is not an average of a property in a particular state you do not take the average value over several states it exists only because there are multiple states and you have a choice if you had exactly one state if Ω was one and that is the that I show the zero law comes up the road law of thermodynamics tells you that entropy of a perfect crystal at zero degrees K is exactly zero and that comes because the number of states in which a crystal a perfect crystal can exist.

A perfect crystal is simply a monatomic substance in the crystalline form at zero degree so it cannot have translational kinetic energy it cannot have vibration rotational energy if it is a monatomic substance such a crystal we can exist only in one state it has no choice therefore entropy 0 what I want to show is that this is equal to e bar we have seen this is okay let me write this out say sum over ei * Pi -T into some more entropy s K into P I log P I what I want to show I have to do someone I have to show a is equal to minus kt log- K log KT log Q.

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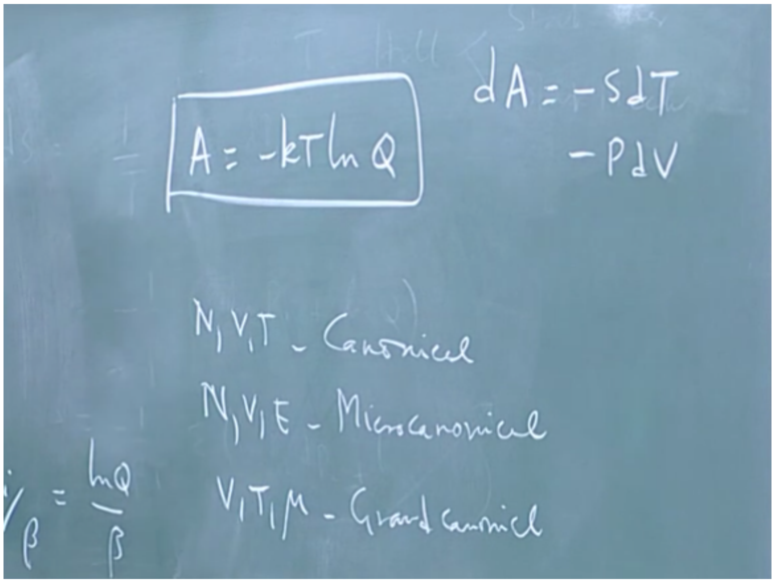

You see that is easy to show yeah this is some over s quite easy e AI plus this is 1 / β I have log P Ix PA but you know log p is, is -βAI +log Q so log P I /β+ I is log Q /β log Q times some our PI b/β so this is simply log Q /β so you have this result Q = -KT I am sorry A =- KT log Q so the whole aim of molecular theory is to calculate Q if you can calculate Q you take the logarithm you get a then you can differentiate with respect to a with respect to V for example at constant and at constant temperature will give you S right you know dAs this is for a closed system da is minus s TP –PDV.

So if you want the pressure your differentiate with respect to V you differentiate a with respect to T same thing you do here should buy new differentiate Q you differentiate with respect to β+β is a more convenient variable so in fact you I could have started with any system I started with N, V, T system this is called the canonical system okay.

I could have done the N, V, E system which is an isolated system so this is called micro canonical because it essentially if you take the n VT system and say all systems will be in TI one particular state it becomes an isolated system so it is called micro canonical you can have an open system you can have sorry V, T, N is not constant but I can have a system in which VT and μT represents equilibrium with the surroundings μ represents again equilibrium mass equilibrium.

So this system would be called grand canonical system and so on these are different ensembles there is also another ensemble it is convenient use which is called the NPT ensemble or isobaric ensemble because it holds the pressure constant the point is molecular theory has very different ways of looking at a system but you know the thermodynamic properties of a closed system when classical thermodynamic properties are completely fixed.

If I give you this and if I take a closed system and give you two variables all other variables are fixed in classical thermodynamics in a pure system you can extend the argument to mixtures readily then the question is if you have different ensembles will you get different answers you are not supposed to so you have to show that you do not actually get different answers the flip side of it is simply here that after all I calculated energy as an average quantity is there a fluctuation in the energy.

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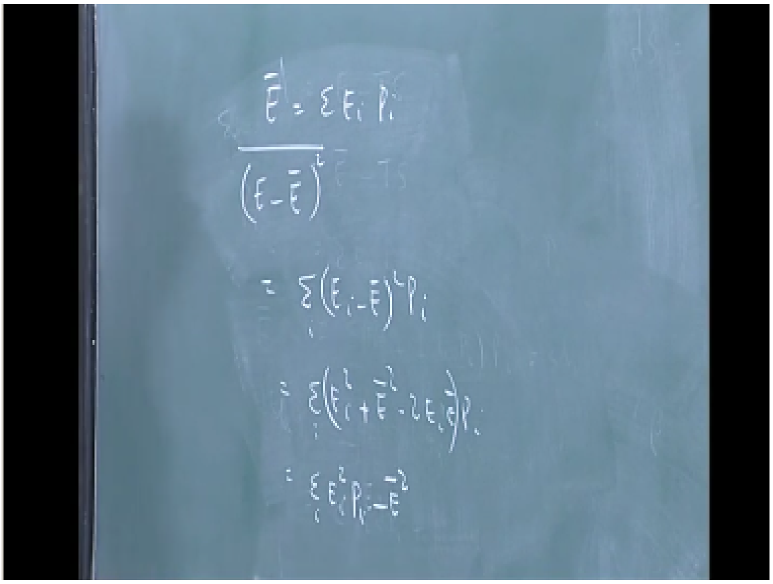

$$\bar{E} = \sum E_i P_i$$

$$\overline{(E-\bar{E})^2}$$

$$= \sum_i (E_i-\bar{E})^2 P_i$$

$$= \sum_i (E_i^2+\bar{E}^2-2E_i\bar{E}) P_i$$

$$= \sum_i E_i^2 P_i - \bar{E}^2$$

So the energy itself is some over ei times pi what is the fluctuation in the energy by fluctuation I want to know what is e -e bar the whole square what I will calculate e- e bar whole essentially what I am going to do is to calculate this average quantity e-e bar average is 0 but e-e bar squared average will give me the fluctuation.

To do this what I do is simply take this Ei- elpi any quantity if I want to find its average I simply find the quantity12 in state I am x so this is some or I this is some our Ei^2-E^2-2EiE.π this Ei π/e so you will get to e but this is plus so these two will cancel I will get simply some Ei^2-E^2 so what

I do is go back to q, q is the source of all inspiration now in the god you worship now is a new God it is called the partition function.

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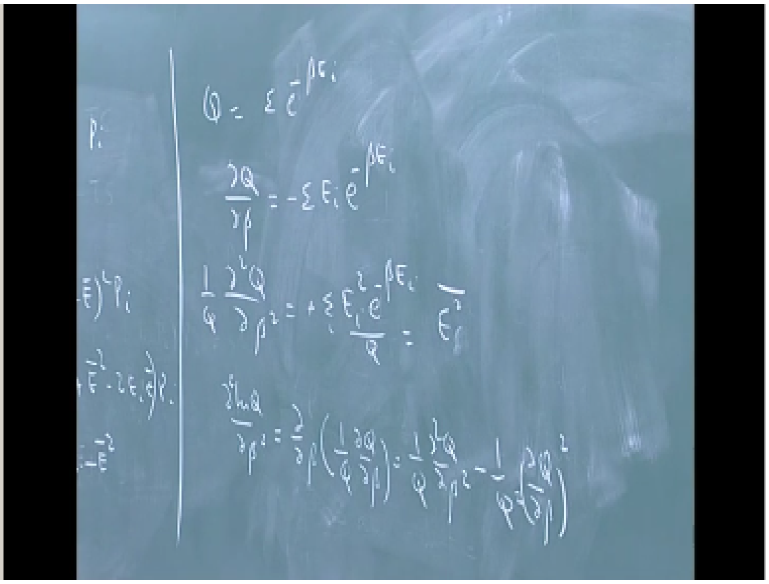

$$Q = \sum e^{-\beta \epsilon_i}$$

$$\frac{\partial Q}{\partial \beta} = -\sum E_i e^{-\beta E_i}$$

$$\frac{1}{Q}\frac{\partial^2 Q}{\partial \beta^2} = +\frac{\sum E_i^2 e^{-\beta E_i}}{Q} = \overline{E_i^2}$$

$$\frac{\partial^2 \ln Q}{\partial \beta^2} = \frac{\partial}{\partial \beta}\left(\frac{1}{Q}\frac{\partial Q}{\partial \beta}\right) = \frac{1}{Q}\frac{\partial^2 Q}{\partial \beta^2} - \frac{1}{Q^2}\left(\frac{\partial Q}{\partial \beta}\right)^2$$

So $q=\sum E^{-\beta i}$ if I want to bring down I differentiate with respect to β so I get $\Delta \log Q/\Delta$-βEI I so the minus sign sorry $\Delta Q/\Delta \beta$ so if I want to bring down one more EIA differentiate again with respect to β^2 it I think we never grow up your kid you do the same thing again and again right you do the same thing here except that you do it in a very sophisticated way with symbols that others do not understand therefore you appear very clear so it is differentiate again with respect to β got EI^2 is so this is the quantity that appears here because if I now / q I get e^2 e but this can be rewritten what is $\Delta \log Q/\Delta\beta$ and take $\Delta^2 \log Q/\Delta\beta^2$this is $\Delta/\beta\Delta \log Q/\Delta\ 1/Q\ \Delta Q$ by $\Delta \beta$ which will give you $1/Q\Delta^2 Q/\Delta\beta^2 - 1/Q^2\ \Delta Q/\Delta\beta^2$ sorry.

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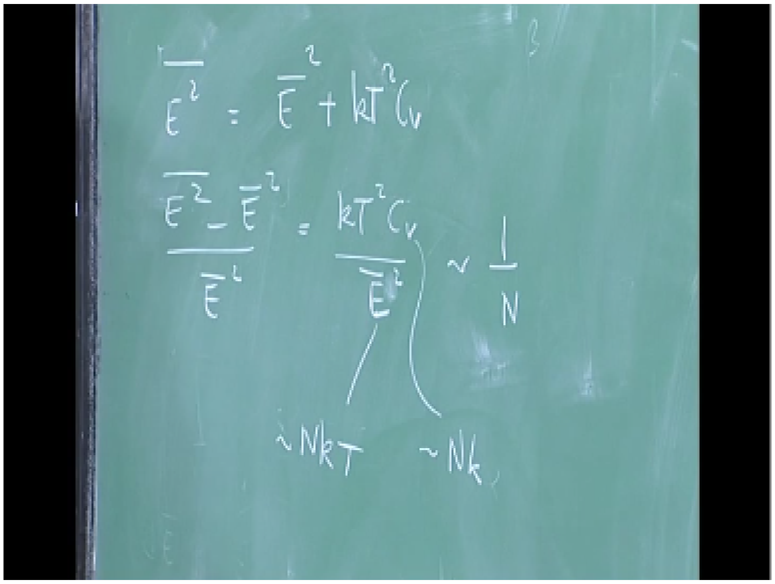

What I am trying to do is find out what e- e AI^2 you know that quantity refutation in the energy that I can expect s in terms of thermodynamic properties to do that I have to always go back to Q log Q and its derivatives now log Q this I know because log Q with respect to βs - y bar - Δ e/Δβ right this is the same as this Δ log Q/ Δβ is simply - ebar this is equal to the quantity I want is this it is equal to this quantity here 1 by Q and this is this is what I want these two are the same this is 1 by Q Δ^2 cube by $\Delta\beta^2$-Δlog Q by $\Delta\beta^2$ that is simply e^2
So I have got both these quantities I wanted ye I^2- PI right which is AI^2 Eai^2 accordingly or e^2 is therefore equal to this is this is e^2 this is e^2 so y^2=e with respect to β what is he with respect to β-Δe bar with respect to β is CV remember this is a canonical ensemble when you differentiate with respect to β you are holding V&T constant I mean V and then constant so it is for a closed system at constant V so you will get CV if you differentiate with respect to e T/ 2 of 1/K T –KT ^{2}t times CB-KT scale.

So e^2 e2+e+ ∂E $\partial\beta^2/\partial\beta$ is this actually it is minus 2e/2 so it is K T ^{2} CB in what you are interested in is e-e^2 you are interested in $e^{2-}e^2$- Ka^2CB and I want to find what this is with respect to you want to find the relative deviation using some things over I want to show you that this is of the order of 1/ n because CV if you are doing it per mole CV is MK this is of the order of NK this is the order of so if you square this you will get an N^2 here you will get only on in the numerator so the ratio will be simply 1 by n.

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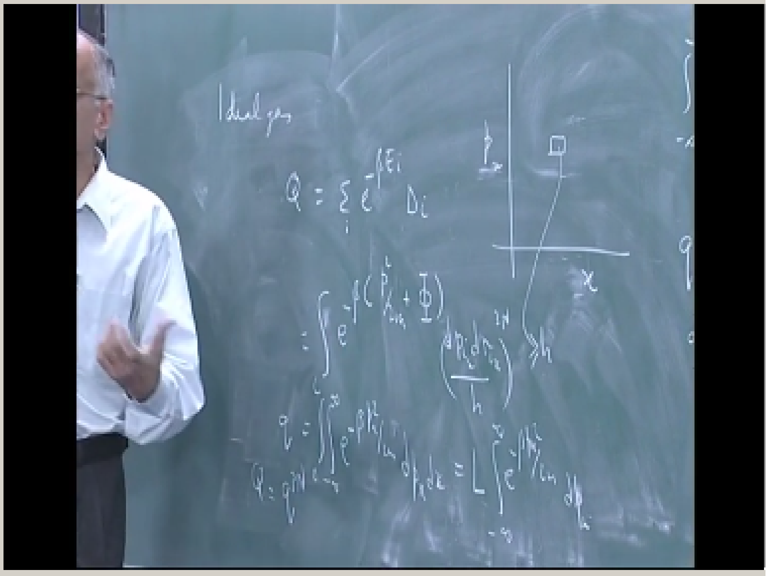

So what it tells you is that σ E is of the order of σe/ e σ 1/√n that means any fluctuations that you observe in the calculated energy will be of the order of 1 by square root of n compared to 1 so if you have 10 to the power 23molecules is unlikely that you see any difference at all if you have 100molecules you have a good chance of seeing ten percent deviation so you get the smaller and smaller and smaller numbers your prediction your assumption basically your assumption in classical thermodynamics is that matter you do not worry about the constitutional matter that all property is very continuously in particular the density varies continuously density never varies continuously.

Because you can only add a molecule and take away a molecule but if you add a molecule to 10 to the power 23 molecules you will notice that the difference is not differential but if you have 10 molecules and we added and take away a molecule you have trouble which is when a no systems are so special in the sense that in nano systems you have number of molecules is so small that if you add or take away a molecule the average property will change significantly that is if you predict an average property for non on systems you could have if you have only 10 molecules in the system then you could have a deviation of 1 √1033% A priori deviation is permitted that is how human behavior is also very predictable.

Because you are talking about billion people in India even more predictable than in a small country but fundamentally you are talking of large numbers all these are laws of large numbers in fact the whole concept of irreversibility and time arrow and all that comes only because of large numbers it is only when you have large numbers because if you had this box right and only two molecules.

And they said in a vacuum on the side and you open this up these two molecules may waive their high probability that they will stay on the left side nothing to make them move so there is no it is very difficult to predict that arrow of time you will say I will watch it after a time if molecules are on both sides then I no time has passed all that bunk amount would not work with two molecules.

But if you have a million molecules moving very sure that about 500,000 will turn up here the law of large numbers is so true that people have applied it to animate systems although the fundamentals of these are not applicable to an imitation because fundamentally you assume here that every system has a state which is described by variables that are not a function of history.

And that is one basic assumption I started with internal energy the proof this two laws of thermodynamics simply establish that you the internal energy and s are functions of state in an animate system they are not functions of state they depend on memory in the system so if you have memory is not applicable.

But one of the schools of thought is called social economic since one is that even in animate systems the law of large numbers is so overwhelming that memory does not matter they will still behave the same way so you can predict social behavior based on that is also a reasonable assumption in except in traumatic cases if you have a second world war and the Jews have been exterminated for a long time Jewish populations behavior will depend very strongly on that persecution soother than such traumatic events it normally seems true that in social dynamics also.

The law of large numbers works to large extent the predictions are valid there is a book by George sq Roma George askew what is his name is Nicholas George is Q sorry count Nicholas you got the Nobel Prize for economics in 60sessentially applying second law of thermodynamics to the equivalent of the second lot economic problems it is a very beautifully written book there is a variation of that by Jeremy Rifkin it is a popular book okay.

Let me get back I will just do thermodynamic properties of an ideal gas very quickly to show you that all this is not just talk I want to calculate $qe\beta e^{i}$ the several ways of doing it I will do it in the classical mold this is summation over I this means you multiply by Δ I which is one right you take integral counts you say state 1 state to state 3etcetera I changes by 1.

So you multiply by one if I want to convert this to an integration I must do it over all the unit cells in phase space so I go to phase space I have p and r I already told you that a cell in units in this space if I have only P X and X for example I know that this cell has to be greater than or equal to H so if it has to be minimum this size that is what quantum mechanics tells me so all I do is divide this phase space into cells of size H then Δ I will actually be alder's I will rewrite this a power β e I will be $p^{2.}$
If I write it in continuous form I am going to write this as integral P^2/ 2 m plus potential energy d of here and integrate over DPI and d RI I have to do this right now I do this by H I have to take a product over many of these cells because one there are actually three n of them so I will write three and if you like actually what I mean is I have PX/ PZ like that for every particle.

So it is p 1 XP 1 YP one and so on since these are independent particles actually know this is going to be q is going to be of the form Q^{n} where q is for individual particles so I can take or all right $Q^{3\ n}$ P- p x^2/m+ the potential energy is zero so I have DP x+ DX I am sorry this is q I will write small Q as this and cap us q^3 this will give me L times this is simply e - $\beta\ x^{\ 2}$ d PX and the momentum in the X direction can go from minus ∞ + ∞ the integration over X also has to be done this will be from zero to the container size let us take a cubicle container eventually the properties do not depend on the shape of the container.

So you will get L times this in text $T\text{-}^{\ \beta\ p\ x}$ / 2 m into DX DPX this is the error integral remember what its magnitude is something like $\pi/\sqrt{}e^{-ax}$ square root DX D remember minus ∞ to plus ∞ $e^{-\ ax}$ DX =√ π/ a do you recall that it is a that form I mean there may be a factor in front put it as proportional to that means if I do this integral I will get q is of the form l times this is to MKT will come the denominator.

So will get $\sqrt{\pi}$ into to MKT so q^3 will be L^3 will be the volume V then $\sqrt{\pi}$ to π MKT so Q will be simply q^{3n} so it is V^3 I am sure we to the power n to π MKT to the power 3 n / $2Q^3$ is this to the power cube this is volume this is cubed at this stage actually if you go back to quantum mechanics you have to in quantum mechanics you will get the correct answer in classical mechanics you make a small mistake.

Because the particles are indistinguishable you have to divide when you calculate this way you have not taken into account that the particles are indistinguishable so this is what is called the correct Boltzmann counting and write down in quantum mechanics you do not need this if I had done it quantum mechanically I have got the correct answer in all this will be the same you have to divide by the number of permutations that are possible of the particles.

And we would not write n factorial because in quantum mechanics in statistical mechanics n factorial is very ugly so we will write it as n/ e^n using Sterling's approximation so this will be if I write this as n/ e I will get EV^n to π MKT 3n / 2/ MN you will get and you can show that entropy is not an extensive property effectively so this does the pier sneaky.

But it actually comes in automatically if you do quantum mechanics because quantum mechanics recognizes the distinguishable and distinguishable states in classical mechanics you do not make that distinction that is only now once I have q I take log Q to get the pressure I am going to furnish it with respect to be to get the energy I am going to do differentiation with respect to t so I am only worried about T&V dependence so I will get n log V on top then T dependences 3 n / 2 3 n K /2 or3 n / 2 in the log π am looking at plus some function of n and if you like mass so what is my energy this if I take K log Q I get the hell knows energy a is simply KT log Q-KT log Q so if all I have to do is multiply by the kt n KT log V-3 k T / 2 log P + n and m MS the molecular weight the mass of a single molecule is not the molecular weight mass multiplied by Avogadro's number will give you molecular weight.

So if I want for example if I know one the pressure p is minus partial away with respect to P at constant volume so I will get NK/ kt by be is something the matter Katie log Q now get some more terms not so I am sorry this is with respect to V and no template yeah partial with respect to be so only one term this is RT/V lo and behold you have the ideal gas so it looks like you start with obscure assumptions.

And get to a beautiful result gives you a complete mechanistic picture it talks I think really you have to look at these things in historical perspective but the whole result is beautiful you can either classical thermodynamics does not have much scope in terms of derivations because you have to imagine mechanisms and do it in statistical mechanics you can go to the equilibrium part and derive these results you can also discuss things like diffusion other things and stop there as far as the course is concerned it is over now formally declared closed.

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