Chemical Principles 2
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Microscopic Equivalent of Heat and Work

Now we are going to talk about the entropy change due to heat and work and before that I would like to remind you our discussions about microscopic understanding of heat and work, so by now you know that any system can be described as particles occupying different energy levels so be it harmonic oscillator, particle in a box are good examples of that even for realistic system one can solve quantum Mechanic problems and can get different energy levels however close they are we know that for very high temperature system levels are very close together and therefore it behaves classically but again it is always we can have different levels always if we want to.

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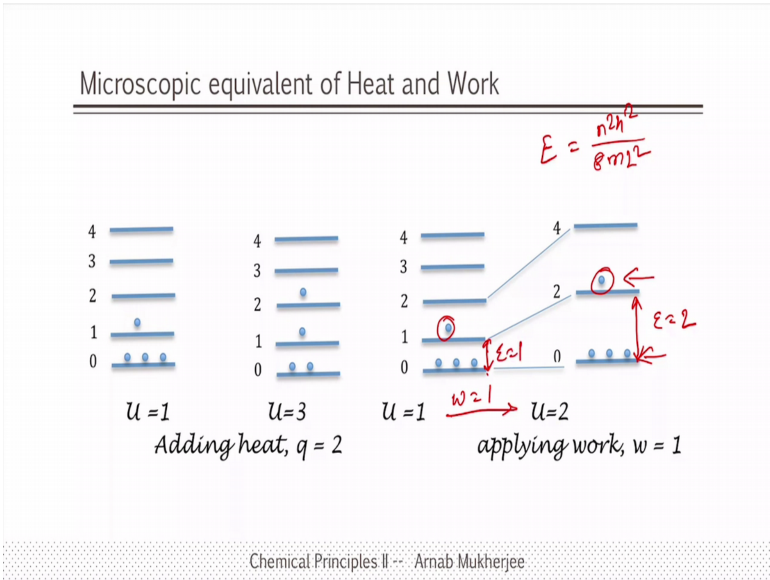

So microscopically if you look at it the internal energy of system is obtain from how the particles are distributed in different levels for example this system the internal energy is one and why is that so because again out of 4 particles 3 are occupying the 0 energy level and one is occupying the 1st energy level. Now when you put heat to the system and you know the heat from the 1st floor heat, internal energy and work they are all equivalent right, so when you put heat to the system then what will happen is that the energy of the system now goes from 1 to 2.

Now how can it go to 2 either one more particle. Okay so we are using 2 units of heat here actually so you know how it can have…then it will have 3 units of heat right, from 1 to 3 now how it can have 3? Either I can take this particular to the 2nd level and one more particle from 0 to this level, I can do that or I can do many different ways I can put all the 3 particles to the 1st level and one particle in the 0th level and many different ways you can do that but the main point here is to show you is that whenever you put heat to the system, the particle get distributed to other levels and that is how the system will observe the heat, however when you do work, does it happen that way?

So when you do work on the system we know that not the heat, just the work on the system we know what happens is that the volume decrease is right, so what happens if the volume decreases? Now from a particle in a box example I would like to remind you is that you know that energy of a particle in a box is n square h square by 8 m L square and L is the length of the box, so wherever L decreases wherever length decreases energy will increase because they are inversely proportional, so what happens when you do walk on the system your length of the box decreases and your energy level which was separated by let us say one unit will increase by large unit.

Here we are using a very simple example I am showing that whenever you do let us say one unit of work W equal to 1 then what happens is that the energy spacing itself increases to the double but you notice that particles remains….distribution remains same that means 3 particles still is in the ground state and one particle is in the next excited state however energy of the next excited state itself is now equal to 2 instead of it was equal to 1, so the gap itself increases, particle distribution did not change just the gap itself changes, so whenever you put heat then particle distribution changes but when you do work then the work itself changes the energy level of the system, energy levels will change and if energy level change you know the overall energy of the system will change and that example you can understand from particle in the box itself. Very good question, so the question is that then will the work change the entropy? We are going to discuss that in a moment.

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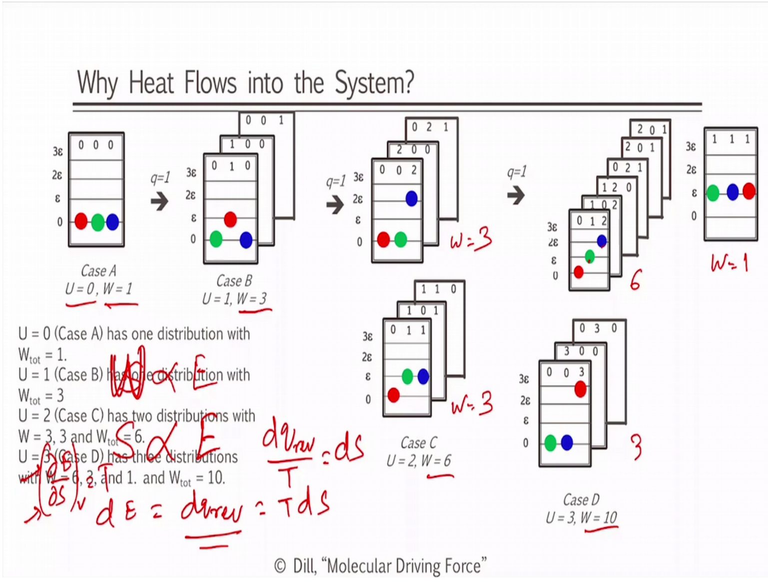

Why heat flows into the system? So why whenever we try to heat a system it actually goes into the system of course not a hot system of course you cannot heat a system by a colder system but always if you bring in hotter system the heat will flow into, so why heat flows into spontaneously into a system and that is what we are going to see because when something drops, the kinetic energy gets dissipated to heat and then it goes to the floor and all, so it is easy for the heat to flow in why is the case that you are going to see, let us take a system and with these examples we have done before.

So you are already familiar with that, so let us start with a system of 0 energy so U equal to 0 and number of micro-state capital W is number of microstate is 1 right now because there is only one possible way of doing so because they are all in the 0 level. Now let us put some heat to the system and you know what happens when you put heat to the system, the particle changes the energy level remains the same, particle distribution changes, so put q equal to 1 so energy now will become 1 and 1 particle hash go to the next level.

Now how many ways you can do that I can put any of the 3 particles, so W becomes 3, so as you can see when you try to heat the system, heat will go into the system because W increases because W increases means entropy increases and entropy increase is a favourable process we know that because there are only possible things to happen. Now put one more heat to the system, now what is going to happen?

Now our total energy of the system now is 2 now I can do it in 2 possible ways, I can either take one particle to the 2nd level and that is 3 possible ways of doing so because I can take any

3 of the particle or I can take 2 particles to the higher level and that is also there are 3 possible ways of doing so because I can take 2 of the 3 particles 3C2 which is 3, so total number of possibilities I get is 6 when we are heating the (())(6:17) system, so you see as and when we are heating the system and as an when the internal energy of the system increases number of micro-states increases, so in a way you can say that entropy is proportional to microstate.

I will give one more example and then I will come back to that. Now put one more heat to the system, now what happens is that now our energy of the system is 3 and now there are 3 possible ways of doing so 3 possible distribution of doing so we already know about that, either we take all the 3 particles to the 1st level and there is only one way of doing so or we can take one particle in 0,1 particle in 1 and 1 particle in 2 and there are as you know 6 possible way of doing so because I can take 3 possible ways for the 2nd one and 2 possible ways of this one, so there are 6 possible ways and I take one particle to the 3rd level and that is 3 possible ways. When I add them up there are 10 possible ways of putting the heat.

So you can see that W is proportional to energy and therefore aces is also proportional to energy, so with the amount of energy entropy also increases, so entropy is actually proportional to energy and that is one of the postulates of thermodynamics when it is starting in apostolate base way that entropy is monotonically increasing function of energy and you will see soon enough or I can already discussed to you because you have already discussed about that is that we know from classical thermodynamics that dq reversible by T is nothing but ds or dq reversible is actually Tds right and then we know that whenever we say that let us say work done is 0 then it will be nothing but dE and then as you can see that dE by ds at a constant volume whenever there is no work it is nothing but temperature.

So because temperature can never be negative you can see that whenever the entropy will increase our energy also have to increase at a constant volume though if there is no work done that is the constrained that we have to put into the system, so without doing the work… here we are not doing the work because there is no change in the energy levels taking place that is why there is no work done here but there is only…heat is going in which means the internal energy of the system is increasing and that is increasing the number of microstate and that has to happen because that is water temperature is and a temperature cannot be negative and that is one interesting thing to really think about and this is I will just clear out the pen marking and you can see exactly the same thing I have written here that we have discussed already.

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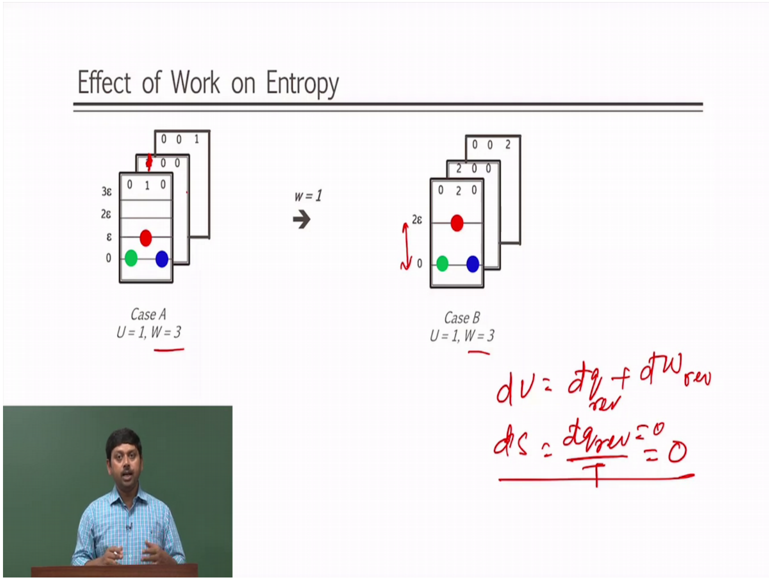

So now let us see how work effects the entropy, now let us say we take the same system where there are 3 particles and one particle is in the level 1 and the 010 they denote just the energy of those particles for example these 2 particles are 0 level that is why I have mentioned 0 and 1 particle is in the higher level that is why it is mentioned in one, so this configuration is where the left particle has energy one and other 2 particles 0 and this configuration is where the last particle is one, so these 3 configurations are denoted by that 010.

Now let us say I do want (())(9:35) work on the system and you know what is expected is that the spacing itself now changes, it absorbs the energy but just the way that the spacing energy changes without changing any distribution of the particle and we see that the number of microstate is not going to change anymore because there are just going to be remain the same even though the energy gap is higher that does not matter.

So does it mean that when you do work on the system the entropy does not change but then that immediately gives us another question that what happens for an expansion process because an expansion process gives more number of micro-states we know that that anywhere whenever we talked about an expansion it is more accessible states for the system and therefore more entropy should have come but we have seen in the carnot cycle that in the adiabatic expansion or compression process there is no change in entropy because dq reversible by T is 0, we see that from the 1st log thermodynamics also that d equal to dq plus dW and when it is done in reversible manner then the entropy changes nothing by dq reversible by T and nothing to do with dw.

So if dq reversible is 0 then entropy is 0 and that is what happens for adiabatic expansion in compression process. Now in expansion process entropy should have increased but they do larger accessible micro-states however at the same time the temperature of the system is decreasing and because of the temperature the system is decreasing, it does not have nearly energy to access the accessible states, so therefore the entropy cannot increase in that case and same thing happens for the compression process.

In the compression process the volume decreases but it should have therefore since decrease the entropy but it has now increased temperature which means that it can now access more number of states and therefore it will compensate that, so this adiabatic expansion and compression process is the opposing phenomena of expansion and not having enough energy to access is actually compensating each other giving rise to the fact that during the work done you do not get to see any change in the entropy.

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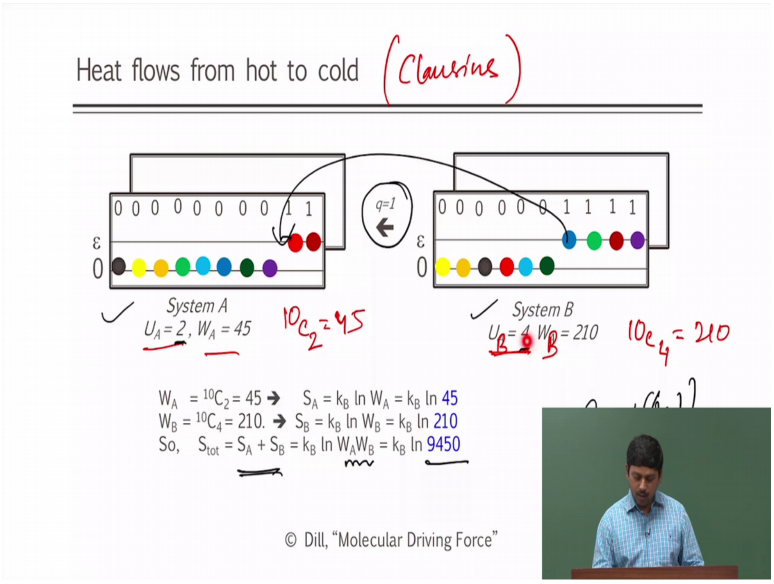

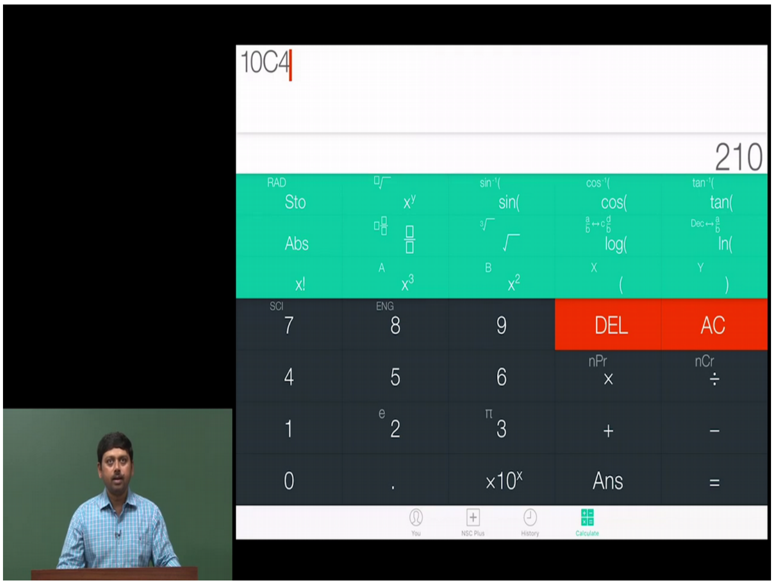

Now let us talk about heat flows from hot to cold, so you remember this heat flows from hot to cold spontaneously is from Clausius theorem of 2nd law of thermodynamics that heat will spontaneously go from high temperature to low temperature or hot to cold and not the other way round spontaneously and that was the basis of classical thermodynamics explanation and there was no microscopic basis to understand that at that point it is just the phenomena just an observation it never happens the other way something always will fall down from up to down and it will not go other way the particle will not fly away or levitate right.

So this is an observation from which they have built the thermodynamics a classical thermodynamics subject whereas from Boltzmann point of view from atoms and molecules and number of microstate a parallel process is going on, a parallel way of understanding is going on however they are connected and we will make those connections between the classical and the statistical laws but right now we are only talking about number of possibilities, number of microstates, so here we see that how the number of microstates can help us understand that heat will always go from high temperature to low temperature.

So let us take a system where internal energy of the system is 4 and we have taken very simple two-level system with 10 particles, so now two-level system 10 particle meaning that 4 out of the 10 particles will have to go to the higher level okay and that is the reason that it will have the 4. Now how many possible ways you can do that because all are distinguishable particles, so I can do…I have to choose 4 out of the 10 in order to put them to the higher level so I do 10C4 ways and you know 10C4 is how much, so let us calculate that and show you 10C4 is 210 and we wrote as 210 here already.

Let us take another system where the energy is only 2 and again I have to choose to out of 10 particle in order to put them to the higher level and that will give us 10C2 number of possibilities and that is 45, so WA is 45 and this should be WB, WA is 45 and WB is 210, so when you make system together we will have how many microstate? This will be product remember never add them because as you know entropy is additive quantity just like volume of A and volume of B combined together will be volume A plus volume B.

Similarly entropy of A and entropy of B will be added together as entropy of A plus entropy of B however when we are talking about microstates the number of possibilities of A and the number of possibilities of B is always a product, so therefore when you do that what happens is that WA is 45 and therefore entropy of A is kB Ln WA which is kB Ln 45 okay. Now WB 210, so entropy of B is kB Ln WB which is kB Ln 210. When you add them together what is happening is we are adding entropy of A and entropy of B and you see what he we are doing we are multiplying them, we are multiplying the microstates and that becomes kB Ln 9450 that is very important point.

Whenever you talking about 2 different systems and that is the reason I told you write that entropy is proportional to W number of microstates but this proportionality comes with an Ln function, a function of W I should say, now comes with a logarithm function the main reason is that while microstate shower multiplicative entropy is additive and that is only possible if you put and Ln function in between and that is why Ln come in between, because so that we can actually add the entropy and multiply the number of microstates that is very important point. Now let us transfer heat from high temperature to low temperature only, so I take this one of the particle and put it here in this level, so now the energy of this system will become 3 and energy of the system also will become 3 now earlier it was 4 and it was 2, now we are taking it 3 to 3 okay.

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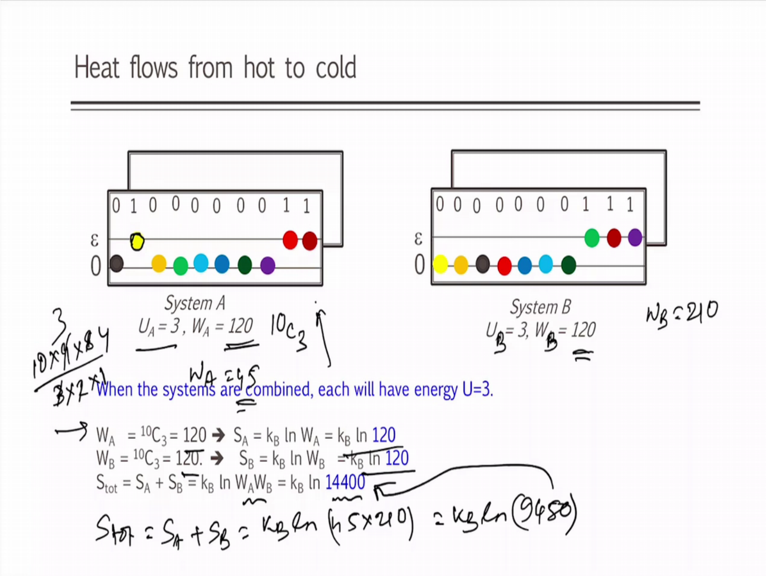

Let us see what will be the repercussions for that, so now UA is 3 and how many ways you can do that? 10C3 ways, so when you do 10C3 ways if you remember earlier how much it was, it was 45, so I have put one more particle you can see here this particle I have put up on the 1st level earlier only 2 particles were there now there are 3 particles, so now it has become 45 10C3, is it modify let me do 10 into 9 into 8 by 3 into 2 into one, so 3 3 za 9 and 2 4 za 8, so 120 ways earlier it was 45 alone but at the same time, so that means the entropy of this A system has increase because earlier it was 45 now it is 120.

So entropy has definitely increased for the left system, however the same time you remember that earlier it was…this should be B and this also should be B, earlier it was WB was 210 and now it has become 120, so it has reduced now so whenever there is a heat transfer do not think that both of them are gaining entropy one is losing and another is gaining but together they are gaining that is the point that we are going to show. It has lost their entropy by giving away heat, it has gain entropy by taking in heat and when you combine them together what we see?

Number of microstates…so again WA is 120 entropy is kB Ln 120, WB is 120 because the same and kB Ln W is 120 together is how much? WA into WB so 120 in to 120 giving rise to 14,400, do you remember how much it was before? How much the combine system entropy earlier was kB Ln 45 multiplied by 210 which was kB Ln 9450. So from 9450 it has increased to 14400, so you see although one part got lesser entropy another part got more entropy in a combined manner they got more entropy and that is the reason the heat will flow from high temperature to low temperature.

Now you should do one calculation instead of like earlier it was 4 2 distribution of energy right, you should transfer heat from low to high that means you make it 15 and see whether the number of microstates for the combined system increases or not and that will tell you that whether it will be possible or not. So now you see that why spontaneously heat will transfer from high to low the reason is that it is just more probable because it will just give more number of micro-states, more possibilities and that is why he will always flow, so microscopic molecule thermodynamics gives some microscopic understanding why heat flows and classically it is just a postulate.

Statistically it is not a postulate it can be shown whereas statistically the postulate lies somewhere else it says that the entropy is proportional to number of micro-states that is postulate for statistical thermodynamics or molecular thermodynamics whereas this can be derivable. In classical thermodynamics the pustules starts with the fact that heat cannot transfer from low temperature to high temperature, yes.

The question is that whatever amount of energy that is being transferred by the hot object it is received by the cold object, so dq is same in both the cases there in one case why together entropy is increasing because we have to remember always the fact that there is in the denominator the temperature that is an integrating factor, so you are transferring heat from a high-temperature which is already having more accessible state to giving it to low temperature object which is not having that many accessible states and somehow the quality of heat becomes better when it is given to a cold object. By quality I mean the number of possibilities that can be, so a rich person is already rich it does not have much revenues to let us say spend it but then if you give it to somebody who does not have that probably have more avenues to spend it.