Chemical Principles 2
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Module 06
Lecture 35
Tutorial Problem - 06

Today we are going to solve some tutorial problems these are the problems associated with both the first law of thermodynamics and second law of thermodynamics we will go over some multiple choice problems, some short answer type problems to get a feel of how to answer certain kind of questions. And also below hopefully it will clear your concepts on these two particular topics because after that we are going to move it to a different one from the next from next module itself so therefore we will go over this one.

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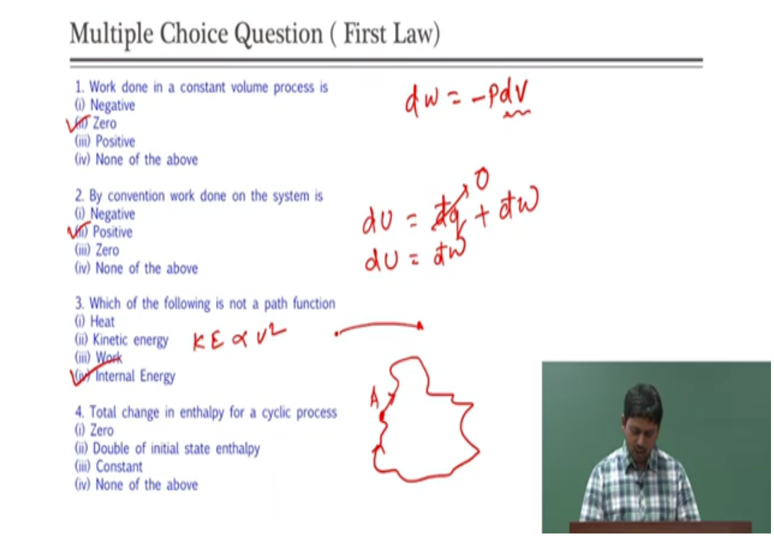

So we will start with some multiple choice questions based on the first law. So multiple choice questions the 1st one is work done in a constant volume process is either negative, 0, positive, or none of the above. So work done in a constant volume process is where you know your volume does not change and if you remember the definition of work done is dW equal to minus PdV, so it is always that is the formula so we have to see the change in volume in order to see the work done.

Since we said that it is a constant volume process which means the dV equal to 0, if dV equal to 0 then the work done will be 0 so 0 will be the answer to the question. So you whenever you are looking at this you should pause the movie, think about the answer and then you can actually see what the right answer is and that way it will be helpful for you to probably get the concept across.

2nd question by convention work done on the system is negative, positive, 0 and none of the above. So this is a question based on totally memory or the concept of the particular law. So we have discussed that always we are going to take conventionally work done on the system as positive. The reason is as we have discussed before first law of thermodynamics is (d equal to) dU equal to dq plus dW now when the dq is 0, then internal energy is equal to the work done, now you know that when work done is work is done on the system the internal energy of this is increases.

So therefore if work done is positive then internal energy will be also positive that is why conventionally work done on the system is always positive. And you can see from from the above expression also that if work done on the system happens then typically dV is a negative negative quantity because volume decreases in that case minus PdV is a positive quantity. So therefore this will also you can see that work done on the system is positive, so positive is the right answer, which of the following is not a path function heat, kinetic energy, work and internal energy?

So as we have discussed heat is a path function because heat can be changed by either constant volume or constant pressure process, work is of course a path function path function because one can do we have already shown by (grano) by graphical ways also that work can be done in one step and multistep so therefore work is also a path function because it depends how you are doing the work.

Kinetic energy is a little bit tricky one you might think that this is energy and therefore it will be a state function, however kinetic energy is nothing but kinetic energy is proportional to mass and velocity square. Now mass is of course intrinsic to the system, however a system can go from one step to another step using different velocities, it can be faster and then slower or it can be slower and then faster, so however at every point that kinetic energy can be different.

Internal energy however by definition is a state function because internal energy is governed by the specific system coordinates. For example we showed that in turn energy depends on (())(4:17) number of molecules, volume, temperature and things like that. So therefore it can have yes therefore it is by definition is a state function so this is the right answer. Total energy in enthalpy for a cyclic process is zero, double the initial enthalpy initial state enthalpy is constant, or none of the above.

So in a cyclic when you talk about the cyclic process which means that we start from somewhere let us say start from A and we do whatever we want to and we come back to the same state. Now this question actually is slightly twisted in the sense that whenever you talk about a cyclic process the state functions are going to be always zero change in the values of the state functions are going to be zero, because state functions depend on the state of the system and not the path, so therefore whichever path it takes it does not matter if it comes back to the same place state function value will be zero.

Now the question actually boils down to this particular thing is enthalpy a state function or a path function? Now we know by definition that enthalpy is nothing but you know heat at a constant pressure, whenever we say that heat at a constant pressure it automatically we are defining the path. So therefore enthalpy is a state function, just like other thermodynamic potentials. Since enthalpy is a state function therefore for a cyclic process the change will be equal to zero.

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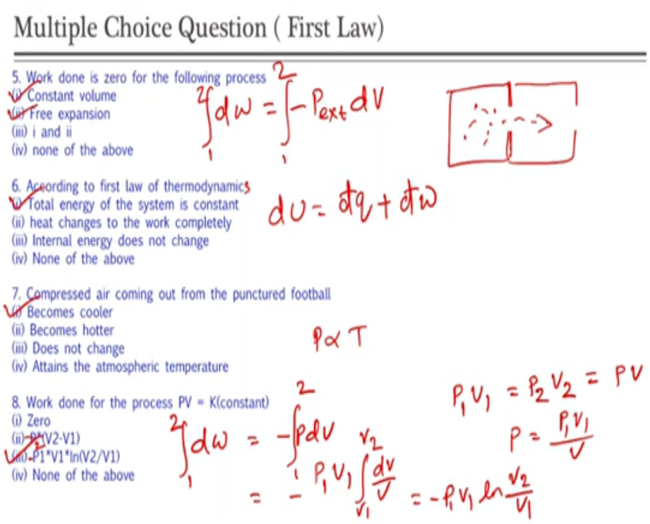

Next question, work done is zero for the following process, constant volume, free expansion, first and second, and none of the above? Anyway so the question now again asking you two things is constant volume work done is zero? Yes, we have explained that in previous questions and free expansion case what is the work done in free expansion? You remember that for free expansion dW is or for any case the definition of work is integration of this particular quantity, work done for going from one step to another step is minus P external dV is the external pressure against which the system expands or contract giving rise to some work done.

Now in case of free expansion as we discussed before external pressure is zero, because let us say the gases are in a particular chamber and there is a barrier here and suddenly if we create a hole then the particles will diffuse to the other side it will diffuse to the other side against any pressure. So P external is zero for a free expansion and therefore that will also be zero so work done will be zero for both constant volume case and free expansion case.

So 6th question, according to the first law of thermodynamics total energy of the system is constant, heat changes to work completely, internal energy does not change and none of the above. Now first law of thermodynamics is the law of conservation of energy. So, therefore it says that that the total energy of the system will always remain constant. So therefore 1 is always right, second one heat changes to work is completely it is not true because you can you know that the internal energy is equal to change in heat plus change in work or work done.

So therefore heat cannot change because there are some processes in which internal energy of the system will change, so this second one cannot be true. And internal it does not change is not true because internal energy will may or may not change depending on you know whether there are no processes in which it may change or may not change for ideal gas we know that if temperature does not change then internal you will not change. However, that is not true for other systems.

So a 7th question, compressed air coming out of a punctured football becomes cooler, becomes hotter, does not change and attains the atmospheric temperature. So although we know that the air inside the football is actually a real gas and not an ideal gas. However, we can understand this kind of questions or which are little bit conceptual questions we can understand by taking an equivalent approach of ideal gas system. Because real gas will be difficult so therefore let us consider that if ideal gas where inside a football and if it came out what would have happened?

Now immediately you can see that there is an expansion in volume, it was compressed therefore it was in a in a smaller volume and it is coming out and in bigger volume and therefore and since we know that the pressure after coming out is actually decreasing because it was in a high pressure before you will have to pump the football right with a pump you have to push the air inside, so the pressure is more than one atmosphere for sure when it is coming out the pressure decreases and therefore since P is proportional to temperature therefore temperature also will decrease and the air will become cooler.

So 8th question work done for the process pV equal to K or K is a constant is zero, P V2 minus V1, and then third option is P1 V1 ln V2 by V1, here P1 means the initial pressure and V1 means the initial volume, similarly V2 means final volume and things like that and none of the above. So to understand that let us just calculate the work done, so what is work done? So dW we can write as minus PdV, so now we know that we are going from once you know initial point to the final point, here also we are going from initial point to the final point.

Now initial point pressure is P1, volume is V1, final point pressure is P2 and volume is V2, which means that at any point along the whole chain it is nothing but PV. So therefore we can take the P as P equal to P1 V1 by V where P1 and V1 are actually fixed points right there are constants P1 V1 P2 V2 they are all constants. Now let us replace P which is a variable, V is also variable, whereas P1 V1 are constants in this equation what will we get is that P1 V1 dV by V going from V1 to V2, which means we are going to get minus P1 V1 ln V2 by V1.

So here it looks like the third option will be correct if I put a minus sign, other options will not be correct. You can think about the case where the second option will be correct because we talked about where the 0 will be correct, the second option will be correct if is done at a constant. However, let us put it at P2 and minus, in that case if it is a constant pressure process then the second option will be correct.

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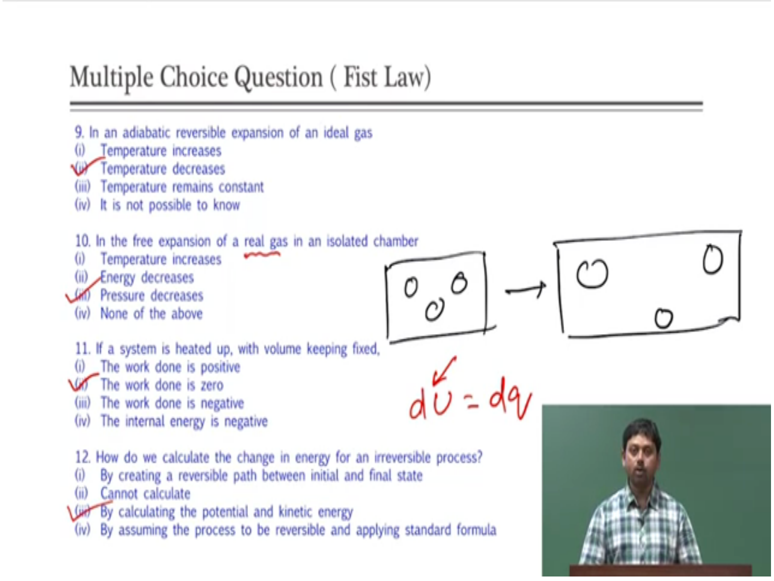

Okay, continuing that let us talk about the 9th question. In an adiabatic reversible expansion of an ideal gas, so it is an adiabatic process, it is a reversible process and is an expansion process you have to think about all the three things, temperature increases, temperature decreases, temperature remains constant and it is not possible to know. Now it is possible to know because it is an ideal gas, so we know all different types of calculations of ideal gas and it is an adiabatic process and we know that in adiabatic process our dq equal to zero.

So therefore from first law of thermodynamics we know dU equal to dW that means change in the internal energy is equal to work done, it is an expansion process and we know that expansion process dW is minus PdV, expansion process means dV means volume increases. Therefore, dW is a negative quantity and if (dW) dU is a negative quantity if dU is a negative quantity we know dU equal to Cv dT and Cv is a constant and that is a negative quantity Cv dT so therefore dT must be a negative quantity.

And you know what it means that dT is negative quantity it means that the final temperature is less than the initial temperature. Therefore, the change in temperature is lesser negative, so temperature decreases is the right answer.

10th question, in the free expansion of a real gas in an isolated chamber, okay what will happen any of this force? See there is there is a catch here, so you have to see the real gas there is a catch. So free expansion that we discussed before, free expansion of an ideal gases in an isolated chamber temperature remains constant, reason is that in an isolated chamber your (Q) dq equal be zero, so dU equal to DW. So when it is a free expansion your work done is also zero, therefore dU will remain 0 and therefore temperature will not change for an ideal gas.

So for an ideal gas here the question is about real gas, however we are talking about ideal gas just to get a premise for understanding this particular thing. So for an ideal gas as you can see the dq is zero, dW is also zero because it is free expansion, therefore dU will be 0 and therefore dT also will be 0, temperature will not change. However, real gas is not the case and the reason is I will explain.

In case of real gas however what happens is that initially the particles were close together and then when the expansion happens they become far separated. So the these particles overcome the attractive interaction between them and therefore it does the system does some work and therefore it because the system does some work the dW becomes negative and therefore dU also become negative decreasing the temperature of the system so temperature decreases is the right answer however there is no option like that.

So energy will not decrease because it is an isolated system, temperature increases is wrong because temperature decreases we know but there is no option like that, therefore the right answer is that pressure decrease because whenever there is an expansion in volume the pressure decreases because pressure is inversely proportional to the volume, of course for ideal gas but also for real gas it may not be exactly inverse but of course it is reciprocal that means if pressure increases volume decreases, if volume increases pressure decreases.

Question number 11, if a system is heated up with volume being fixed what are the things that is going on the work done is positive, the work done is 0, the work done is negative and internal energy is negative? Now if a system is heated up with volume keeping fixed that is the idea. So you are putting heat to the system and the volume you are not allowing to change which means your work done is 0, because there is no volume change means we already discussed that work done will be zero, which means your dU is nothing but dq and is DQ positive? Yes, because we are heating up the system, we are putting heat to the system.

So therefore your internal energy has to increase, the change in energy is negative is wrong because it will be positive. So work done is negative, we have already discussed that if volume is fixed then there is no work done, the work done is zero is the right answer therefore and work done is positive again is wrong.

12th question, how do we calculate the change in energy for an irreversible process by calculating reversible path between initial and final state, cannot calculate, by calculating the potential and kinetic energy, and by assuming the process to be reversible and applying standard formula? Now this is a trick question because whether the so energy of the system is the is property of the state of the system.

So if we know the kinetic energy and potential energy of the system we can always calculate the total energy of the system or change in energy of the system we need not really look into the path because the internal energy so change in energy by that we mean internal energy of the system, it does not depend on the path. So therefore it does not matter which path it took we just need to know the final value and the initial value and it will be all right. So by calculating the potential energy and the kinetic energy will be the right answer.

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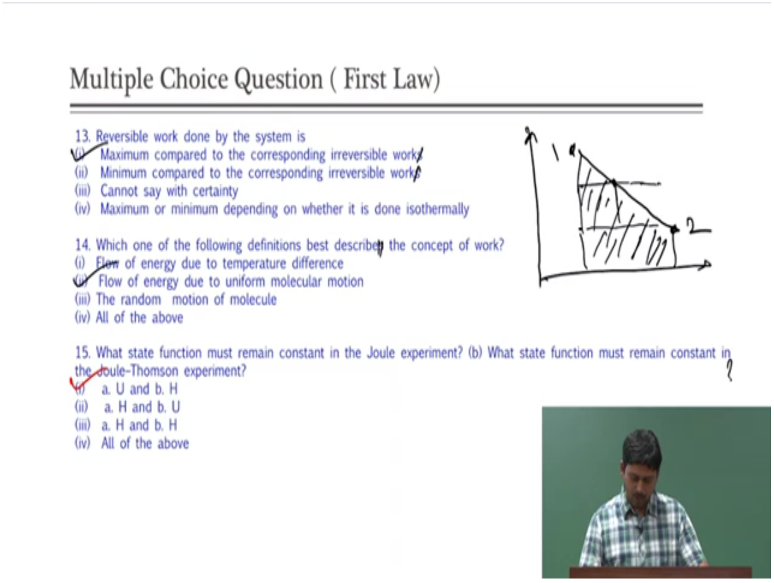

Okay, question number 13, reversible work done by the system is maximum compared to the corresponding irreversible work, minimum compared to the corresponding irreversible work, cannot say with certainty, and maximum or minimum depending on it is done isothermally? So I will remind you again that how we calculate the work done for you know two processes. Let us say we are talking about work done by the system, so work done by the system is typically an expansion work, we start from 1 and go to 2.

If it is done in one step you know the work done will be this much and we have discussed that if we do it in two step process then let us say we come here and then work done of the system will be this much so let us say you come here so it will be this much and then finally if you do in a multiple step process then it will be all the area under the curve, so therefore it is maximum compared to the irreversible work.

Which of the following definitions best describe the concept of work? Flow of energy due to temperature difference, flow of energy due to uniform molecular motion, the random motion of molecule and all the above. Now what is work? Work is unlike heat work has certain direction. For example if it is an expansion going from a smaller volume to larger volume then the molecule is going to move in a particular uniform directions, if it is heat then you know when you increase little bit more heat into the system molecules motions will be more random, it will be you know jumping with higher vigour when the heat is inserted into the system.

However, if it is work then the molecules has to move in a certain directions in order to expand the system from one size to another size. So therefore I would go with this answer that flow of energy due to uniform molecular motion and flow of energy due to temperature difference again that is called heat right. So when you do that, due to temperature difference we know that heat flows and depending on whether talking about solid system or gas systems the flow of heat will be different.

Okay, question number 15, what state function must remain constant in the Joule experiment? And question b is what state function must remain constant in the Joule-Thomson experiment? This is an easy question, you know that in Joules experiment the internal energy remains constant and Joule-Thomson experiment the enthalpy remains constant. So let us see a. U and b. H will be the right answer, but let us see the other options yeah the second question is wrong and the other options are also wrong.

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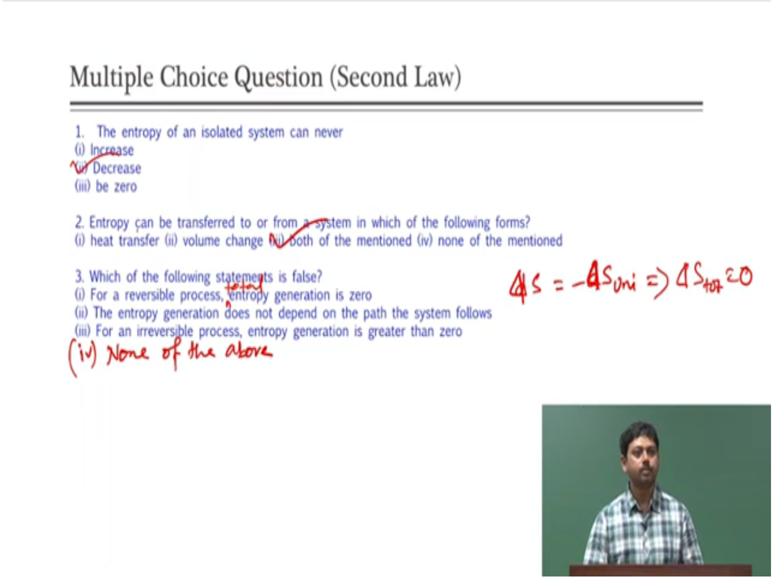

So now we have finished the multiple choice questions for the first law, now coming to the multiple choice questions for the second law. 1st question the entropy of an isolated system can never increase, decrease, or be zero what does it mean? An isolated system is a system in which the heat cannot come from outside to inside or it cannot go. However, an isolated system still can expand just like you know our universe is an isolated system it is still expanding.

So if it expands we know that entropy can change, so it can increase, can it decrease however? We have discussed this during the second law of thermodynamics that an isolated system like our universe for example the entropy cannot go to zero, it cannot become lesser, it is always increases, why? Because any spontaneous changes will increase the entropy and any change which is reversible will not increase the entropy but nothing will actually decrease. So therefore an entropy of an isolated system can never decrease is the right answer.

2nd question, entropy can be transferred to and from a system by which of the following forms? Like heat transfer, volume change, both the above mentioned and none of the above mentioned? So we know that entropy is proportional to the reversible change in heat divided by the temperature. Now if you transfer a heat let us say non reversibly will it change the entropy still?

It turns out that of course we can always define a path which is reversible meaning we can always define a path by which a reversible change in heat will take place. And therefore we can calculate the corresponding change in the heat when it the process is done reversibly and we can calculate an estimate the entropy. But if the volume change also takes place when it change the entropy, now it turns out that indeed if the volume change happens then also entropy will change.

So therefore I will go with above that both of the above mentioned, because we will show that a change in the volume also will give rise to and the reason is that imagine a situation in which the heat flow happens and the internal energy remains same, then that this change in the heat also correspondingly related to the change in work or work done and work done also is related to the change in the volume. So therefore whenever there is a change in the volume there is a possibility that entropy can change.

Another example of change in entropy by volume is free expansion. For example let us say the particles are there in one part of a big bigger volume and suddenly a partition is removed and the particles expand to the full volume in that case they occupy much larger area and we will show you later on that that changes or that increases the entropy of the system. So therefore by changing both the volume and by changing heat one can change the entropy to and fro from the system.

3rd question, which of the following is false? For a reversible process the entropy generation is zero, the entropy generation does not depend on the path of the system follows, and for an irreversible process the entropy generation is greater than zero. Now let us understand each point for a reversible process entropy generation is zero, so we know that to be true. For example we talked about Carnot cycle done in a reversible manner and then first step there is entropy increases so it does not mean that the entropy generation will be zero but however yet to we are talking about here the entropy of the universe.

Now in a Carnot cycle if it is done in a reversible manner the change in the entropy of the system is equal to the negative of the change in the entropy of the universe I will write Delta S. So therefore the total change so you should write the question that for a reversible process total entropy, entropy generation here we mean that the change in the total entropy. So total entropy change will be zero for a reversible process, so therefore this is true given that we are talking about total entropy.

The entropy generation of the total entropy does not depend on the path it follows. Now the thing is that if it is an irreversible path then what will happen is that we have to construct a different path that is reversible and calculate the entropy. So therefore, so first of all the first statement is right, second statement seems to be right as well does not depend on the path that the system follows meaning it is a straight function it is not a path function it does not depend on the path. For an irreversible process entropy generation is greater than zero and that is also true, so all are true. So I would say that the answer is none of the above.

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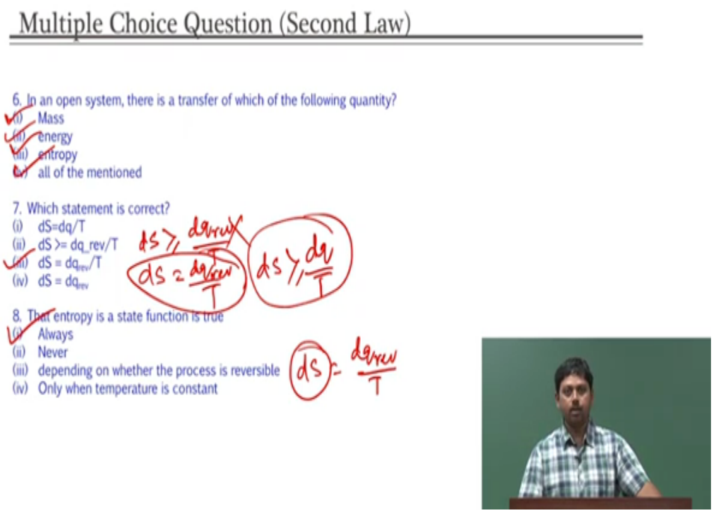

Next question in an open system there is a transfer of which of the following quantity? Mass, energy, entropy, and all the above mentioned. Now you know that this is a simple problem because it is by definition whenever we talk about open system then there is a change in of course both mass and energy. Now will the entropy also will change? Now let us say we talk about an open system, now there may or may not be change in entropy you know it depends on the process.

So when you are talking about a particular system it has a particular entropy because entropy the state function, the open system allows the change in mass change in energy and it will allow of course change in entropy because even an isolated system allow change in entropy right. So I would say all the above mentioned. Which statement is correct? dS equal to dq by T, now you will be tempted to always write dS equal to dq by T, but no it is not true, days greater equal to dq reversible by T meaning if I write it like this dS greater equal to dq reversible by T yes I think that is no that is not true because because we will discuss that because this is the right one dS equal to dq by T dq reversible by T.

And we can also write that dS greater equal to dq by T, which means that whenever it is reversible the equality sign holds, whenever it is irreversible then the greater than sign will hold. So this is right and this is right, however that is not right so therefore third option is right on so this is. So if you don't pay attention there might be mistakes in this kind of questions as was I was just about to make.

The entropies is a state function is true, is it always, never, depending on whether the process is reversible or not, only when the temperature is constant. Since you know we talked about the entropy dS is dq reversible by T and there is only one reversible path therefore entropy is always a state function and option one is right.

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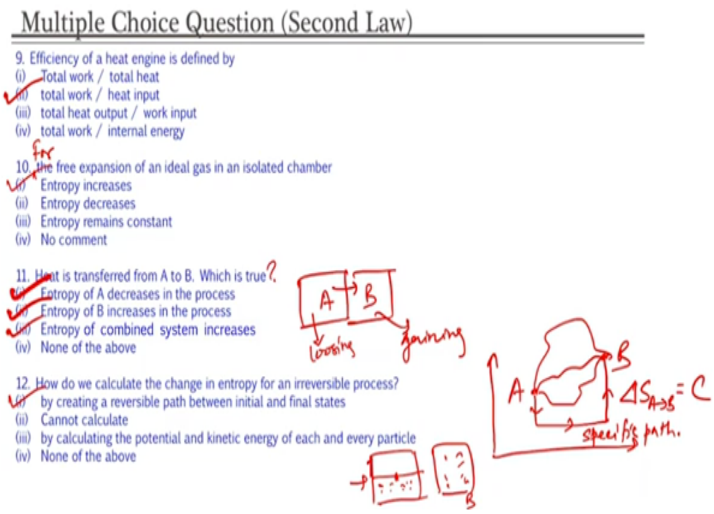

Continuing with the multiple choice question, efficiency of a heat engine is defined by it is very important to remember that it is always work output by heat input, so option two is right. The free expansion of an ideal gas in isolation chamber what will happen in the free expansion of an ideal gas in an isolated chamber or for the free expansion of an ideal gas in either chamber? Entropy increases, entropy decreases, entropy remains constant, and comments. So of course will be entropy increases will be the right answer because is free expansion will fill the volume.

Heat is transferred from A to B which is true? Entropy of A decreases in the process, that is a good question because you see what happens is that this question typically tells you that that the sub part of a combined system A and B sub part may lose entropy. However, overall there will be there will be you know an increase in entropy. For example we will talk about A and we will talk about B. Now heat is transferred from A to B, what happens in this process is that A is losing heat so A is losing entropy and B is getting heat so B is gaining entropy, now when you add the gain and the loss there will be an overall gain.

So I would say that entropy of A decreases in the process that is the right one, entropy of B increases in the process that is right one, entry of a combined system increases that is also right one, Next question how do we calculate change in entropy for an irreversible process? By calculating reversible path between initial and final states, cannot calculate, by calculating the potential and kinetic energy of each and every particle, and none of the above this is a very important thing for you to remember is that entropy is a state function therefore it has to be associated with some state variables.

Now if I talk about an irreversible process going from A to B there can be many reversible path. However, entropy of B has to be some specific value and A has to be some specific value. Therefore, change in entropy between A to B has a very specific value let us call it C. Now which means that in order to get C we need a very specific way to change from A to B and that specific way is a particular reversible path for which we can calculate so it is a specific path which is a reversible path and therefore we will be able to calculate the reversible change in heat and by definition entropy is reversible change in heat by temperature and we will be able to estimate the value of entropy even though we are using a very different path.

I can give an example let us take I think we have talked about that but I will still mention it here let us say that we are talking about free expansion of gas. So what happens is that whenever you make a hole here the gas will expand and fill the whole volume this is an irreversible process, how do we estimate the entropy? We go from same half or same you know unfilled box to a filled box by using a reversible path, we can do it reversible by expanding this volume very slowly let us say under pressure and finally you can reach this particular state B and therefore we will be able to estimate change in the reversible heat and therefore change in entropy. So the right answer to this question is that by creating a reversible path between the initial and final states.

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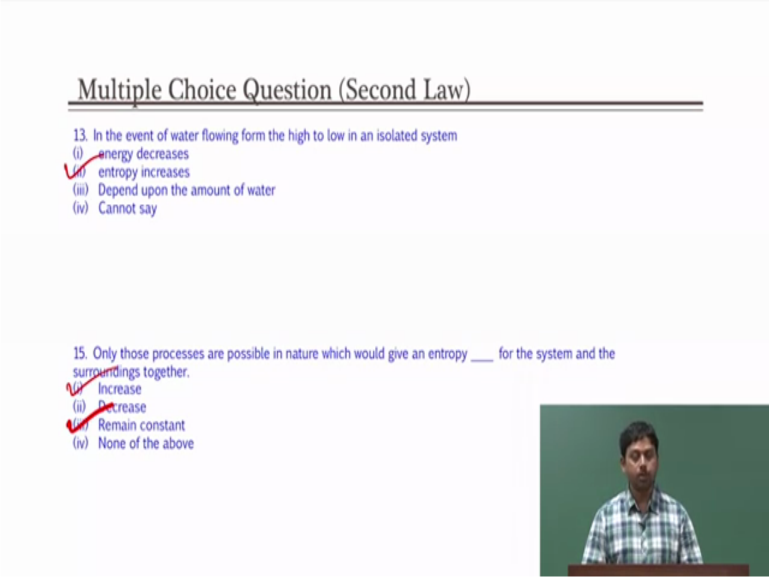

Question 13 in the event of water flowing from high to low in an isolated system what will happen in an isolated system remember that is the key. Energy decreases? No it is not possible because it is an isolated system so energy is conserved. Entropy increases? We will come back to that, depends upon the amount of water, no cannot say, we can still say. The thing is that whenever water flows from high to low in an isolated system it is very you know spontaneous process, so it is flowing water flowing from high to low is a spontaneous process just like heat transfer from high to high temperature to low temperature.

So therefore I will go with the entropy increases, because energy is not driving the change so the change that is driven is basically the entropy. For example when heat transfers from high temperature to low temperature, energy remains conserved because the total change in the energy is fixed and you know total change in energy is zero. However, is the process still happens and it happens due to entropy.

Only those processes are possible in nature which would give an entropy dash for the system and the surrounding together. So we know the system and surrounding together means entropy of the universe and we know that those processes are possible in which entropy change of the universe are either zero or positive. So but it says increases which is right, decreases not possible, remain constant possible, so these two options are correct.

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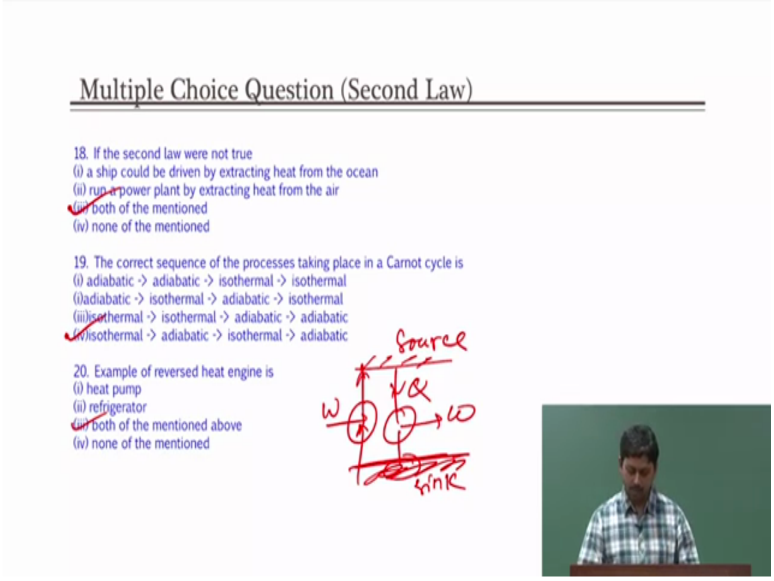

Next question, if second law were not true. Then a ship could be driven by extracting heat from the ocean, run a power plant by extracting heat from the air, both the above mentioned and none of the above mentioned. So the idea is that second law of thermodynamics prohibits us to take the heat from the ocean and run a ship or extract the heat from the air because it is only we will solve one heat source, but in second law of thermodynamics we need two heat, one heat source and another heat sink working at two different temperature.

So which means that the engine could take heat from the ocean but it has to throw the heat at a lower temperature. Now where do you get the lower temperature? Because if we are in room temperature and taking heat from our room temperature reservoir then something has to be cooler than the room temperature and that is only possible by using a refrigerator to cool that, that means we have to use work to cool the system and that will now drive the change of another engine and if you combine them together the efficiency will be even lower.

So therefore with one heat source or one heat sink it is not possible to run any engine and therefore unfortunately even though we have so much you know energy sources available around us we are not going to just simply take the energy from the environment and do the work. So therefore I would say that if it were not true then (both) we could have done both of the above mentioned but it is not true.

Next one the correct sequence of the process taking place in a Carnot cycle is adiabatic adiabatic isothermal isothermal and we the process. So first is isothermal, then adiabatic and then isothermal and then adiabatic so this is a question that will test your knowledge whether you remember the Carnot cycle or not. Next one example for reverse heat engine is heat pump, refrigerator, both the above mentioned and none of the above mentioned.

So I would say that both above mentioned because engine is where you take the heat and do the work and throw away some heat to the sink this is sink, this is source, refrigerator is just the opposite where you take the heat and then take the heat from high (temp) you take the heat from the low temperature, do some work and throw the heat to the high temperature. For example you take the heat from inside of a refrigerator where the temperature is 4 degree Kelvin and throw the heat to room temperature where the temperature is a 30 degree centigrade.

And you do that by doing some work which is done of course by the refrigerator with the help of the electrical energy that makes the work, does the work and the heat pump is also the same thing where you put the heat from low temperature to high temperature.