Chemical Principles 2 Professor Dr. Arnab Mukherjee Department of Chemistry Indian Institute of Science Education and Research, Pune Module 6 Lecture 37 Tutorial Problem-08

Ok so let us now discuss some of the long tutorial problems for entropy calculation.

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So the first question says that a reversible heat engine operates between two reservoirs at 827 degree centigrade and 27 degree centigrade. The engine drives the Carnot refrigerator maintaining minus 13 degree centigrade and rejecting heat to a reservoir kept at 27 degree centigrade. The heat input to the engine is 2000 kilo joule and the net work available is 300 kilo joule. How much heat is transferred to the refrigerator and what is the total heat rejected to the reservoir at 27 degree centigrade ok.

So in order to understand the problem first then will go step by step but remember that during the second law of thermodynamics we discuss that particular heat engine can also drive refrigerator where heat can be transfer from low temperature to high temperature. So when the purpose of the

heat engine is to drive heat from high temperatures of work and do the work, now this work can be fed into a refrigerator which will then take the heat from low temperature and through it to the high temperature (())(01:27).

Now will draw the diagram and then will explain this so this is the high temperature reservoir T1 from where T1 heat is taken in and w amount of work is being done and lets say Q2 amount of heat is thrown into the low temperature reservoir T2 and the correspondingly there is a refrigerator which will now lets call it W1 now there is a refrigerator which will now take heat from low temperature and it will require some work W2 to throw heat to the high temperature.

Now lets call that lets call this as T3 lets call that as T4 and we know the values of T1, T2, T3 and T4 so T1 is 27 degree centigrade, T2 is 27 degree centigrade, T3 is minus 13 degree centigrade and T4 is 27 degree centigrade. We don't know about W1, W2 but we know the value of (Q) Q1 which is 2000 kilo joule and we know the difference between W1 and W2 as 300 kilo joule that is the net work. Now we have to find out how much heat is transferred to the refrigerator? That means we have to find out so lets call this Q3 and lets call that Q4. So we have to find out that what is the value of Q3 and so how much heat is transferred to the refrigerator is Q4 and what is the total heat rejected to the reservoir at 27 degree centigrade, so that is this is Q4 because this is minus 13 degree centigrade and how much heat is transferred to the refrigerator, which is I would say W1 minus that is the W1 that we have to get ok.

So basically you have to calculate Q3 and Q4 so let us say do that. Now how do we start solving the problem? So first you have to understand that this kind of problems you need you have to know that in Carnot cycle the ratio of heat input and heat output is equal to the ratio is of the temperature of the reservoirs T1 and T2 (and) remember we talked about the thermodynamic temperature and which is based on the heat input and output from high temperature reservoir and low temperature reservoir so Q1 is 2000 kilo joule Q2 we don't know T1 is 827 degree which is converted into Kelvin it will become 1100 and 27 degree will become 300 this we know.

So this will give us Q2 so Q2 by 2000 is equal to 300 by 1100 which is 3 by 11 so Q is 6000 by 11 that is the that much kilo joule is Q2. Now once we know Q1 and Q2 will can then calculate the W1 so W1 is Q1 minus Q2 which is 2000 minus 6000 divided by 11 which is 22000 minus 6000 is 16000 divide by 11. So we know the W1 and we know the difference between W1 and

W2 as 300 and ofcourse that means all the W1 is not being fed into the refrigerator so this is the refrigerator and this is the engine Carnot engine. So 300 less is being fed so we know the W2 which is W1 minus 300 which is 16000 divide by 11 minus 300 which is 16000 minus 3300 divided by 11 which will give us so (3000) so 13000 so 12700 so 13000 (())(06:01) by 11, so that is the W2 that you got.

Now comes our last part we know that T Q, 3 by Q4 is equal to T3 by T4 which is equal to so T3 is minus 13 degree so minus 13 so T3 is minus 13 degree means (27) 273 minus 13 will be 260 and T4 is 27 degree centigrade which is 300 kelvin. So Q3 by Q4 also we know and we also know that W2 which is Q3 minus Q3 plus W2 is equal to Q4 so therefore Q3 is Q4 minus W2. So let us see how can we do that? So again so we have this (())(07:01) some little bit more space.

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$$\frac{Q_3}{Q_4} = \frac{260}{300} \cdot 1 \quad u_2 = \frac{12700}{11}$$

$$\frac{Q_3 - Q_4}{Q_4} = \frac{260 - 200}{300}$$

$$\frac{1}{Q_4} = \frac{260 - 200}{300}$$

$$\frac{1}{Q_4} = \frac{140}{200} \cdot 1$$

$$\frac{1}{200} = \frac{1}{200} \cdot 1$$

$$\frac{1}{200} = \frac{1}{200} \cdot 1$$

$$\frac{1}{200} = 8659 \cdot 09$$

$$\frac{1}{10} = 7504 \cdot 545$$

So I will be writing it here, Q3 by Q4 is equal to 260 by 300 and W2you got to be 12700 by 11 Q3 by Q4 so let us subtract 1 from both sides of this equation one you are going to get Q3 minus Q4 by Q4 is equal to 260 minus 300 by 300. Q3 minus Q4 is minus W2 by Q4 is equal to minus 40 by 300 2 15 so Q4 is 15 by 2 into W2 and you know 15 by 2 is 7.5 and W2 is 12700 by 11. So let us calculate that 12700 by 11 into 7.5 giving us 8659.01. so we got Q4 so then you can get Q3 also we have to just add the value of W2 with that so Q4 plus W2 which is 8659.09 plus 12700 by 11. So let us do that and we get 7504.54 (())(09:06) so this is what we wanted to get from that. So you see that in this problem the most important was to understand that the heat input and heat

output ratio is equal to the ratio of the temperature. Once you know that other things is just manipulations nothing else ok.

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Ok let us talk about the next problem, so three irreversible engine, engines of Carnot type are operating in series meaning, they are operating based on the output one engine the input of engine is you know happening so operating in series between the limiting temperatures of 1100 kelvin and 300 kelvin. Determining the intermediate temperatures if the work output from engine is in the proportion of 3:2:1 now you see the setup of the engine is that heat is coming from Q1 going to Q2 then from Q2 is going to Q3 and things like that and that information is given is that the work output is in the ratios of 3:2:1 so that is important, so that we are going to use.

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So I am going to need little bit extra space for that so let us see that the third one the T one lets say that is our 1100 kelvin and then the heat Q1 is taken in from that and some work is done W1 if Q2 is thrown into the second one which is again passing to the next one lest say W2 work is done and then heat Q3 is going to the next one which is again going to go to the next engine in series W3 work is done and then finally that is going to Q4 is going to the final temperature T4 and the T4 temperature is 300 kelvin the third one is 1000 kelvin. Ok so this information is given another information given is that the work outputs are in the ratios of 3:2:1 which means that so we know that W1 is nothing but Q1 minus Q2 and W2 is nothing but Q2 minus Q3.

So W1 by W2 is 3:2 similarly W3 is Q3 minus Q4 and W2 by W3 is given as 2:1 means 2 so now using this information we can write down a few equations, what one you can write down equation 1 lets say and equation 2. So from 1 we get q1 minus Q2 by Q2 minus Q3 is equal to 3 by 2 rearranging that will get 3 Q1 minus Q2 is sorry it will be 2 3 Q2 minus Q3. So now I can divide both sides by Q2 and I get Q1 by Q2 minus 1 is 1 minus Q3 by Q2 ok.

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So I can continue with that so 2 Q1 by Q2 minus 2 equal to 3 minus 3 Q3 by Q2 and we know another information we have that this ratios are in the ratios of the temperature. You can write that as T1 by 2T1 by T2 minus 2 is equal to 3 minus 3 T3 by T2. So lets simplify little bit more 2T1 by T2is equal to 5 minus 3 T3 by T2 simplifying further will give us 2T1 equal to 5 T2 basically multiplying by T2 on both sides 5 T2 minus 3 T3. Now the information of T1 is given to me which is then 5T2 minus 3 T3 is equal to 2 into 1100 kelvin so 2200 kelvin k into 100. So lets write that equation as equation 3. Now we are going to use equation number 2 W2 by W3 equal to 2.

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So W2 by W3 is equal to 2 which is Q2 minus Q3 by Q3 minus Q4 is equal to therefore Q2 minus Q3 is equal to 2 Q3 minus Q4 now you can divide both sides by Q3 Q2 by Q3 minus 1 is equal to 2 1 minus Q4 by Q3 and I can write them as their (())(14:48) temperature so T2 by T3 minus 1 is equal to 2 minus 2 into T4 by T3. Simplifying further T2 by T3 equal to 3 minus 2 into T4 by T3 multiply both sides by T3 it give me T2 equal to 3 T3 minus 2 T4 I take it on the left hand side so T2 minus 3 T3 is equal to minus 2 into 300 because T4 we know so minus 600 lets call that as equation number 4. So we have two equations now equation 3 is 5 T2 minus 3 T3 equal to 2200 and T2 minus 3 T3 is equal to minus 600.

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So subtracting will get 4 T2 is equal to 2800 or T2 as 700 kelvin. Now we are going to get the T3 so we can use any of this equation so 700 kelvin minus 3 T3 is minus 600 or 3T3 is equal to 1300 or T3 is equal to 1300 by 3 which is going to give me 0.33 kelvin. So now we got all the (())(16:37) temperatures in the series that is working again we use a simple principle of Q1Q2 equal to Q1 by Q2 equal to T1 by T2 and that is true for Carnot thing in alone by the way it is not true for other engines ok so that we have to remember.

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So next question a close system executed irreversible cycle 1 2 3 4 5 6 just like it is shown here 1 to 2, 2 to 3, 3 to 4, so it is like a (())(17:13) diagram 1 to 2, 2 to 3, 3 to 4, 4 to 5 and 5 to 6 and going back to 1 consisting of 6 processes, during process of 1, 2 and 3, 4 the system receives 1000 kilo joule and 800 kilo joule. So at this stage it receives 1000 kilo joule at this stage it receives 800 kilo joule heat at a constant temperature of 500 so this state is 500 and this state is 400 temperature kelvin.

Processes 2 3 and 4 5 are adiabatic so 2 3 is adiabatic ofcourse because there is no (())(18:06) that you can see and that is you know temperature is changing 2 3 and 4 5 are adiabatic expansions in which the system temperature reduces from 500 to 400 and 400 to 300 respectively during the process 5 to 6 the system rejects the heat and that is the place lets say I call it Q2 system rejects the heat at temperature 300 kelvin so this is 300 kelvin as shown in the diagram, process 6 to 1 again is adiabatic compression process right the temperature will come so from here till here the temperature will come to again back to 500 kelvin so it is adiabatic compression process. Determine the work done by the system during the cycle and thermal efficiency of the cycle ok so now that we know the problem will go back to this page to work out on this particular problem.

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W = Rinp - Rout Rinp = R12 + R34 = 1000 + 800 = 1800KJ $Q_{out} = Q_{57} + Q_{77} = T_5 \times (S_2 - S_7) + T_5 \times (S_2 - S_7)$ = 300 × (53-54) + 300 × (51-52) = 300 × 241 + 300 × 241 - 500 = 306 × - 200 + 300 × - 1000 = $\frac{3}{4} \times (800) + \frac{300}{500} \times (-1000)$ - -600 -600

Ok so we have discussed about how to calculate the work done and heat in from a T S diagram so it is much easier to do from T S diagram than from P V diagram. For example we can graphically itself we can say that the work done in the whole cyclic process is the area that is enclosed by the curve that you can immediately say ok. Now only thing we have to have is that we have to calculate the area and how do we that, that we have to see.

Another thing that we can already mention is that the work done in the process is the total heat input minus total heat output. Heat input is already given because heat can be can come through this only two steps 1 2 and 2 4 and 3 4 so Q input is nothing but Q 1 2 plus Q 3 4, Q 1 2 is given as 1000 and Q 3 4 is given as 800 which makes it 1800 kilo joule that is given. All that we need to calculate is the 5 6 then that means the area under this particular curve 5 6 tat is what we have to calculate. Now how do we do that? So in order to do that we have to also remember that heat Q is nothing but T into delta S that means by knowing the delta s will be able to calculate that.

So like I see how we can do that so as you can see that as you can see that we can calculate the heat that is going out in 5 6 process by breaking into two parts one is the 3 4 another is 1 2 for example I use another color just to identify that lets call this point as 7 so you see that the entropy change between 5 7 so let us write first the formula so Q out is equal to Q 5 7 plus Q 6 7 ok so Q 5 7 and Q 7 6 not 6 7 should be 7 6 so Q 5 7 is temperature at the level of T5 lets say I can say T5 multiplied by S 7 minus S 5 plus the temperature remain same so T5 again into S 6

minus S 7 you see because the process is happening from 5 to 6 so therefore you have to subtract the entropy from the final minus initial ok.

So we know the temperature T5 which is 300 what is S 7 minus S 5? Now if you look at S 7 minus S 5 it is same as you know S 3 minus S 4 because they are parallel lines right so we can write that as S 3 minus S 4 plus T5 is again 300 and we can write that as now what is 6 7? 6 7 is same as as you can see 1 2. So it will be S 1 minus S 2 so 300 into S 3 minus S 4 so S3 minus S4 how do we get that? We can get that again by using the formula that it is dq by t. So S3 minus S4 if we have to calculate then we can see the heat input during 3 4 process which is Q 3 4 divided by temperature at that level which is 400 plus again 300 into S1 minus S2, how do we get?

We have to take the input at 1 2 level divide by the temperature so again Q 1 2 by 500 just notice one thing during the input process it was S2 minus S1 but now we are doing S1 minus S2 so it will be the negative of that ok. So now continuing that it is 300 by 400 multiplied by Q 3 4 now what is Q 3 4? Q 3 4 is negative of Q 4 3, actually it should be 4 3 so Q 4 3 is negative of Q 3 4, Q 3 4 is 800 so it will be minus 800 by 400 plus 300 into Q1 2 is opposite of Q 2 1 I should write 2 1 not 1 2 just to denote that the process is happening from 2 to 1 rather than 1 to 2 again it will be negative of that 500. Now we get all our values so it is nothing but 3 by 4 into minus 2 plus 300 into yeah so I made a mistake here I will just change that. So I have already divided by 400 here so I should not divide here so I will just write it again which is 3 by 4 multiplied by minus 800 plus 300 plus 300 by 500 multiplied by minus 1000.

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Ok so it should be then minus 600 minus this is also 600 so it is minus 1200 (kilo joule). Let me see (())(25:03) 800 400 is 2 minus 600 that is 300, 1000 so minus 1200. So the heat output is minus 1200. So now what is the work done? So work done is now Q input plus Q output and what is the efficiency? Is 1 plus Q output by Q input so it will be 1 plus minus 1200 divided by plus (800) 1800 which is 1 minus 12 by 18 which is 1 by 3 that is the efficiency of this whole particular engine.

So you have got both the things again so you see that it is extremely straight forward to calculate the work done for any complicated cycle as long as you write that in the T S level and remember that for Carnot engine is especially is very simple if it is an isothermal process if it is entropy is increasing then heat will (())(26:17) system and if it is if the entropy is decreasing then heat is going out of the system and by working the area under the curve which is very simple for this kind of system because it is just a rectangular graph it is a line under which you will have to calculate the area so it is simple enough that one can calculate the whole thing ok.

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So going to the problem determine entropy change of the universe if two copper blocks of 1 kg so two copper blocks I have 1 kg and 0.5 kg kept at 150 degree centigrade and 0 degree centigrade respectively are joined together specific heat of the copper at 150 degree is 0.393 kilo joule per kg kelvin and then this one is 0.381 kilo joule per kg so we are assuming that the it capacity is constant or anything at different temperature. So what will be the change in entropy? Now you see that it is simple problem of heat transfer from high temperature to low temperature. So let us say so this at high temperature right T1 and this is at low temperature T2 lets say.

Let us say T1 is greater than T2 and dq amount of heat is transferred from first block to the second block. So what will be the change in entropy for the whole process is that change in entropy of the first system which is minus dq by or minus q let us say by t and entropy increased will be plus T1 and entropy increased would be Q by T2. So that is what we were going to calculate so it will be Q1 by T2 minus 1by T1. So we have to calculate the q and we know that q is nothing but cp dt ofcourse here we have to here we cannot take Q to be the same for both the processes so let us use this particular formula and do the calculation.

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So in order to calculate the final temperature so we can have in this particular formula is that let us say the final temperature equal to T f so then the first block how much heat it will lose? Let us calculate that, so first block will lose the specific heat 0.393 into T f it will lose therefore it will be 150 minus 150 degree centigrade you should first convert it to kelvin. So 150 degree centigrade is equal to 150 plus 273 423 so 0.393 into 423 minus T f equal to that is the same as the heat gain or the low temperature system which is kept at 0.381 the specific heat ofcourse and it is 1 kg oh there is mass associated with that also so this system is 1 kg and this is only 0.5 kg so m c dt so what is the formula of Q? Q is mass into specific heat into delta t change in temperature.

So mass for the first block which is losing is 1kg and then specific this (393) 0.393 and the temperature changes this much. There is other block is on the 0.5 kg and specifically this 0.381 and it will increase from 273 kelvin to T f. once we equate them we are going to get the final temperature T f, so let us try to calculate that so 0.393 into 423 minus 0.393 T f is equal to 0.381 into 0.5 T f minus 0.381 into 0.5 into 273 so or what you are going to get? We are going to use calculate now 393 into 423 is equal to 166.24 minus 0.393 T f is equal to 0.381 into 0.5 is 0.19 T f minus 52 approximately 52.0 or you can get that 166.24 plus 52 is equal to 0.19 T f plus 0.393 T f or 166.24 plus 52 is 218.24 is equal to 0.19 plus 0.393 is 0.583 T f or T f is 218.24 divided by 0.583 which is 374.34 lets say kelvin.

So this is what we got so once we got our final T f temperature now we have to now we can think into different ways either we can think of you know direct heat transfer as we discussed above at this point but in this particular case we are assuming that the whole heat is transferred at the same point however if we see take reversible process then the heat is transferring slowly and the temperature also increases slowly.



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So in order to account for that we have to integrate the system from initial temperature to the final temperature. So let us calculate the change in entropy for the block one which is S1 so S1 we know that it is going from T1 to T f and the formula for that is them M C dt is the change and the entropy is dq by T so M C dt is the dq reversible by T so that is the formula that we were using that we have to used in order to calculate that which is giving us m C ln T f by T.

We know the n which is 1 kg and C we know as 0.393 and we have to calculate ln of T f which is 373.34 by T1 which is around 423. Similarly for S2 we have to calculate from T2 to T f as you can see that S1 will be a negative quantity because the heat is going out of the system and S2 will be a positive quantity because it is coming in this is 0.5 into 0.381 if I remember correctly 0.381 multiplied by 1 n of ok sorry just wrote it fast enough so it just let me write it once more so it is M lets say this is M1 C1 this is M2 C2 dt by T giving us M2 C2 1 n T f by T2.

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And we know the values 0.5, 0.381 multiplied by 1 n of T of T f is again 37403 4.34 and initial temperature is 0 degree so 273. Now let us calculate S1 and S2 separately using calculator so we have to calculate 1 n of this quantity so we have a function 1 n here and we can calculate the ratios also it is 374.34 by 423 bracket closed multiplied by 0.393 that is giving us 0.048 as you can see it is a negative quantity. Now delta S2 will be 1 n of 374.34 by 273 multiplied by 0.381 into 0.5 giving us 0.06014 ok now total S1 plus S2 as you can see pad is losing entropy another part is gaining. So now if I just subtract this one I will get that 0.048 approximately we are going to get plus 0.0121 or 0.21 yeah so that is much kilo joule per kelvin if initial value (())(37:47) so you can see that overall change in entropy is possible and therefore it is an irreversible process because which means that you know it will not go back so we have our experience right.

An hot body and a cold body is brought together then what happens is the heat transfers but one cannot get back again hot body and cold body so this is an irreversible process that happens and that happens because overall change of the entropy total change of the entropy has increased. Assuming ofcourse that there is no dissipation is going to the universe outside surrounding or not we are just thinking that the whole heat from one (())(38:25) has come to the other that is an assumption that we are taking here so with that we you know we are finishing the classical second law of thermodynamics we are going to start with statistical description of the second law of

thermodynamics with a twist classical approach of second law of thermodynamics with twist using free energies and thermodynamics relations later on.