

**Chemical Principles II**  
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**Module 06**  
**Lecture 33**  
**Tutorial Problem - 04**

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Efficiency from T-S diagram directly

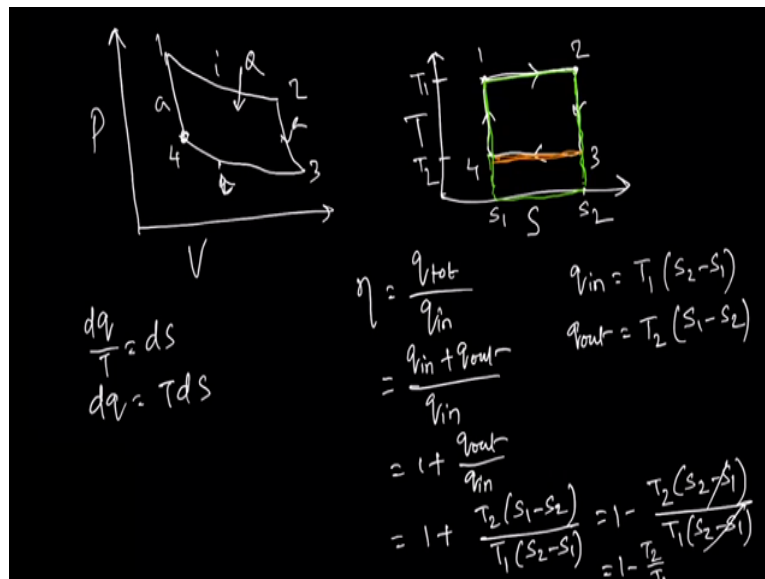
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Derive the expression for the efficiency of a Carnot engine directly from a TS diagram. Compare the efficiencies of cycles A and B of the figure below.

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So let us continue with the problems that we were doing on the second law of thermodynamics. So here is a problem on the efficiency calculation from TS diagram directly. So the question says that derive the expression for the efficiency of Carnot Engine directly from TS diagram, compare the efficiencies of the cycle, A and B in the figure below. So before we actually can do that, we should calculate the efficiency of the Carnot Engine first from the TS diagram.

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So for that we are going to first draw the PV and TS diagram. So first draw the PV diagram, so it is isothermal process, adiabatic expansion process, isothermal compression process and adiabatic compression process. Let us call it 1, 2, 3, 4 and we can write the corresponding TS diagram. So between the 1 and 2, temperature remains constant because in isothermal process however since it is an expansion process heat comes in in the reversible manner and the system's entropy increases, so it should be flat like this.

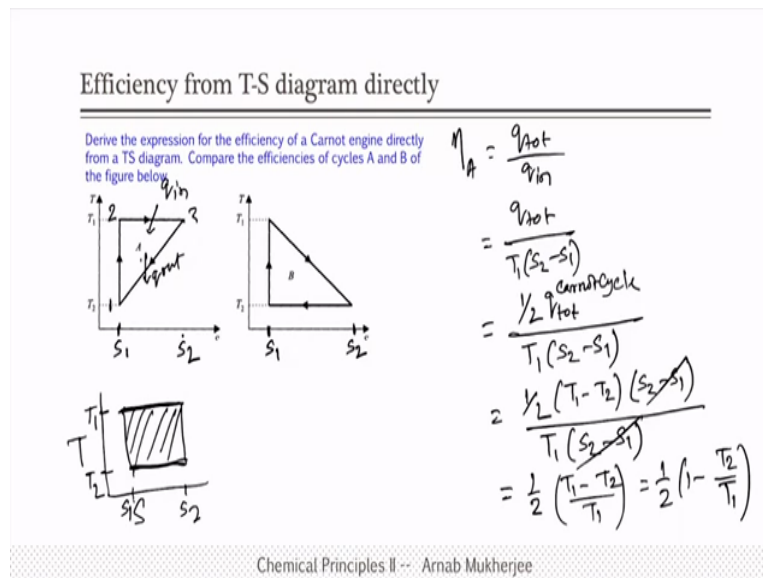
And then 2 to 3 is an adiabatic compression process, sorry it is an adiabatic expansion process, since it is an adiabatic process entropy remains fixed. However since it is an expansion process, then it cools down, so temperature decreases. So it will be like this, then 3 to 4 is just the opposite of 1 to 2. So this is 1, this is 2, this is 3 and this is 4 and we get 4 to 1 like this. Now what is the, in order to calculate the efficiency, we know the efficiency calculation, it is the Q total divided by Q input.

So we have to calculate Q total and Q input, so let us calculate that. And we know what is Q because we know that  $dQ$  by  $T$  equal to  $dS$ , so  $Q$  is,  $dQ$  is nothing but  $TdS$ . Therefore when we calculate the entropy for the heat input which is coming between 1 and 2 steps, the heat coming in should be area under the curve 1, 2. Let me draw that and show you. So the whole green region is the area corresponding to the heat input. And how do we get that? We can get that from the expression.

So let us say this temperature is  $T_1$ , let us say this temperature is  $T_2$ , this is entropy  $S_1$  and let us say this is  $S_2$ . So then our  $Q_{in}$  is going to be  $T_1$  multiplied by  $S_2$  minus  $S_1$ . It is a positive quantity and  $S_2$  is greater than  $S_1$ , so therefore  $Q_{in}$  is a positive quantity. Now we have to do  $Q_{tot}$ , so in order to get the  $Q_{tot}$ , we know that it is  $Q_{in}$  plus  $Q_{out}$ . But this  $Q_{out}$  also we can calculate,  $Q_{out}$  is the, I will show in a different color, orange color.  $Q_{out}$  is the area under this line and the temperature of that is  $T_2$ , however it is a negative quantity because the entropy decreases there. So it is  $S_1$  minus  $S_2$ , that is  $Q_{out}$ .

So we can also calculate the efficiency using  $Q_{out}$  and  $Q_{in}$  as well, so we can do that, let us do that. So this is  $Q_{tot}$  is  $Q_{in}$  plus  $Q_{out}$ , remember  $Q_{out}$  itself is a negative quantity divided by  $Q_{in}$  which is 1 plus  $Q_{out}$  divided by  $Q_{in}$ , equal to 1 plus, now  $Q_{out}$  is  $T_2$ ,  $S_1$  minus  $S_2$  and that is  $T_1$ ,  $S_2$  minus  $S_1$ . Taking the negative sign on the numerator we get  $T_2$   $S_2$  minus  $S_1$  by  $T_1$   $S_2$  minus  $S_1$  which cancels giving us  $1$  minus  $T_2$  by  $T_1$ . So that is the efficiency of the Carnot Engine calculated directly from the TS diagram. Now given that we know how to calculate that, let us calculate the two problems that we were discussing. So let us go back to that and calculate that.

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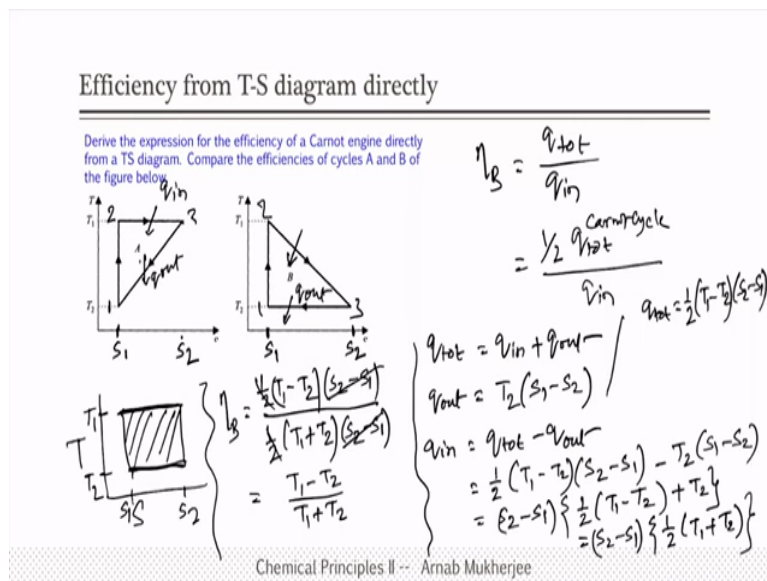
So for the first problem I will just mention the values. This is let us say  $S_1$  and this value corresponding to this value is  $S_2$ , for this also  $S_1$  and  $S_2$ . Temperature is also mentioned and everything is mentioned. Now let us calculate for cycle A. So for the cycle A as you can see, that if I start from here to here, there is no change in entropy. Temperature increases but entropy remains constant. So this is an adiabatic step where nothing happens, no heat input or output takes place.

Now as you can see, this point to this point, so let us write it as 1, 2, 3. So 1, 2 and 3, so between 1, 2 entropy is 0 and 2 to 3 this is where entropy increases at constant temperature, so it is basically an isothermal expansion process in which heat comes in. So our  $Q_{in}$  is this, and obviously 3 to 1 is our  $Q_{out}$ . Now how do we calculate the  $Q_{out}$ ? This is our  $Q_{out}$ . How do we calculate the efficiency? So efficiency of the engine A we can write again as  $Q_{tot}$  by  $Q_{in}$ .  $Q_{in}$  is same as what was there for the Carnot Cycle which is  $T_1$  multiplied by  $S_2$  minus  $S_1$ . But what is  $Q_{tot}$ ?

Now you can see interestingly that the  $Q_{tot}$  is from the Carnot Cycle was the area enclosed by the rectangle. So if we remember that, when we added in the TS diagram,  $Q_{tot}$  is this one.  $Q_{in}$  is area under this curve,  $Q_{out}$  is area under this curve, so therefore  $Q_{tot}$  was the area enclosed by the rectangle. And you can see this is half of that, so here the  $Q_{tot}$  is half of  $Q_{tot}$ , sorry this should be  $Q_{tot}$ ,  $Q_{tot}$  half of  $Q_{tot}$  of the Carnot Cycle divided by  $T_1 S_2$  minus  $S_1$ . So now what was the  $Q_{tot}$  of the Carnot Cycle? Again from here also you can see  $T_1$ , this is  $T_2$ , this is  $S_1$  and this is  $S_2$ . So therefore it is  $T_1$  minus  $T_2$  multiplied by  $S_2$  minus  $S_1$  divided by  $T_1 S_2$  minus  $S_1$ .  $S_2$  minus  $S_1$  cancels giving us half  $T_1$  minus  $T_2$  by  $T_1$ . It is half  $1$  minus  $T_2$  by  $T_1$ . So we get exactly half the efficiency of the Carnot Cycle.

And the reason is clear because input is the same as that of Carnot Cycle for engine A. However the total work output is half that of the Carnot Cycle because in Carnot Cycle we get the whole rectangle as the output but here we are getting half the rectangle as the output, work output, so therefore the efficiency will be half that of the Carnot Cycle. Now let us talk about the engine B. Let me remove the A just to get more space.

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So we can see that for engine B again it is half that of the, so let us write that engine B efficiency. Again engine B efficiency is  $Q_{tot}$  by  $Q_{in}$ . Now  $Q_{tot}$  again is half that of the  $Q_{tot}$  of Carnot Cycle. But what is the  $Q_{in}$ ? So we have to understand where the heat comes in. Heat comes in through this path or this section, so 1, 2 and 3, so heat comes from the process 2 to 3 because 3 to 1 is the process in which heat goes out,  $Q_{out}$ , so  $Q_{in}$  is only 2 to 3 because 1 to 2 there is no heat exchange happening as you can see clearly.

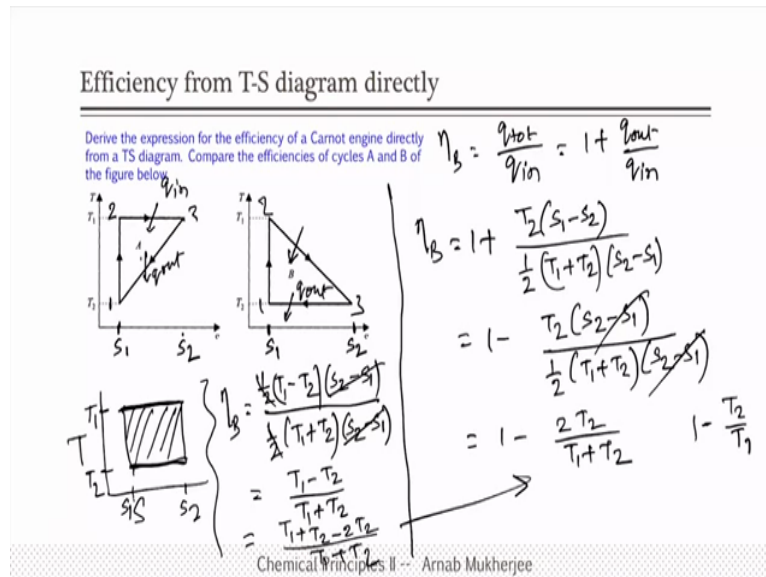
So what is the value of 2 to 3? So we can calculate that again by knowing that the value of  $Q_{out}$ . So  $Q_{tot}$  we know is  $Q_{in}$  plus  $Q_{out}$ . And we know the  $Q_{out}$  from Carnot Cycle expression itself that  $Q_{out}$  is  $T_2 (S_2 - S_1)$ , it is a negative quantity remember. So therefore  $Q_{tot}$ , we need  $Q_{in}$  right? So therefore  $Q_{in}$  is  $Q_{tot}$  minus  $Q_{out}$ . And what is  $Q_{tot}$ ?  $Q_{tot}$  is half that of the Carnot Cycle which is  $T_1 - T_2, S_2 - S_1$  minus, what is  $Q_{out}$ ?  $Q_{out}$  is  $T_2 (S_2 - S_1)$ .

I will do this, I will take  $S_2 - S_1$  common giving me half  $T_1 - T_2$ . Since I took this thing, it will be plus  $T_2$  giving me  $S_2 - S_1$  multiplied by half  $T_1 + T_2$ . So we got  $Q_{in}$ , now we have everything available to us. So let us write it here. We have some space here.

So  $\eta_B$  is  $Q_{out}$  or  $Q_{tot}$  is given here, yeah  $Q_{tot}$  I have not written here but okay, we can write it many ways. We can write  $1 + Q_{in}$  by  $Q_{out}$  also. But let us write it by  $Q_{tot}$ . So again we will just write  $Q_{tot}$  value which is half  $T_1 - T_2, S_2 - S_1$ , half  $T_1 - T_2, S_2 - S_1$  divided by  $Q_{in}$  which is here, half  $T_1 + T_2, S_2 - S_1$ .

cancels, half cancels giving us  $T_1$  minus  $T_2$  by  $T_1$  plus  $T_2$ . So now that we got half  $T_1$  plus  $T_2$ ,  $S_2$  minus  $S_1$ , we will write that way also.

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So efficiency Because can also be written as  $Q_{tot}$  by  $Q_{in}$  or  $1 + Q_{out}$  by  $Q_{in}$ . And then  $1 + Q_{out}$  how much we got? Half,  $Q_{out}$  is not half,  $Q_{out}$  we just got, right? That it is  $T_2$ ,  $S_2$  minus  $S_1$  and this one we got as half  $T_1$  plus  $T_2$ ,  $S_2$  minus  $S_1$ . We take a minus, so we get  $T_2$ ,  $S_2$  minus  $S_1$  by half  $T_1$  plus  $T_2$ ,  $S_2$  minus  $S_1$ , giving us  $1 - 2T_2$  by  $T_1$  plus  $T_2$ . Now at the same we can easily check that. We can just take  $T_1$  plus  $T_2$ , so here we can just take  $T_1$  plus  $T_2$  minus  $2T_2$  by  $T_1$  plus  $T_2$  and we are going to get this one.

So this is the efficiency of the engine B. Now you see, is this efficiency be more or less than Carnot Engine? So we have seen here obviously that the efficiency is less than Carnot Engine. Why? Because the input is same, output is half. But here output, heat out is same but heat in, is it more or is it less by this way? Is this efficiency, so what is the Carnot efficiency?  $1 - T_2$  by  $T_1$ . Now is it more or less than this thing? The output is also less, and the input is it more or is it less? Of course, it will depend on, so  $Q_{in}$  is half,  $T_1$ ,  $T_2$ ,  $S_2$  minus  $S_1$ . So since  $T_1$  is greater than  $T_2$ , obviously the input is also less than the Carnot input.

So total is also less than the Carnot input. Now it all depends on the value of  $T_1$  and  $T_2$ , whether it will, this construction will have more or less than the efficiency of the Carnot Engine. Let us say for example, we can take arbitrarily close temperature, let us say both of them are very close to  $T_1$ , then it will have efficiency 1. So when they will come closer and

closer, then, no, no, so if  $T_1$  equal to  $T_2$ , what will happen? No,  $T_1$  it will be 1 minus  $2T_2$  by  $2T_1$ . It will be 0, yeah, so they will come closer and closer of course.

Then, that of course it will not work, that is right. So that means if the  $T_1$  and  $T_2$  come arbitrarily close together, the efficiency will go towards 0, that is fine. Efficiency will go towards 1 only when the  $T_2$  will go to 0, that is also fine according to Carnot this thing. Now the question is that whether this one will have more or less the efficiency of the Carnot Engine. So this is 1 minus  $2T_2$  by  $T_1$  plus  $T_2$ , right?

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Handwritten notes on a blackboard:

$$\eta_B = 1 - \frac{2T_2}{T_1 + T_2}$$

$$\eta_C = 1 - \frac{T_2}{T_1} \quad T_1 > T_2$$

$$\frac{2T_2}{T_1 + T_2} \rightarrow \frac{T_2 + T_2}{T_1 + T_2} \quad T_1 > T_2$$

$$\frac{2T_2}{T_1 + T_2} > \frac{T_2}{T_1}$$

$$\frac{3}{7} \rightarrow \frac{4}{8}$$

$\eta_B < \eta_C$

So this is the efficiency of the engine B. And efficiency of a Carnot Engine is 1 minus  $T_2$  by  $T_1$ . Now the difference is that I am adding, sorry it should be  $T_2$  by  $T_1$  because  $T_1$  is larger than  $T_2$ . Yeah, we can do some analysis here. We can say that look, this one is, let us analyze this quantity,  $2T_2$  by  $T_1$  plus  $T_2$ . This comes from  $T_2$  plus  $T_2$  by  $T_1$  plus  $T_2$ . Now you see this, I will just write it properly. This is the ratio that is there in the Carnot. We are adding  $T_2$  value. Now since  $T_1$  is larger than  $T_2$ , by adding the same amount  $T_2$  on numerator and denominator, so for example I am talking about let us say 3 by 4, 3 by 7, I add 1 to both of them. We are going to get 4 by 8.

Now adding 1 is more, will have more value, so is 4 by 8 bigger or 3 by 7 bigger? 4 by 8 bigger, right? So adding this one will have larger effect. So this quantity,  $2T_2$  by  $T_1$  plus  $T_2$  will be larger than  $T_2$  by  $T_1$ . Therefore efficiency of B will have lesser efficiency than C, that is my analysis of that.

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### Efficiency from T-S diagram directly

Derive the expression for the efficiency of a Carnot engine directly from a T-S diagram. Compare the efficiencies of cycles A and B of the figure below.

$\eta_B = \frac{q_{tot}}{q_{in}} = 1 + \frac{q_{out}}{q_{in}}$   
 $\eta_B = 1 + \frac{T_2(s_1 - s_2)}{\frac{1}{2}(T_1 + T_2)(s_2 - s_1)}$   
 $= 1 - \frac{T_2(s_2 - s_1)}{\frac{1}{2}(T_1 + T_2)(s_2 - s_1)}$   
 $= 1 - \frac{T_2}{\frac{T_1 + T_2}{2}}$   
 $= \frac{T_1 - T_2}{T_1 + T_2}$

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This will have half the efficiency, this will have slightly lesser efficiency depending on the value.

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### Entropy variation with temperature (For Expansion Process)

Prove that the slope on a T-S diagram of  
 (a) An isochoric curve is  $T/C_v$   
 (b) An isobaric curve is  $T/C_p$   
 Then compare the change in entropy with temperature for the following processes:  
 (a) Isothermal (b) adiabatic (c) isobaric (d) isochoric

$(a) dq_{rev} = T ds$   
 $C_v dT = T ds$   
 $\frac{dT}{ds} = \frac{T}{C_v}$   
 $dT = \frac{T}{C_v} ds$   
 $\frac{dT}{T} = \frac{ds}{C_v}$   
 $\ln T = \frac{s}{C_v}$   
 $T = e^{s/C_v}$

$(b) C_p dT = T ds$   
 $\left(\frac{dT}{ds}\right) = \frac{T}{C_p}$   
 $T = e^{s/C_p}$   
 $C_p > C_v$

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Prove that the slope on a TS diagram of an isochoric curve is T by Cv and Isobaric curve is T by Cp. So we know that dQ reversible is TdS. Now what is dQ for a constant volume process, isobaric process? Is Cv dT, So Cv dT is TdS or dS is, or dT dS rather, dT dS is T by Cv. So that is proven. And similarly Cp dT is TdS for isobaric process. So dT by dS is T by Cp. So this is A and this is B, proof of A and B. This is the slope, right? When you calculate the slope, you will take the differentiation. So we got that.



But now the second question is that then, compare the change in entropy with temperature for the following processes. So let us draw that, temperature and entropy. And an isothermal process, how does the temperature change in the isothermal process? Does not change, right? This is the isothermal process, it does not change at all. Temperature does not change, entropy changes. How does it change for an adiabatic process? Temperature changes but entropy does not change, so this is adiabatic process, this is isothermal process.

How does it change in an isochoric and isobaric process? For that we need to take the help of this one. So  $dT$  equal to  $T$  by  $C_v dS$  or  $dT$  by  $T$  equal to  $dS$  by  $C_v$ . So  $\ln T$  is  $S$  by  $C_v$ . So  $T$  is  $e$  to the power  $S$  by  $C_v$ . So temperature as goes as  $e$  to the power  $S$  by  $C_v$  in case of isobaric process. Similarly temperature will be  $e$  to the power  $S$  by  $C_p$  in case of, sorry this is isochoric process, this is isobaric process. Which will go in a steeper manner? Both are exponential but which will go in steeper manner?

We know that  $C_p$  is greater than  $C_v$ , right? So therefore  $S$  by  $C_p$  is a smaller number,  $S$  by  $C_v$  is a bigger number, because  $C_v$  is small. So therefore isobaric process will go exponentially, isochoric process will be even higher, with higher exponential it will move. So this is isobaric process, this is c and isochoric process, this is d. Did you understand this one? So these are the four ways that, this is isothermal process a, I am just denoting by a, b, c, d on the top. And this is b, do not confuse a by adiabatic. So a is denoting is isothermal, b is denoted by adiabatic, c is isobaric and d is isochoric.