

**Chemical Principles II**  
**Professor Dr Arnab Mukherjee**  
**Department of Chemistry**  
**Indian Institutes of Science Education and Research, Pune**  
**Module 03**  
**Lecture 20**  
**Tutorial Problem 01**

So we start today so we have again already discussed about different types of work done P-V work done both isothermal and adiabatic work. And also we have looked into Joules Thomson and Joules expansion and we have worked out certain other problems, so today we are going to do some more simple problems and then if there is time we will go to the next topic ok.

(Refer Slide Time: 0:49)

Application of isothermal and adiabatic work: TQ1

---

Calculate the work done for this cyclic process.

$$W_{A \rightarrow B} = -P_1(3V_1 - V_1) = -P_1 \times 2V_1 = -2P_1V_1$$

$$W_{C \rightarrow A} = 0$$

$$W_{B \rightarrow C} = ?$$

$$\frac{dP}{dV} = \frac{6P_1}{-2V_1} = -\frac{3P_1}{V_1}$$

$$dP = -\frac{3P_1}{V_1} dV$$

$$P = -\frac{3P_1}{V_1} V + C \quad \text{--- (1)}$$

$$P_1 = -\frac{3P_1}{3V_1} \times 3V_1 + C$$

$$P_1 = -9P_1 + C \Rightarrow C = 10P_1$$

$$\textcircled{1} \Rightarrow P = -\frac{3P_1}{V_1} V + 10P_1$$

$$W_{B \rightarrow C} = -\int_{3V_1}^{V_1} P dV$$

Chemical Principles II -- Arnab Mukherjee

So the first problem is for this particular cyclic diagram A goes to B, B goes to C and C goes to A, we need to calculate the work done in the whole process okay, so how you are going to approach this particular problem? So is given that what you are going to do for example, if we want to do work done for A to B system it should be pretty simple because it is constant pressure work, see the pressure is not changing it is remaining fixed at P1 value so it should be minus P1 and change in the volume which is 3 V1 is the final volume minus initial volume is V1 so that gives us minus P1 into 2 V1 or -2 P1 V1 correct so you can see that the work is negative, which means that the work is done by the system ok.

Now let us to the other simple one which is C to A, what will be the work done in this particular case? The work done should be 0 in this particular case. Now we are going in a cycling process; A to B, B to C and C to A so we have to do B to C now can you tell me what will be the work done in case of B to C, how you are going to do that? So notice one thing that B to C is a linear change right and there is some information in the graph to find out the relation between pressure and volume so we need to find out that relation ok.

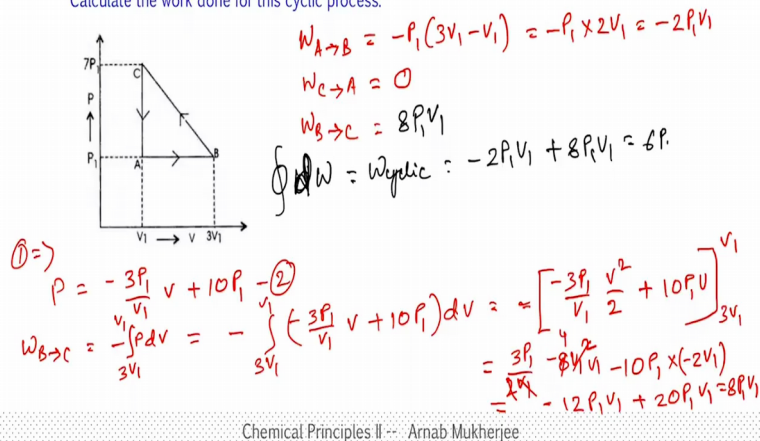
So as you can see it is a linear graph right, so change in pressure versus change in volume which is  $dP$  by  $dV$  that is the slope of the curve right? And what is the change in pressure, so let us say I am going from B to C so I am going from B to C so I will get  $6 P_1$  change and going from B to C, I will get a change of  $-2 V_1$  right, so the slope is  $-3 P_1$  by  $V_1$  right, it is a negative slope it should be negative because when pressure increases volume decreases so that means  $dP$  is equal to  $-3 P_1$  by  $V_1 DV$ . When integrateing, it will give  $P$  is equal to  $-3 P_1$  by  $V_1$  into  $V$  plus  $C$  so we need to find out the value of  $C$  right. So in order to find out the value of  $C$  we need to put some points, let us take the point B.

So at B the pressure is  $P_1$  so I write  $P_1$  equal to  $-3 P_1$  by  $V_1$  and at B volume is  $3 V_1$  right so  $3 V_1$  plus  $C$ . So what happens is then  $V_1 V_1$  cancels, it gives us  $P_1$  equal to  $-9 P_1$  plus  $C$  which gives us  $C$  is equal to  $10 P_1$ . Now we get that equation, now let us see the equation number 1 so from 1 we get  $P$  is equal to  $-3 P_1$  by  $V_1$  into  $V$  plus  $10 P_1$ , so  $P_1 V_1$  they are all fixed values where as  $P$  and  $V$  are variables okay  $P$  is a function of  $V$  or  $V$  is a function of  $P$ . So now that we get our  $P$ , the work done from B to C can be written as minus  $P dV$  integration going from  $3 V_1$  to  $V_1$  because we are going from B to C right. So I will just I am just going to erase this particular part right-hand side space.

(Refer Slide Time: 4:59)

### Application of isothermal and adiabatic work: TQ1

Calculate the work done for this cyclic process.



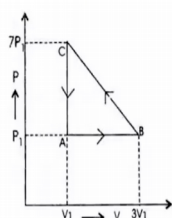
So which means now I am going to substitute P from equation number 2 which is integration 3 V1 to V1 and substitute P as minus 3 P1 by V1 into V + 10 P1 this one total dV which gives us minus now I will just straightaway put the bracket, minus 3 P1 by V1 into V square by 2, integration of V gives us V square by 2 + 10 P1 into V that is going from 3 V1 to V1 ok. So now we are going to do again so minus minus becomes plus so 3 P1 by V1 and 2 I will just put it here so now I get V square. V square is V1 square minus 9 V1 square right, which gives us - 8 V1 square. First step is done, 2<sup>nd</sup> step, -10 P1 this minus has come here -10 P1 now V1 - 3 V1 gives us -2 V1.

Now this is the last step, now I have 2 V1 and 8 V1 square so 2, 8, 4 V1, V1 square is V1 so I am getting -12 P1 V1 plus 20 P1 V1 so 8 P1 V1, is it correct? Ok so now that means now I can write here as 8 P1 V1, now what will be the total work done for the cyclic process, which means I can say that I can write as integration of dW over the cycle or I can write total work in the cyclic process whichever way I want to write so I have to add all that together will give us -2 P1 V1 plus 8 P1 V1 is 6 P1 V1 so I am just going to erase it.

(Refer Slide Time: 7:45)

### Application of isothermal and adiabatic work: TQ1

Calculate the work done for this cyclic process.



$$W_{A \rightarrow B} = -P_1(3V_1 - V_1) = -P_1 \times 2V_1 = -2P_1V_1$$

$$W_{C \rightarrow A} = 0$$

$$W_{B \rightarrow C} = 8P_1V_1$$

$$\oint dW = W_{\text{cyclic}} = -2P_1V_1 + 8P_1V_1 = 6P_1V_1$$

$$\oint dU = 0$$

$$\oint dQ = -6P_1V_1$$



Chemical Principles II -- Arnab Mukherjee

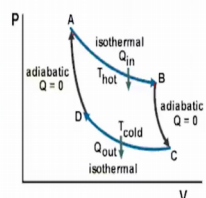
So if that is the case so you know what is the total internal energy change in the cyclic process, so if I go from A to B, B to C and C to A, what will be the change in the internal energy, 0 because it is a straight function so therefore what is the total heat change in the whole process? It will be  $-6 P_1 V_1$  so we do not have to calculate the heat so it is not always easy to calculate the heat change ok because heat change formula we know either  $CV DT$  or  $CP DT$ , so constant pressure process we have only one here which is going from A to B ok.

And this is a constant volume process is also there C-A that is also fine but we do not have anything between A-C that we will not be able to calculate, it is neither constant pressure process nor constant volume process, nor adiabatic process nor isothermal process so in that case it will not be possible to calculate the heat change so but here total heat change we can calculate by using the 1<sup>st</sup> law of thermodynamics formula.

(Refer Slide Time: 9:08)

### Application of isothermal and adiabatic work: TQ2

Calculate the work done for this cyclic process.



$$T_A = T_B = T_h \quad T_C = T_D = T_c$$

$$W_{A \rightarrow B} = -nRT_h \ln \frac{V_B}{V_A}$$

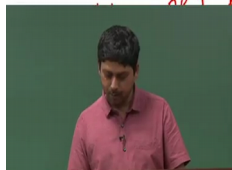
$$W_{B \rightarrow C} = C_V (T_c - T_h)$$

$$W_{C \rightarrow D} = -nRT_c \ln \frac{V_D}{V_C}$$

$$W_{D \rightarrow A} = C_V (T_h - T_c)$$

$$W_{total} = nRT_h \ln \frac{V_B}{V_A} - nRT_c \ln \frac{V_D}{V_C} + C_V (T_h - T_c + T_c - T_h)$$

$$= nR \left[ T_h \ln \frac{V_B}{V_A} + T_c \ln \frac{V_D}{V_C} \right]$$



Chemical Principles II -- Arnab Mukherjee

Ok so now let us study one more problem of calculating the work done. So here you will learn later that it is called the Carnot cycle where A to B is an isothermal process, then B to C is an adiabatic process so 1<sup>st</sup> there is an isothermal expansion. And you know in isothermal expansion heat goes inside because otherwise temperature will not remain constant I told you that for an expansion process temperature will cool down if you do not put heat, so in order to maintain the temperature you have to put in heat, so this is the step where the heat goes in.

Now next is adiabatic step where there is no heat going in or coming out because that is why it is adiabatic and since it is an expansion process the temperature will cool down. And then C to D is a compression isothermal compression process just opposite of A to B in which case the heat will go out, just like it is going in between A-B and C-D it will go out, and D to A then this no exchange of heat it is just the opposite of B to C, it is a compression process so the temperature will increase ok. So AB and CD are complimentary to each other or just the opposite process of each other and BC and DA are opposite process of each other.

And interestingly the temperature of AB is same, temperature of CD are same, but the temperature between B and C and A and B are different okay. These are different facets of this particular Carnot cycle you know that was designed and you will learn later that this kind of an engine that works. So any engine means you know you give in heat and you get some work, our main task of working with engine is that that we will get the work done whether it is a train in which we ride or whether it is a pump with which we take out water or whatever you can think of, and engine or a car, engine is made to do some work you know they

substitute manual labor by using the available energy. So this is the heat engine where heat will be used to do the work so let us see how much work this engine can get.

(Refer Slide Time: 11:39)

Application of isothermal and adiabatic work: TQ2

---

Calculate the work done for this cyclic process.

$$T_A = T_B = T_h \quad T_C = T_D = T_c$$

$$W_{A \rightarrow B} = -nRT_h \ln \frac{V_B}{V_A}$$

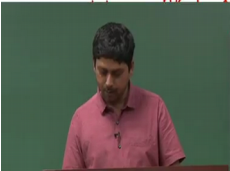
$$W_{B \rightarrow C} = C_V (T_C - T_h)$$

$$W_{C \rightarrow D} = -nRT_c \ln \frac{V_D}{V_C}$$

$$W_{D \rightarrow A} = C_V (T_h - T_c)$$

$$nRT_h \ln \frac{V_B}{V_A} - nRT_c \ln \frac{V_D}{V_C} + C_V (T_h - T_c + T_h - T_c)$$

$$T_h \ln \frac{V_B}{V_A} + T_c \ln \frac{V_D}{V_C}$$



Chemical Principles II -- Arnab Mukherjee

Now you see in order to calculate the total work we have to do it again stepwise, what is the work than in  $W_{A \rightarrow B}$ , if you remember the formula it is an expansion process remember so work done on the system will be negative, we always calculate work done on the system right and since it is an expansion process work done on a system is a negative work done that means system is doing the work. So it is  $-nRT_h$ , A or B basically the same because it is a constant temperature process so I am just writing as  $T_h$ . I will just note it down here that  $T_A$  is equal to  $T_B$  and  $T_C$  is equal to  $T_D$ .  $\ln \frac{V_B}{V_A}$  by  $V_A$  okay that is the formula I am using that which we have already derived for isothermal work, we have already derived that so that is why I am not doing it.

Now for B to C we have also derived this what was that,  $T_C - T_h$  let us call it  $T_h$  because  $T_B$  and  $T_h$  are same in fact, since  $T_B$  and  $T_h$  are same we can call that as  $T_h$  high-temperature, and  $T_C$  and  $T_D$  are same let us call as  $T_c$  cold, here the C is cold you know high-temperature hot reservoir and cold reservoir basically okay. So we are just going to replace A by H and C by cold ok. And we will also explain what is a hot reservoir and a cold reservoir, hot reservoir is something in which like where the reservoir is supplying new energy, it is kept at high-temperature.

A cold reservoir is where reservoir is colder than the system which will take out the heat from that that is the definition and reservoir is as I told you is a very big system therefore its

temperature is not going to change if you give in little bit heat or take out a little bit of heat ok. So now what is the work done from C to D? No, we have gone to B to C right so C to D it will be exactly opposite of A to B so it will be plus N R T or rather you use the same formula so minus N R T C LN VD by VC. You see volume of D is smaller than volume of C so this particular term is already negative, and negative and negative will make it positive so it is actually a positive work done on the system ok but we do not have to worry about which is positive and which is negative, we can use the same formula and the formula is minus N R T LN V final by V initial.

Now the last step D to A, again CV TH minus TC okay, is it correct? Now what is the total work done then? minus N R TH LN VB by VA minus NR TC LN VD by VC + CV TC - TH plus TH minus TC, so we can see that this gets cancelled out and only this is remaining and we can take minus common and it will be TH LN VB by VA + TC LN VD by VC.

(Refer Slide Time: 16:13)

The image shows a handwritten derivation of the work done in a Carnot cycle. The derivation is as follows:

$$W = -nR \left[ T_h \ln \frac{V_B}{V_A} + T_c \ln \frac{V_D}{V_C} \right]$$

$$= -nR \left[ T_h \ln \frac{V_B}{V_A} + T_c \ln \frac{V_A}{V_B} \right]$$

$$= -nR \left[ T_h \ln \frac{V_B}{V_A} - T_c \ln \frac{V_B}{V_A} \right]$$

$$W = -nR \ln \left( \frac{V_B}{V_A} \right) (T_h - T_c) \quad (4)$$

The efficiency  $\eta$  is given by:

$$\eta = \frac{-W}{Q_{in}} = \frac{-W}{nR \ln \left( \frac{V_B}{V_A} \right) (T_h - T_c)}$$

$$= \frac{nR \ln \left( \frac{V_B}{V_A} \right) (T_h - T_c)}{nR \ln \left( \frac{V_B}{V_A} \right) (T_h - T_c)}$$

$$= 1 - \frac{T_c}{T_h}$$

The final result is boxed in red:  $\eta = 1 - \frac{T_c}{T_h}$ .

Other equations shown include:

$$W_{AB} = -\int p dv = -nR T_h \ln \frac{V_B}{V_A}$$

$$Q_{in} = Q_{AB} = -W_{AB} = nR T_h \ln \frac{V_B}{V_A} \quad (5)$$

Adiabatic relations for points B and C:

$$T_B V_B^{\gamma-1} = T_C V_C^{\gamma-1} \quad (1)$$

$$T_h V_B^{\gamma-1} = T_c V_C^{\gamma-1} \quad (2)$$

$$T_A V_A^{\gamma-1} = T_D V_D^{\gamma-1}$$

$$T_h V_A^{\gamma-1} = T_c V_D^{\gamma-1} \quad (3)$$

$$\frac{V_B}{V_A} = \frac{V_C}{V_D} \quad (3)$$

A P-V diagram of the Carnot cycle is shown, with points A, B, C, and D. The cycle consists of four processes: A to B (isothermal expansion), B to C (adiabatic expansion), C to D (isothermal compression), and D to A (adiabatic compression). The temperatures  $T_h$  and  $T_c$  are indicated at points A and C respectively.

So we can simplify it even further and we can write W, writing it again we can say that W is equal to  $-N R T_h \ln V_B$  by  $V_A + T_c \ln V_D$  by  $V_C$ . Now just to remind us the Carnot cycle in P-V diagram is A to B is an isothermal process, B to C is an adiabatic process, C to D is an isothermal process and D to A is an adiabatic process. I will denote by I as an isothermal and A as an adiabatic. Now I can use the relation between B and C which are 2 points connected by adiabatic reversible path, so the connection that you know between them the relation is that the temperature at point B and then volume to the power gamma - 1 at point B is temperature at point C and volume at point C to the power gamma - 1.

And we know that TB is nothing but TH, both A and B have same temperature TH which is the high-temperature and VB to the power  $\gamma - 1$  is TC, C is now cold C means cold now, so this is TH and this is TC VC to the power  $\gamma - 1$  so that is equation 1. Similar relation we can have between D and A and we can write TA VA to the power  $\gamma - 1$  is TD VD to the power  $\gamma - 1$ . TA is nothing but TH VA to the power  $\gamma - 1$  and TD is TC VD to the power  $\gamma - 1$  let us call it 2. And then dividing 1 by 2 we get VB by VA to the power  $\gamma - 1$  is VC by VD to the power  $\gamma - 1$  or VB by VA is VC by VD, let us call that 3.

Now use this equation relation in 3 in this equation we can get minus  $N R TH \ln VD$  by VA + TC LN it is VD by VC will be VA by VB and then we can take we can write it again using the formula as minus TC LN VB by VA. And then we can take L and VB by VA as common and write TH minus TC, so this is the work done for the cyclic process in a Carnot cycle going from A to B to C to D and this is the simplest possible relation that you can write down. And now we can also calculate the efficiency from this, so efficiency of that particular engine is work done by heat input.

Now heat input has happened as you know between the 1<sup>st</sup> isothermal processes going from A to B. Now we have done already the work done from A to B so work done from A to B as we have seen is minus  $P DV$  and then we have written that as  $N R TH \ln VB$  by VA. And we know that  $U_{AB}$  is 0 because there is no temperature change so therefore heat input Q in equal to  $Q_{AB}$  that is negative of  $W_{AB}$  which is plus  $N R TH \ln VB$  by VA, let us is called this as equation 4 and this as equation 5.

So therefore this one we get as minus  $N R$  as  $W \ln VB$  by VA TH minus TC divided by Q in we got from 5 as plus  $N R \ln VB$  by VA. Now  $N R \ln VB$  by VA cancels and TH is also there, they cancels each other and we get minus TH minus TC by TH or we get this as minus  $1 - \frac{TC}{TH}$  so there is you have to see there is minus should not be there. So if I say that W is work done on the system so therefore work done by the system will be minus W, so minus W is the work that the system is doing, there will be plus there will be + and there will be plus. So the efficiency of the engine now if I use a different color is  $\eta$  is equal to  $1 - \frac{TC}{TH}$  so this is the efficiency of the Carnot engine.