Chemical and Biological Thermodynamics: Principles to Applications

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Lecture – 06

Adiabatic Processes

Today, we are going to discuss the adiabatic processes. In the previous lecture, we talked about how to get the work done in an isothermal process. Adiabatic processes are the one in which no heat is allowed to either enter or leave the system. And we will develop several equations and show that when we want to calculate the work done in an adiabatic process. We do not actually need to work through pressure and volume, if it is a pressure volume change, we can actually work through changes in internal energy.

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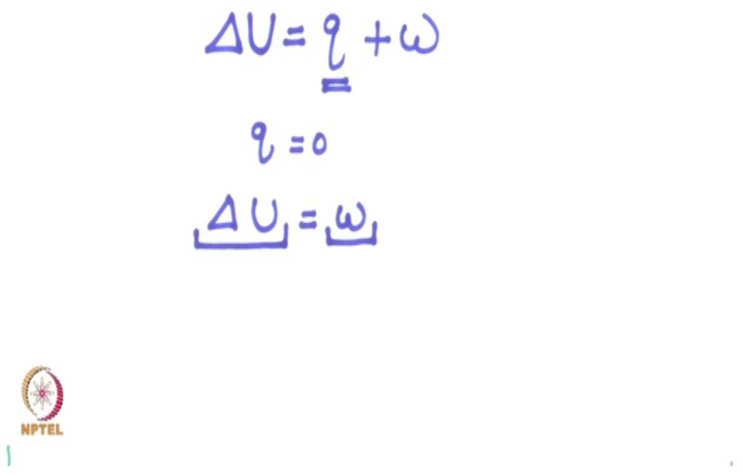

$$\Delta U = \underline{\underline{q}} + w$$

$$q = 0$$

$$\underbrace{\Delta U} = \underbrace{w}$$

The reason is that let us recall that the change in internal energy delta U is equal to q plus w; and for an adiabatic process q is equal to 0, therefore, delta U is equal to w. So, in order to calculate work if i can simply calculate the change in internal energy that does the work that does the job of calculating the work.

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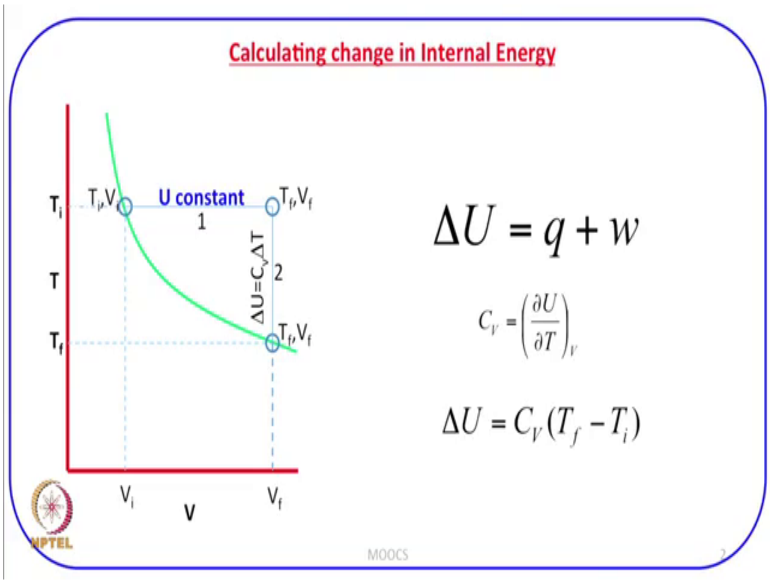

Calculating change in Internal Energy

$$\Delta U = q + w$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$\Delta U = C_V(T_f - T_i)$$

Let us take a look at the slide. Since, in order to calculate the work, we need to calculate the change in internal energy. Let us see how we can do it. This is a plot of temperature versus volume, and this is how the temperature will fall when the volume increases. Why the temperature falls when the gas expands under adiabatic conditions or why the temperature will increase when the gas is compressed under adiabatic conditions. The reason is if you allow a gas to expand under adiabatic conditions, we are not allowing any heat to either enter or leave the system.

Therefore any work which is done at the cost of internal energy. That means, if the work is done by the system and you are not allowing any heat exchange, and then during expansion, the internal energy of the system must decrease. And since the internal energy will not just depend upon the changes in the volume, and since here we are not allowing any heat exchange, therefore, the temperature of the system must fall during expansion.

And that is what is seen here in this figure. You see when the volume is changing from V i to V f the temperature changes from T i to T f, there is a fall in the temperature. And if I divide this process into two steps that is a step one where I keep the temperature constant it remains constant T i, but the volume changes. And since we will refer to ideal gases, the internal energy does not change in an isothermal expansion, so U remains constant. And the second step can be now let the temperature change from T i to T f and the volume is remaining constant and here I can use delta U is equal to C v times delta T. This is how you can change you can calculate the change in internal energy.

Let us take a look at step-by-step. This is the first law of thermodynamics. And since q is equal to 0, I can set w is equal to delta U. So, calculations of delta U become very important. From the definition of the heat capacity at constant volume C v is equal to dou U by dou T at constant volume. And this can be rearranged to get delta U for a final change which is C v times the difference in the temperature. And this calculation requires the knowledge of final temperature, the knowledge of initial temperature and the value of the heat capacity. Now, we will discuss how to calculate the work done during an adiabatic change. And most of my discussion unless I specify it my discussion will refer to ideal gases.

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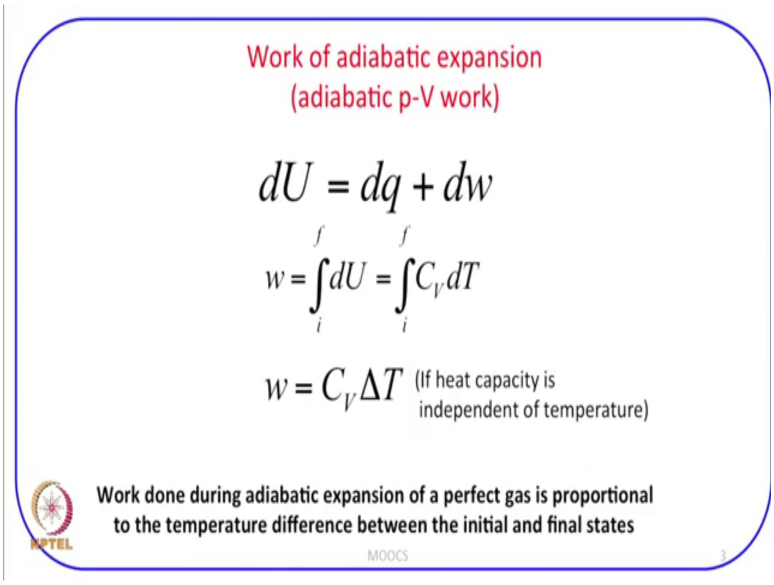

Work of adiabatic expansion
(adiabatic p-V work)

$$dU = dq + dw$$

$$w = \int_i^f dU = \int_i^f C_V dT$$

$$w = C_V \Delta T$$ (If heat capacity is independent of temperature)

Work done during adiabatic expansion of a perfect gas is proportional to the temperature difference between the initial and final states

MOOCS

Let us talk about the work of adiabatic expansion or if I call it as a adiabatic pressure-volume work. Once again let us recall the first law of thermodynamics. This will be important throughout the discussion d U is equal to d q plus d w. And work done will be equal to integration of d U from initial state to final state because d q is equal to 0 and instead of d U, now I write C v times delta T. And if C v is independent of temperature, it can come out of the integral and what we get is this expression that w is equal to C v times delta T.

So, in order to calculate the work what we need is the information on delta T and we need the information on heat capacity at constant volume, this is how we calculate the work of adiabatic expansion. So, the work done during adiabatic expansion of a perfect gas is proportional to the temperature difference between the initial and final state. Remember that this work is being done at the cost of internal energy, therefore this w will be same as delta U and that conclusion; we must remember that in adiabatic changes work is directly equal to changes in internal energy.

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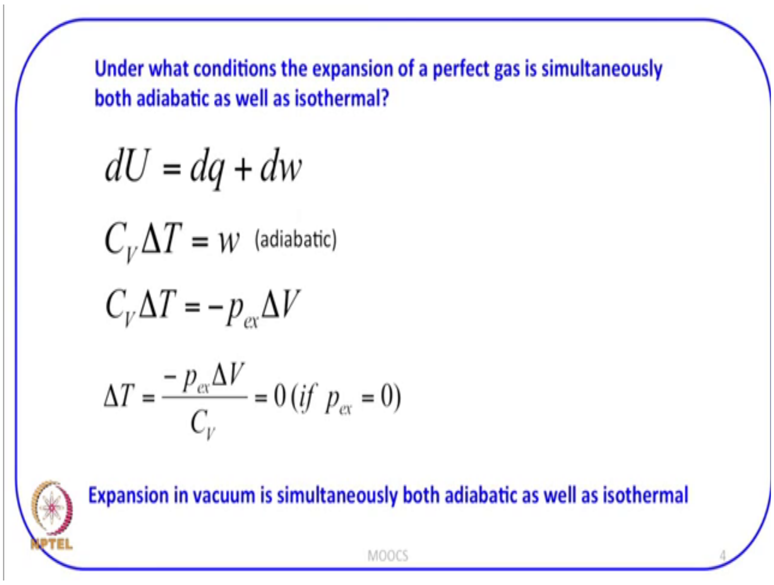

Under what conditions the expansion of a perfect gas is simultaneously both adiabatic as well as isothermal?

$$dU = dq + dw$$

$$C_V \Delta T = w \text{ (adiabatic)}$$

$$C_V \Delta T = -p_{ex} \Delta V$$

$$\Delta T = \frac{-p_{ex} \Delta V}{C_V} = 0 \, (if \; p_{ex} = 0)$$

Expansion in vacuum is simultaneously both adiabatic as well as isothermal

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Let us consider this special case. Under what conditions the expansion of a perfect gas is simultaneously both adiabatic as well as isothermal. Let us try to solve this question. As I said that the mathematical form of the first law of thermodynamics is very important in addressing such problems; d U is equal to d q plus d w, since process is adiabatic d q is equal to 0.

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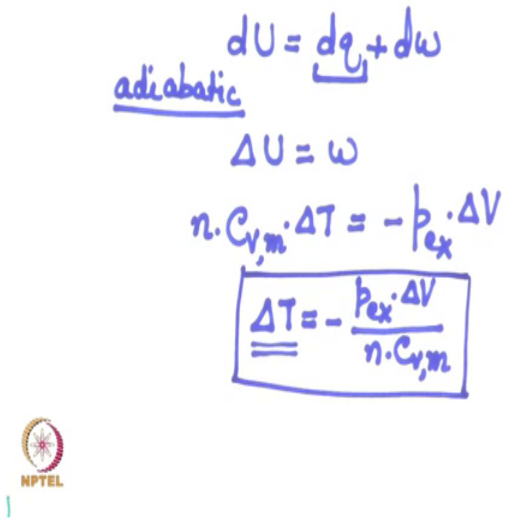

<u>adiabatic</u>

$$dU = \underbrace{dq} + dw$$

$$\Delta U = w$$

$$n \cdot C_{v,m} \cdot \Delta T = -p_{ex} \cdot \Delta V$$

$$\boxed{\underline{\underline{\Delta T}} = -\frac{p_{ex} \cdot \Delta V}{n \cdot C_{v,m}}}$$

And for a finite change, I can write delta U is equal to w. For delta U, I can write n times C v, m times delta T we just discussed and w is minus p external times delta V. From this step to this step, what we assumed is that the process is adiabatic. From this expression, I get delta T is equal to minus p external times delta V divided by n times C v, m. So, if I know the external pressure changes in volume and the heat capacity, I can calculate the change in temperature. From this expression, I can immediately tell that under what conditions the process is going to be isothermal.

Let us take a look at the slide this is why it what I just described that d U is equal to d q plus d w. And then immediately for an adiabatic change, I can write that work done is equal to C v times delta T. Remember that C v is the heat capacity for a given size of a substance. And this C v is equal to n times C v, m number of moles times molar heat capacity. So, there should be no confusion when I write C v or I write C v m that is why when I discussed here I talked in terms of C v m. So, delta T will be equal to 0, if the p external is equal to 0.

So, here you have the answer that when the gas expands against zero pressure, what is that zero pressure means expansion in vacuum. So, you have the conditions we started with an adiabatic process, and we find found out that if external pressure is equal to 0, then there is no change in temperature. Therefore, expansion in vacuum is simultaneously both adiabatic as well as isothermal.

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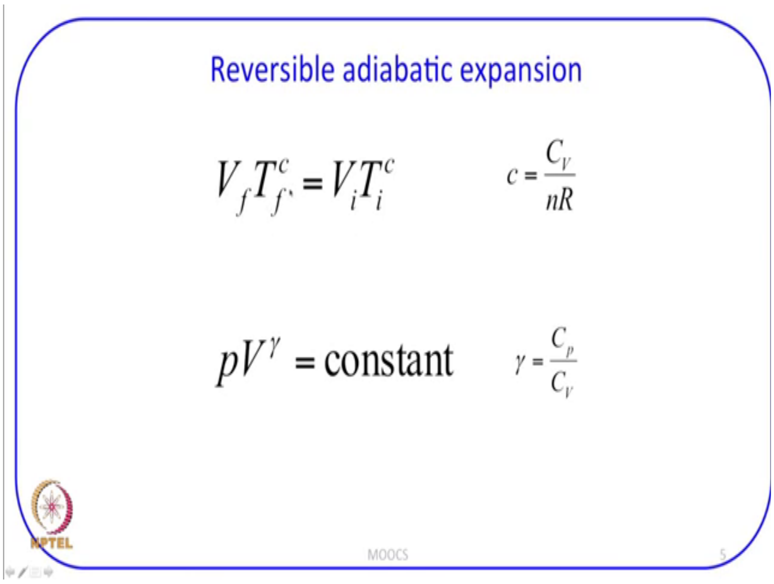

Reversible adiabatic expansion

$$V_f T_f^c = V_i T_i^c \qquad c = \frac{C_V}{nR}$$

$$pV^\gamma = \text{constant} \qquad \gamma = \frac{C_p}{C_V}$$

Next, let us now talk about the special case of reversible adiabatic pressure-volume changes. Remember that when we were talking about isothermal expansion of perfect gases, we showed that the maximum work is available from the system when it is operating under reversible isothermal conditions. And now let us see what happens if we remove that condition of being isothermal and carry out the process under adiabatic conditions. Here we are going to derive two equations, V f T f raised to the power c is equal to V i T i raise to the power c, where the c is the ratio of heat capacity and n R. The second equation that we are going to derive is p V gamma is equal to constant, where gamma is the ratio of heat capacities at constant pressure and constant volume, very easy derivation.

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$$dU = \underbrace{dq}_{} + dw$$

$$dU = dw$$

$$\underline{n \cdot C_{v,m} \cdot dT} = -\underline{p}\, dV = -\underline{\frac{nRT}{V}}\, dV$$

$$C_{v,m} \cdot \frac{dT}{T} = -R\,\frac{dV}{V}$$

$$\frac{C_{v,m}}{R}\int_{T_i}^{T_f}\frac{dT}{T} = -\int_{V_i}^{V_f}\frac{dV}{V} \quad \Bigg| \quad \frac{C_{v,m}}{R}\ln\frac{T_f}{T_i} = \ln\frac{V_i}{V_f}$$

Let us see how to get it. Once again d U is equal to d q plus d w and adiabatic since we are talking adiabatic changes d q is equal to 0. So, I have d U is equal to d w. And d U is n times C v, m times d T, and d w is equal to minus p d V, I am keeping p because the process is reversible. And this I can say minus n R T by V into d V. Now using these two, I can write that C v, m into d T by T is equal to minus R into d V by V or I can write this as C v, m by R into d T by T is equal to minus d V by V. And if I now integrate from T i to T f V i to V f then what I get is I will write here that C v, m by R log T f by T i is equal to log V i by V f, I am consuming the negative sign.

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$$\frac{C_{v,m}}{R}\ln\frac{T_f}{T_i} = \ln\frac{V_i}{V_f}$$

$$\ln\frac{T_f}{T_i} = \ln\left(\frac{V_i}{V_f}\right)^{C_{v,m}/R}$$

$$\frac{T_f}{T_i} = \left(\frac{V_i}{V_f}\right)^{C_{v,m}/R}$$

$$V_f T_f^{c} = V_i T_i^{c} \;;\quad c = \frac{C_{v,m}}{R}$$

Now, from this equation, the equation that we just derived that C v, m by R is a log T f by T i is equal to log V i by V f, I can write log T f by T i is equal to log V i by V f raise to the power C v m by R. And then I can further rearrange this that is T f by T i is equal to V i by V f raise to the power C v m divide by R. Or I can write this as V f T f raise to the power c is equal to V i T i raise to the power c with c equal to C v, m divided by R.

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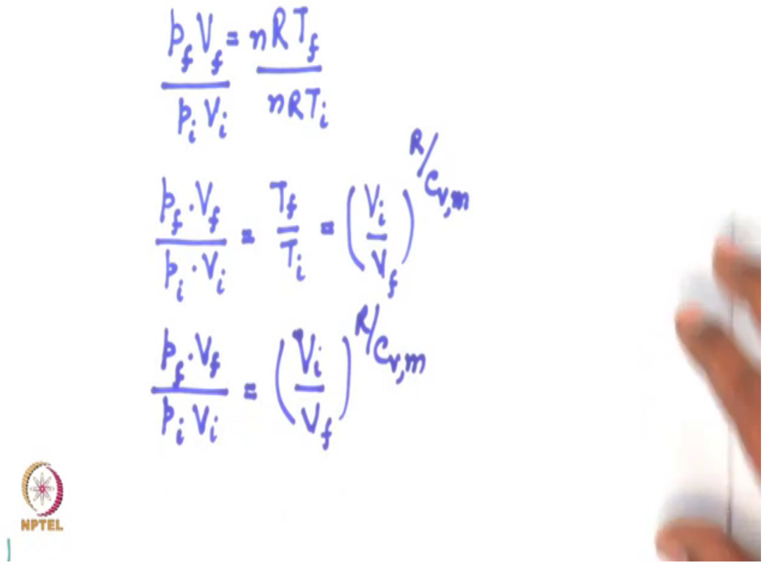

$$\frac{p_f V_f}{p_i V_i} = \frac{nRT_f}{nRT_i}$$

$$\frac{p_f \cdot V_f}{p_i \cdot V_i} = \frac{T_f}{T_i} = \left(\frac{V_i}{V_f}\right)^{R/C_{v,m}}$$

$$\frac{p_f \cdot V_f}{p_i \cdot V_i} = \left(\frac{V_i}{V_f}\right)^{R/C_{v,m}}$$

So, now let us look at the second equation that p V gamma is equal to constant this is what we need to now derive. Let us see now how to get that equation that is very easy p f V f is equal to n R T f that will anyway be valid and p i V i is equal to n R T i that will be valid. So, from here I can write p f V f p i V i is equal to T f by T i. So, therefore, T f by T i is equal to we have V i by V f raise to the power R by C v, m. Now, I when I rearrange p f V f over p i V i is equal to V i by V f raise to the power R by C v, m.

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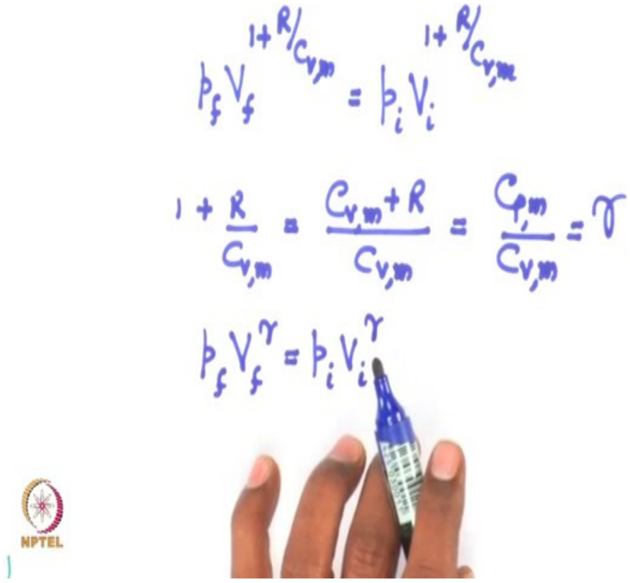

$$p_f V_f^{1+R/C_{v,m}} = p_i V_i^{1+R/C_{v,m}}$$

$$1 + \frac{R}{C_{v,m}} = \frac{C_{v,m}+R}{C_{v,m}} = \frac{C_{p,m}}{C_{v,m}} = \gamma$$

$$p_f V_f^{\gamma} = p_i V_i^{\gamma}$$

From here, I get p f V f raise to the power 1 plus R by C v, m is equal to p i V i raise to the power 1 plus R by C v, m. Now, 1 plus R by C v, m is equal to C v, m plus R divided by C v, m and this is equal to C p, m because C p, m minus C v, m is equal to R divided by C v, m and I call this as gamma. So, therefore my equation now becomes p f V f gamma is equal to p i V i raise to the power gamma. Now, let us go back what we have in this is p V gamma is equal to constant where gamma is the ratio of C p and C v.

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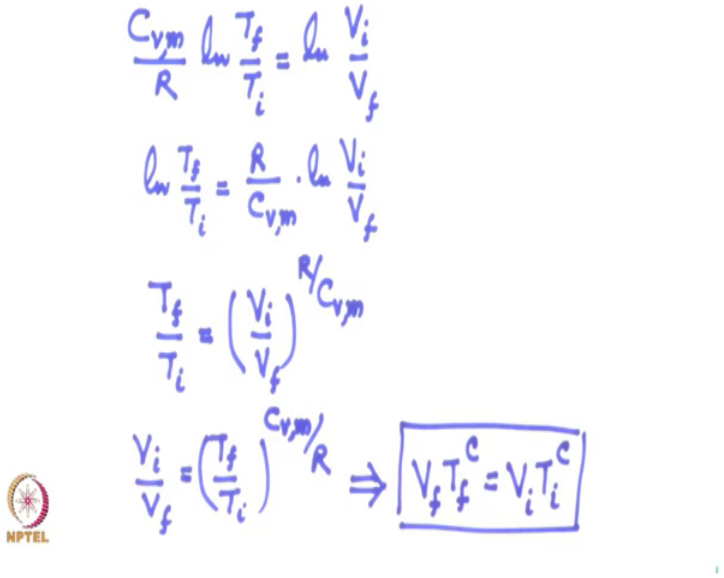

$$\frac{C_{v,m}}{R} \ln \frac{T_f}{T_i} = \ln \frac{V_i}{V_f}$$

$$\ln \frac{T_f}{T_i} = \frac{R}{C_{v,m}} \cdot \ln \frac{V_i}{V_f}$$

$$\frac{T_f}{T_i} = \left(\frac{V_i}{V_f}\right)^{R/C_{v,m}}$$

$$\frac{V_i}{V_f} = \left(\frac{T_f}{T_i}\right)^{C_{v,m}/R} \Rightarrow \boxed{V_f T_f^{c} = V_i T_i^{c}}$$

So, what we have is C v, m by R log T f by T i is equal to log V i by V f. This rearranges to log T f by T i is equal to R by C v, m into log V i by V f. This further rearranges to T f by T i is equal to V i by V f raise to the power R by C v, m. This I can rearrange now to write in this form that V i upon V f is equal to T f upon T i raise to the power C v, m divide by R which suggest the equation V f T f raise to the power c is equal to V i T i raise to the power c. And this is the equation that we were planning to derive with c is equal to C v by n R or C v, m by R.

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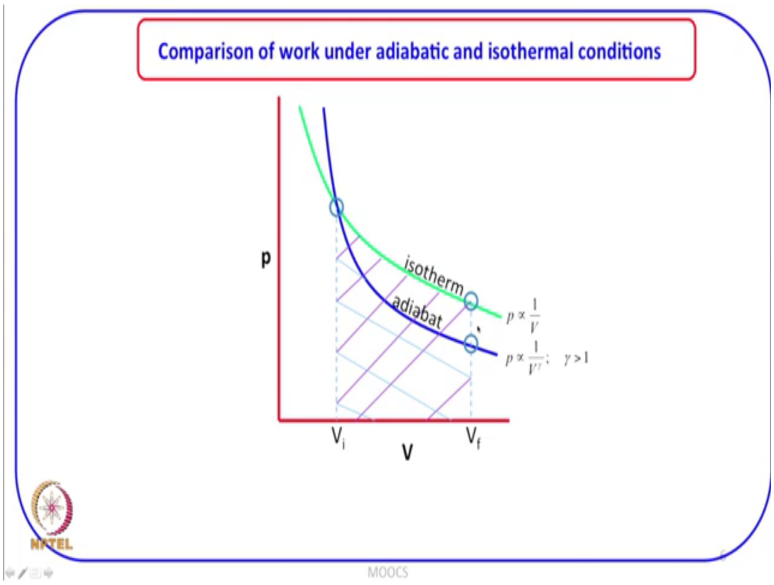

Comparison of work under adiabatic and isothermal conditions

Now, let us see under what conditions the work available from the system is more, is it under isothermal conditions or under adiabatic conditions. Let us take a look at this figure. Let us take a look at the green curve which is according to p V is equal to n R t.

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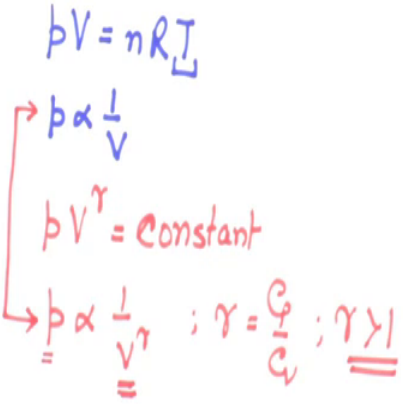

$$pV = nRT$$

$$p \propto \frac{1}{V}$$

$$pV^{\gamma} = \text{Constant}$$

$$p \propto \frac{1}{V^{\gamma}} \; ; \; \gamma = \frac{C_p}{C_v} \; ; \; \gamma > 1$$

See, for an ideal gas p V is equal to n R T. So, if the process is isothermal temperature is constant, then the pressure is inversely proportional to volume, because n is constant, R is constant and that is what you see in this green line that as the volume increases the pressure decreases this way. Now, for an adiabatic, we just showed that p V gamma is constant that means p is inversely proportional to volume raise to power gamma where gamma is equal to ratio of C p and C v. C p’s since is greater than C v therefore, gamma is always greater than 1.

Now, if gamma is greater than 1 and then if you compare- this versus this here with increase in volume the pressure is going to decrease more sharply, because gamma is greater than 1. And that is what we see in this blue line which is for a perfect gas adiabatic that as the volume increases the pressure is decreasing more sharply. And then as we discussed in the previous lectures that the area under the curve between the specified limits represents the work available from the system.

So, obviously, here the area under adiabatic between V i and V f is less than the area under an isothermal case. Therefore, more work is available from the system when the gas is expanding under isothermal reversible conditions compare to that when the gas is expanding against reversible adiabatic in reversible adiabatic conditions. Otherwise, also if the process is isothermal, isothermal means the temperature is being kept constant therefore, the internal energy of the system is continuously being replenished, and hence the system can do more work, whereas in an adiabatic process the internal energy decreases, therefore the work available from the system will be less.

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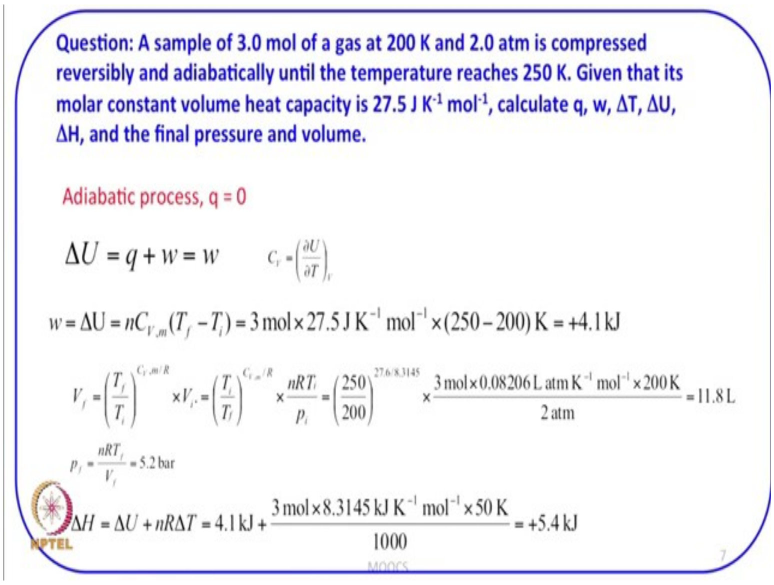

Question: A sample of 3.0 mol of a gas at 200 K and 2.0 atm is compressed reversibly and adiabatically until the temperature reaches 250 K. Given that its molar constant volume heat capacity is 27.5 J K^{-1} mol^{-1}, calculate q, w, ΔT, ΔU, ΔH, and the final pressure and volume.

Adiabatic process, q = 0

$$\Delta U = q + w = w \qquad C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$w = \Delta \mathrm{U} = nC_{V,m}(T_f - T_i) = 3\,\mathrm{mol} \times 27.5\,\mathrm{J\,K^{-1}\,mol^{-1}} \times (250 - 200)\,\mathrm{K} = +4.1\,\mathrm{kJ}$$

$$V_f = \left(\frac{T_f}{T_i}\right)^{C_V,m/R} \times V_i = \left(\frac{T_i}{T_f}\right)^{C_{V,m}/R} \times \frac{nRT_i}{p_i} = \left(\frac{250}{200}\right)^{27.6/8.3145} \times \frac{3\,\mathrm{mol} \times 0.08206\,\mathrm{L\,atm\,K^{-1}\,mol^{-1}} \times 200\,\mathrm{K}}{2\,\mathrm{atm}} = 11.8\,\mathrm{L}$$

$$p_f = \frac{nRT_f}{V_f} = 5.2\,\mathrm{bar}$$

$$\Delta H = \Delta U + nR\Delta T = 4.1\,\mathrm{kJ} + \frac{3\,\mathrm{mol} \times 8.3145\,\mathrm{kJ\,K^{-1}\,mol^{-1}} \times 50\,\mathrm{K}}{1000} = +5.4\,\mathrm{kJ}$$

Let us look at one of its application in the form of this question. A sample of three mole of a gas at 200 Kelvin and 2 atmosphere is compressed reversibly and adiabatically until the temperature reaches 250 Kelvin. Given that it is molar constant volume heat capacity is twenty seven point five joules per Kelvin per mol calculate q, w, delta T, delta U, delta H and the final pressure and volume. So, many quantities need to be calculated.

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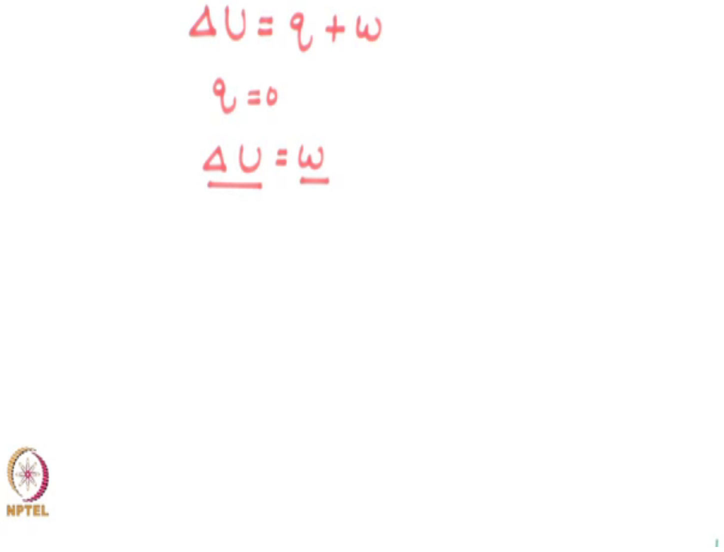

$$\Delta U = q + w$$

$$q = 0$$

$$\underline{\Delta U} = \underline{w}$$

However, as I expressed earlier also that we can straightaway start with the first law of thermodynamics delta U is equal to q plus w. And since the process is adiabatic q is equal to 0, therefore, delta U is equal to w. So, when we calculate delta U then we do not need to calculate w through p and V because delta U will be equal to w. And let us see how to calculate that. Let us take a look at the slide. Adiabatic process q is equal to 0. So, therefore, delta U has to be equal to w, we can use again here the definition of heat capacity C v which is dou U by dou T at constant volume which will give us delta U which is equal to n times C v, m times delta T. And it has to be equal to work by the arguments given above. Now, you substitute the numbers n is 3 mol, C v, m is given 27.5 joules per Kelvin per mol, temperatures are also given 250 and 200 Kelvin's as the final and initial temperature, and this turns out to be 4.1 kilo joule.

Next, we need the final volume. And final volume can be calculated from this expression, because you remember we just showed that V i T i raise to the power c is equal to V f T f raise to the power c. And if we rearrange that we will have this expression V f is equal to T f by T i raise to the power C v, m by R into V i, V i can be calculated from n R T i by p i because this is an ideal gas. And once we substitute all the numbers with a suitable value of R, a liter atmosphere per Kelvin per mol the volume comes out to be 11.8 liter, this is the final volume. Then immediately if I know the final volume, and since it is an ideal gas I can calculate p f which is equal to n R T f by V i, this is 5.2 bar.

Now, the only thing that is left over is to calculate the change in enthalpy. And change in enthalpy again we can calculate from this expression delta h is equal to delta U plus n R delta T. and here we have the value of delta U we have already calculated we know the value of n R delta T you substitute the numbers. And here I am converting joules into kilojoules by dividing by 1000 the number comes out to be 5.4 kilojoules. So, the way to solve these type of questions when the process is adiabatic, it is always a good idea to start with the first law of thermodynamics, and then to see how we can use the different definitions to get the answers for the various thermodynamic quantities that have been asked.

So, in this lecture, we discussed how to calculate the work done in an adiabatic process. We discussed that we actually do not need to work through pressure and volume; we can work through the changes in internal energy because q is equal to 0. And then once we know the changes in internal energy, we can get the other thermodynamic quantities. We will discuss more in terms of numerical problems in the future lectures. And if there are any questions or queries, we will discuss those in the help session.

Thank you very much.