Introduction to Atmospheric Science
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Lecture - 29
The Second Law of Thermodynamics - Clausius Clapeyron Relation

Okay, Good Morning. Welcome back. So do not be so surprised. So we will start with the second law of thermodynamics. We will try to complete it also. In the next class we will start off with radiative transfer in the atmosphere right. So second law of thermodynamics, Carnot cycle, entropy all that you all know it very well. So we will quickly go through this.

The most important thing for us is the Clausius Clapeyron equation helps you to find out how the saturated vapour pressure changes with temperature that is related to the latent heat right. People who are in mechanical engineering must have studied the Clausius Clapeyron equation in one course, somewhere it is ringing a bell alright. So now, the second law of thermodynamics. What is the, basic goal of today's lesson basically is to introduce the Carnot cycle and get the efficiency of the function of T 1 and T 2. But there is no heat engine.

We are not going to use the heat engine here. It is not mechanical engineering. From the Carnot cycle, the absolute temperature scale is devised. From that we can and then we move on to the concept of entropy and then we prove that the constant potential temperature is the same as the isentropic lines. So we will say that isentropic lines, constant potential temperature lines or dry adiabat or saturated adiabat can be used as a surrogate or as a proxy for an isentropic process which you already know. You have discussed it so many times, reversible and adiabatic.

The reversible and adiabatic process is also known as the isentropic process. That you already know. But we will have to for the sake of completeness we will go through those arguments and then we will say the delta s is greater than equal to 0 of the universe right the principle of increase of entropy that we will see and towards the end of the lecture we will derive the Clausius Clapeyron equation from first principles using the Carnot cycle. The Clausius Clapeyron equation tell you how much the vapour pressure will change with temperature okay. What is it actually?

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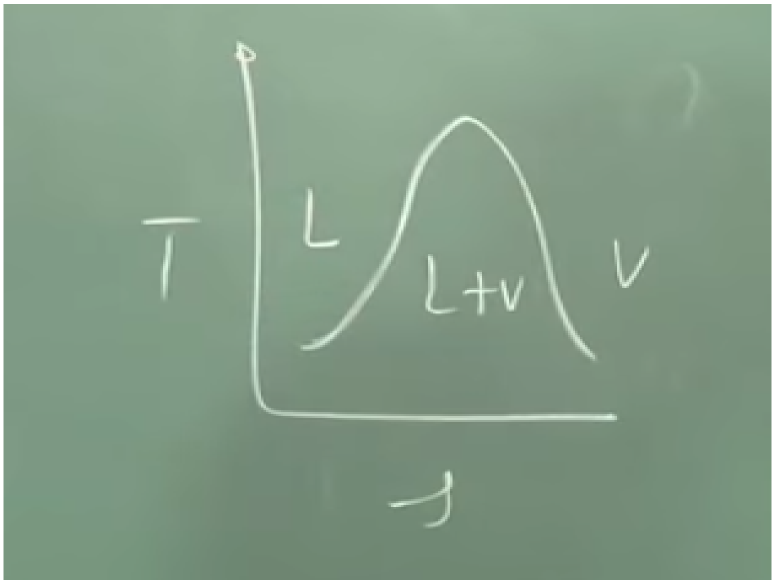

Your T s diagram of the steam okay with (()) (02:13) vapour and wave. This shape how do you get this curve, that is basically coming from the Clausius Clapeyron equation okay. So we will so that is the program. Now Sadi Carnot devised a hypothetical cycle which was never tested. It is an hypothetical cycle consisting of 2 reversible adiabats and 2 reversible isothermal process. A reversible process is one which is very slow.

That means when you take it from A to B it is possible for you to bring it back from B to A without any change in the system or in the surroundings. If it is an irreversible process you can bring it back from B to A but there will be change in the surroundings okay. If there is no change in the system and surroundings then it is a reversible and adiabatic process. If a balloon is filled with air and you prick it then it is a irreversible process.

It is not so easy to get the air back from the balloon. It is possible to do it but with work. But for pricking if you assume that the energy the work done in pricking is 0 then there is no work done in this. But to bring to fill the balloon back is a big job for you. So that is a so any sudden process an irreversible process. So the reversible processes are also called quasistatic processes, a succession of equilibrium states and the process proceeds very slowly.

This is the cornerstone of thermodynamics. We start with a quasistatic process. Since all of you have taken ME 1100 in the first semester, is there anybody who has not taken that, everybody has taken. So I think all this you know. Now, the second law.

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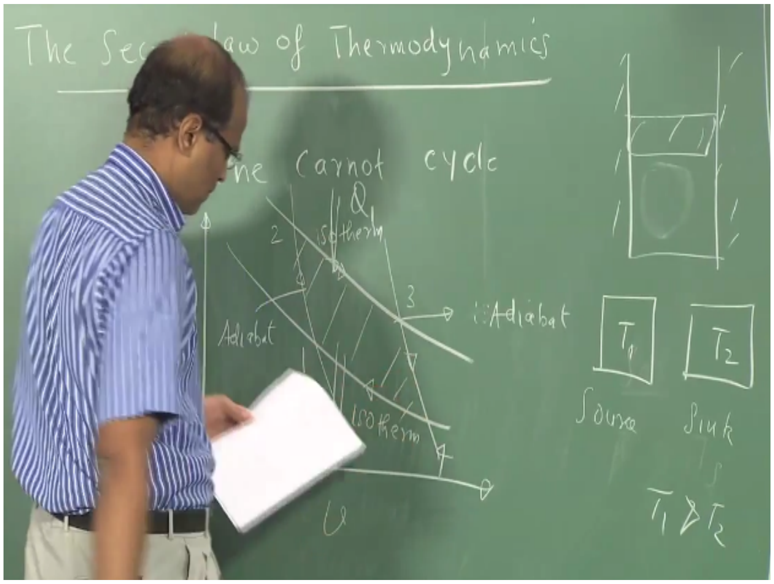

Consider a cycle consisting of 4 processes 1, 2, 3 and 4; 2, 3 is an isotherm; 4, 1 is an isotherm; 1, 2 is an adiabat that means no heat transfer, isotherm is a constant temperature process, this is an adiabat. So there is a isothermal heat addition of Q 1 into the cycle in the process 2, 3 and there is a isothermal heat rejection of Q 2 okay. I am not going into how do you do this. Actually there is a piston and cylinder. There is a medium here. It is insulated everywhere.

Bottom is allowed to exchange heat. There are 2 reservoirs T 1 and T 2. This is the source okay. So you can make this go from one position from here to some other position so it is compressed. Then you make into contact with T 1. Then there will be heat addition. It will be heated up. Then because of this it will again expand. It will do the work. It will go back to some position 3. Then it will come back and the cycle gets repeated and so on alright. So this is basically the cycle.

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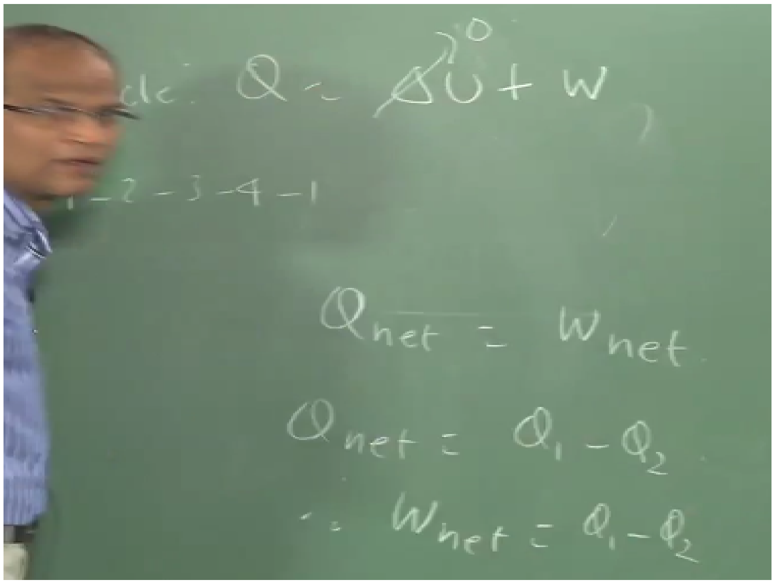

Now you know that the cycle is basically 1, 2, 3, 4, 1. So from 1 you start and you get back to 1. So if you start from 1 and get back to 1 what is delta u, very good. So for the cycle Q net equal to W net. What is the Q net in this process, in the cycle? So in a 1000 megawatt power plant okay let us say in a 500 megawatt power plant if 1000 megawatts is input or 1200 megawatts is input to the plant and 500 megawatts is produced how many megawatts are rejected to the surrounding, 700 megawatt.

So if you actually improve the efficiency of a power plant the amount of heat which is rejected will reduce and therefore the global warming will decrease okay. So apart from increasing the plant efficiency how mechanical engineers can contribute to reduce global warming is to improve the efficiency of the power plants. Not only we will have more realization, more bang for buck, what do they say, more bang for the buck that is for 1 kg or 1 ton of coal you can get more power. Also, it will be environmentally less polluting alright. Now what is this Q net anyway?

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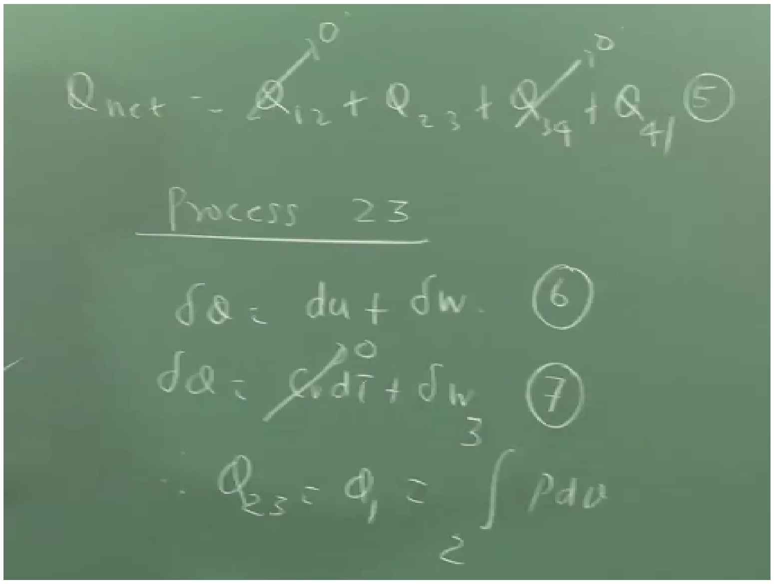

$$Q_{net} = \cancel{Q_{12}}^{0} + Q_{23} + \cancel{Q_{34}}^{0} + Q_{41} \quad ⑤$$

Process 23

$$\delta Q = du + \delta w \quad ⑥$$

$$\delta Q = \cancel{C_v dT}^{0} + \delta w \quad ⑦$$

$$\therefore Q_{23} = Q_1 = \int_2^3 P\,dv$$

Is that okay. Now which are the two zeros. An adiabatic process is no heat transfer. Very good. Now consider process 23. What is the C v d T of process 23? What process is it? What is C v d T of that. Very good. I think you should start doing this. If you want you write your own notes why it is 0 okay. So therefore Q 1 that Q 2 3 actually we are calling it as Q 1 that is heat added to the cycle. Is it okay with you?

Okay that I am putting small v, everything can be 1 kilogram or something that you adjust that is not central to our discussion here. People who want to be clinically correct and use P v V m whatever you are free to do that. That would not affect our logic alight.

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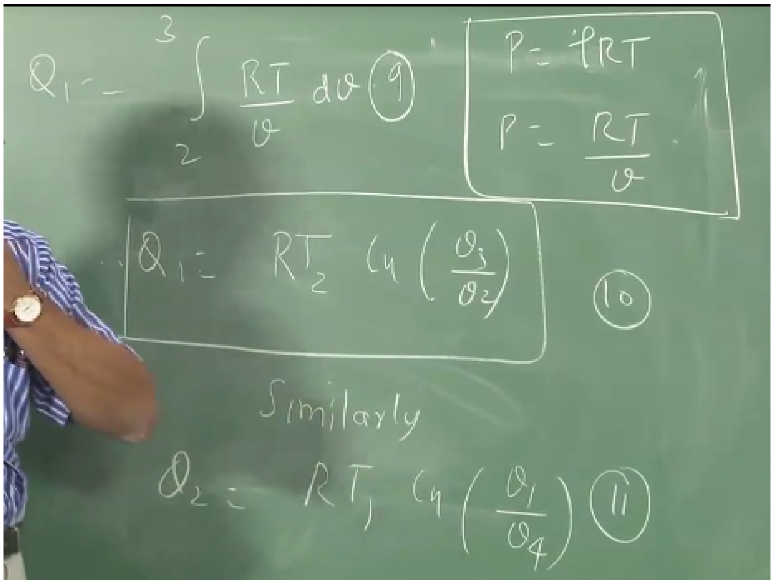

$$Q_1 = \int_2^3 \frac{RT}{v}\,dv \quad ⑨$$

$$\boxed{\begin{aligned} P &= \rho RT \\ P &= \frac{RT}{v} \end{aligned}}$$

$$\boxed{Q_1 = RT_2 \ln\left(\frac{v_3}{v_2}\right)} \quad ⑩$$

Similarly

$$Q_2 = RT_1 \ln\left(\frac{v_1}{v_4}\right) \quad ⑪$$

For an ideal gas what is P? Correct. Are you doing fine? R T, ln v 1 by v 4 or that minus plus you have to adjust then keep it. Now what I am trying to do is, I want to prove that Q 2 by Q 1 is T 1 by T 2 or something. I want to prove, then I will get the Carnot, there is no problem. But to do that it is an elaborate process.

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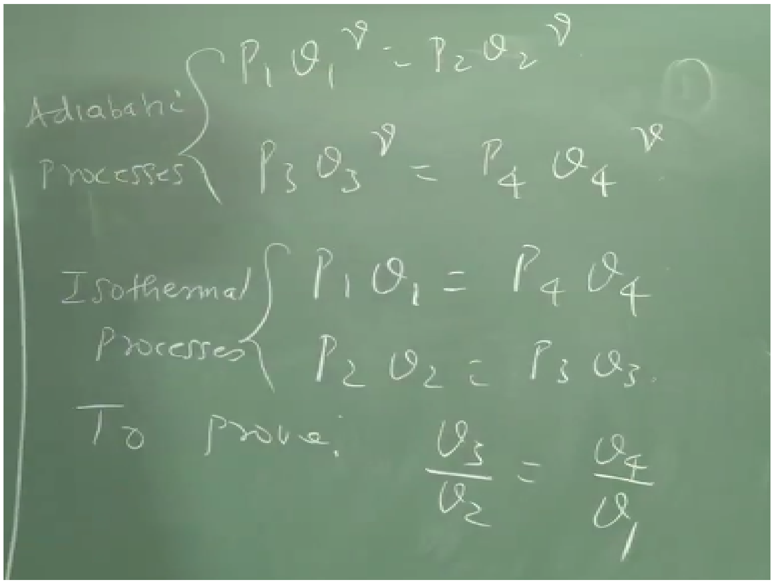

Adiabatic Processes

$$P_1 v_1^\gamma = P_2 v_2^\gamma$$

$$P_3 v_3^\gamma = P_4 v_4^\gamma$$

Isothermal Processes

$$P_1 v_1 = P_4 v_4$$

$$P_2 v_2 = P_3 v_3.$$

To prove: $\frac{v_3}{v_2} = \frac{v_4}{v_1}$

Is V 3 greater than V 2? Ya. V 1 is less than V4. So some minus will come. So we can make it into V4 by V 1 whatever you want. That we will. Now the whole idea is basically I want to prove, can you do that? P 1 V 1 is P 2 V 2 is it? That is a adiabatic process, correct and P 3 V 3 to the power of gamma that is correct right. Got it? Vishwajeet. You have done it before right.

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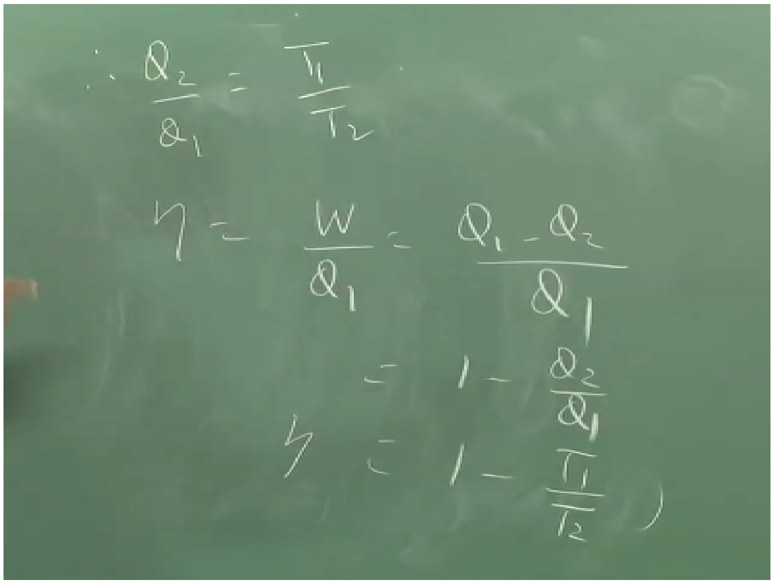

$$\therefore \frac{Q_2}{Q_1} = \frac{T_1}{T_2}$$

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1}$$

$$= 1 - \frac{Q_2}{Q_1}$$

$$\eta = 1 - \frac{T_1}{T_2}$$

Therefore, I am proceeding. Which is the higher temperature T 1 or T 2? Is this correct? Q 1 is more than okay. Efficiency is normally 1 is considered to be the higher temperature okay. Fine Normally, we will do it as T 2 - T 1 because we have taken the. So this is the Carnot efficiency okay. Now it is time to define a new quantity called you take it as homework. I think you are getting it right. How many of it got it already? Very good okay. I am sorry I did not give enough time but it is okay we have to move on.

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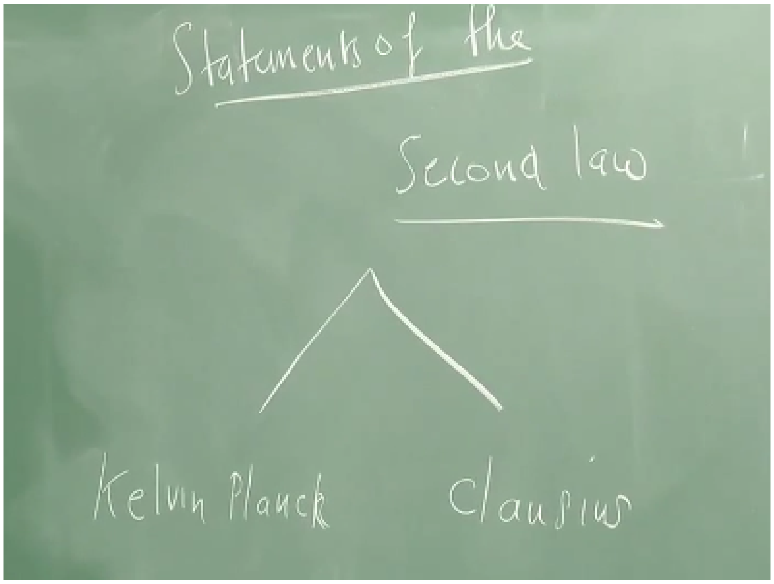

Now you have to define, there are 2 statements the Kelvin Planck and the Clausius statement. Just take down the statements. The Kelvin Planck statement of the second law, KP statement. It is impossible to construct a device which when operating in a cycle, it is impossible to construct a device which when operating in a cycle produces work by having heat interaction, produces work by having heat interaction with a single reservoir.

It is impossible to construct a device which when operating in a cycle produces work by having heat interaction with a single reservoir at a fixed temperature okay. Clausius statement, it is impossible to construct a device, you just put it as impossible dash device which when operating in a cycle all that no sorry. It is impossible to construct a device which when operating in a cycle has followed by as which has as its sole effect the transfer of heat which has as its sole effect the transfer of heat from a reservoir at low temperature to a reservoir at high temperature.

Which has as its sole effect the transfer of heat from a reservoir at low temperature to a reservoir at high temperature. That means heat by itself will flow from high temperature to low temperature. From a reservoir at low temperature to a reservoir at high temperature. The law does not forbid you from doing this which has as its sole effect. If you supply work it can be done. It is happening right now. Outside is hotter, we are cooler.

But you are continuously removing heat from a colder place and putting it to hotter place why we have a device called the air conditioner. If we stop the air conditioner quickly that heat will come, in 1 or 2 hours we will reach, in a couple of hours we will reach the temperature of the outside okay. Now, life is not always about cycles. Many people do not have a cycle. In thermodynamics also we can have processes without a cycle.

So what is the story of those process without a cycle. No I am saying something serious. So if the first law of thermodynamics is extended to a noncyclic process you got the property energy because heat is equal to work. The algebraic sum of heat is equal to algebraic sum of work only for a cycle. What about those fellows who do not have a cycle. I mean for those processes which are noncyclic. Noncyclic we have del Q = del u + del w okay.

So if we introduce a noncyclic process we got energy or internal energy much in the same way as we got internal energy or energy if we extended the first law of thermodynamics to a noncyclic process we got a new property which is e in its special in special avatar it is the internal energy which can be written as C v into d t so which gives you a framework to solve many problems with just temperature okay.

Because the u it is possible for you to make it as C v d T for d u equal to. So if the second law or thermodynamics forget about Kelvin Planck and Clausius who are always concentrating on cycle if somebody does not have cycle if there is no cyclic process if you extend it to a noncyclic processes a new property call entropy emerges. So the entropy is a consequence of the extension of the second law of thermodynamics to noncyclic processes. Entropy much like energy is a property of the system. So it is a point function, it is not a path function okay and the okay we will do the okay.

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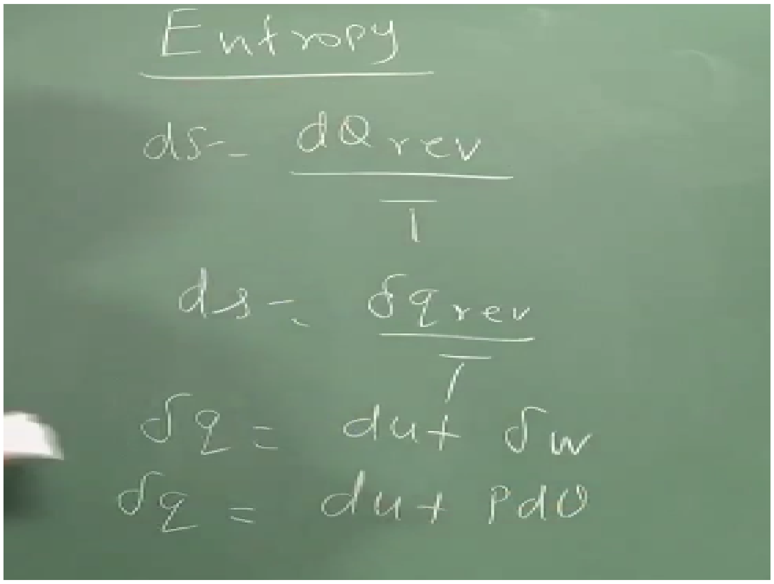

Entropy

$$ds = \frac{dQ_{rev}}{T}$$

$$ds = \frac{\delta q_{rev}}{T}$$

$$\delta q = du + \delta w$$

$$\delta q = du + P\,d\vartheta$$

So d s. So the heat transfer in a reversible process that is why I put d q reversible. What is a small d q. That means per unit mass. So the entropy per unit mass is d small s okay. Now please note that religiously I am putting del and del for q and w and d for this. This is a property, these 2 are not properties. IIT students you should not make d q = d u + d w you should not do that right. It is a fatal mistake; d q = d u + Pd v okay; d s okay.

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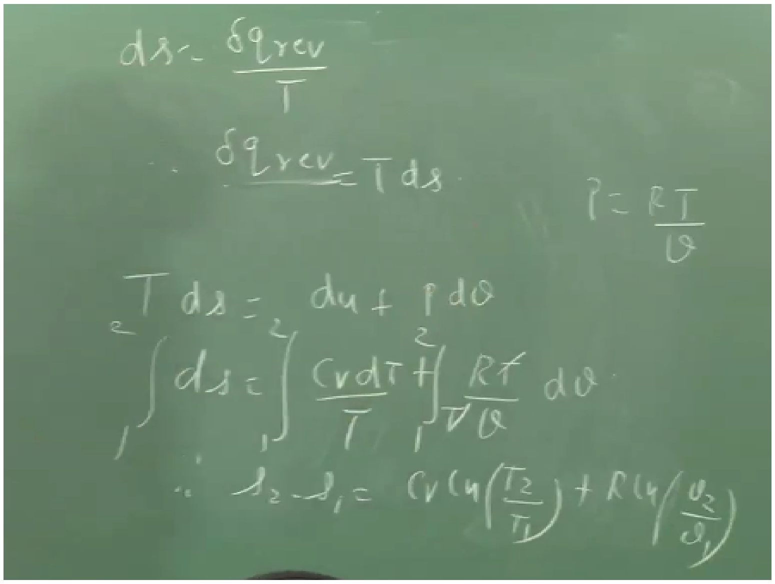

$$ds = \frac{\delta q_{rev}}{T}$$

$$\therefore \delta q_{rev} = T\,ds$$

$$P = \frac{RT}{\vartheta}$$

$$T\,ds = du + p\,d\vartheta$$

$$\int_1^2 ds = \int_1^2 \frac{C_v dT}{T} + \int_1^2 \frac{RT}{T\vartheta}\,d\vartheta$$

$$\therefore s_2 - s_1 = C_v \ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{\vartheta_2}{\vartheta_1}\right)$$

You studied all this correct; s 2 - s 1 is C v so if you give me the 2 temperatures and you either give me the pressure of volume I can always play with P equal to rho or P v equal to R T and I can manage. I can calculate the entropy change. It is it can be calculated only for a reversible process but since it is a property for an irreversible process also it is okay. s1 and s 2 but generally it will be more than what is taken through a reversible process.

Let us not get into all that. Now the goal of introducing all this for a atmospheric science course is we are going to look at entropy of steam, entropy of water and what happens in a boiler, what happens in a turbine and so on. But we want to be quickly able to link it to what happens in atmospheric science.

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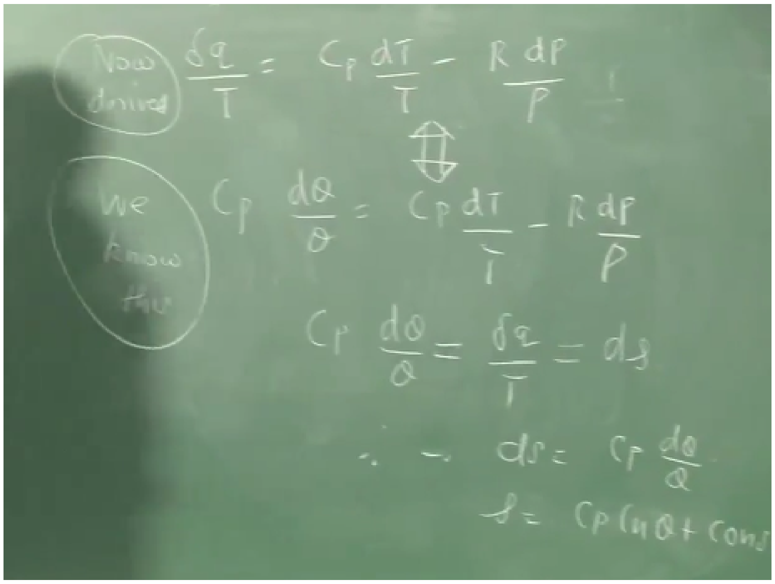

Now derived

$$\frac{\delta q}{T} = C_p \frac{dT}{T} - R \frac{dP}{P}$$

$$\Updownarrow$$

We know this

$$C_p \frac{d\theta}{\theta} = C_p \frac{dT}{T} - R \frac{dP}{P}$$

$$C_p \frac{d\theta}{\theta} = \frac{\delta q}{T} = ds$$

$$\therefore \; ds = C_p \frac{d\theta}{\theta}$$

$$s = C_p \ln \theta + \text{cons}$$

So del q by T is we can also write it as C p please do not ask me how u = h - P v, d h - P d, P d P will get cancelled v d P all that you know that okay. Let us quickly go through this. But we know that C p we derived it right. This one we derived in an earlier class when we got the potential temperature. Look at this. This is now derived. This we know. RHS is the same. Therefore, the fun is not that. The fun is let me check whether you are following the lecture.

The fun is C P d theta by theta equal to d q by T which is also equal to. Therefore whatever right. Is it correct. Or I will simply make it like this. So in an adiabatic process which usually takes place in the atmosphere if the potential temperature is conserved it goes without saying that the entropy remains constant. Therefore the potential temperature which is remaining constant a reversible adiabatic process with which you are taking the air parcel all the way up and all that.

So when the air parcel undergoes this and this process and goes up all the way up to its LCL following a dry adiabat it is also following an isentropic. So the potential temperature is used as a surrogate for an isentropic process. Surrogate is a proxy or a replacement for. So the isentropic process and the constant potential temperature, the dry adiabat are one and the same in atmospheric science.

So that brings us the link, the second law of thermodynamics why we should study second law of thermodynamics in relation to atmospheric science okay. So the moral of the story is a not very good example is CGPA is a surrogate for learning. You may not agree with me that is a belief right. That is a common belief. CGPA or percentage is the surrogate for how much learning you have taken, it is questionable. I am not opening up a Pandora's box.

Like that the instead of entropy please use theta okay. Because there is something called anyway I get into philosophy so I was just reading a new book, The Art of Thinking Clearly, okay where he proposes various syndromes and this thing. He calls it as in science the fallacy of a single cause. There is something called the fallacy of a single cause which is called the causal oversimplification.

If an effect is produces by produced by several causes quickly we will try to identify one cause. What is the cause for the Uttarakhand rain. There may be many causes and we quickly put the blame okay. So in a and actually if we go deeper there are 2 sets of causes. There can be a proximal cause, there can be a distal cause. And the proximal cause seems to say please choose me I mean you want to almost you want to fall into the trap and choose that.

There are lot of distal variables. So this is called I mean you reduce everything for everything there is only one effect. Then if you speak if you start talking like this then only you are an expert no for everything you have a theory I mean there is only one cause but there are cross correlation between the causes. Even the learning, CGP there are multiple reason, multiple causes are there okay. So this why did I say all this okay so there is some surrogate okay.

We have to be very careful. Anyway in this case it is very innocuous and harmless. So instead of entropy we will use the theta alright. So the Carnot cycle must be represented on a T-s diagram.

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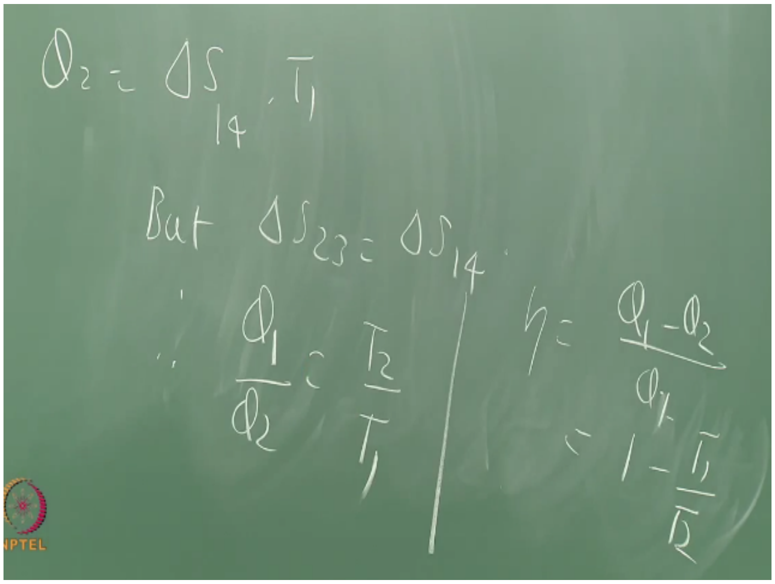

$$Q_2 = \Delta S_{14} \cdot T_1$$

$$\text{But } \Delta S_{23} = \Delta S_{14}$$

$$\therefore \frac{Q_1}{Q_2} = \frac{T_2}{T_1}$$

$$\eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{T_1}{T_2}$$

So we represent it on a T- s diagram. So correct. Q equal to T d s. Now when the temperature is integral T d s, T can be taken out because it is isothermal process. Yes. You must have studied this right. Okay. The Carnot cycle becomes a rectangle. The net area under a T-s diagram is a heat added but since it is a cyclic process it is the same as the work done. The net area under a P v diagram is work done.

Again in a cyclic process since heat added since it is a cycle del u equal to 0 the net work done is equal to the net heat added okay. Now the last part of the lecture basically is the Clausius Clapeyron equation which we will derive now. Physics people call it as the first latent heat equation. Thermodynamicist call it as a Clausius Clapeyron equation in honor of the 2 scientists.

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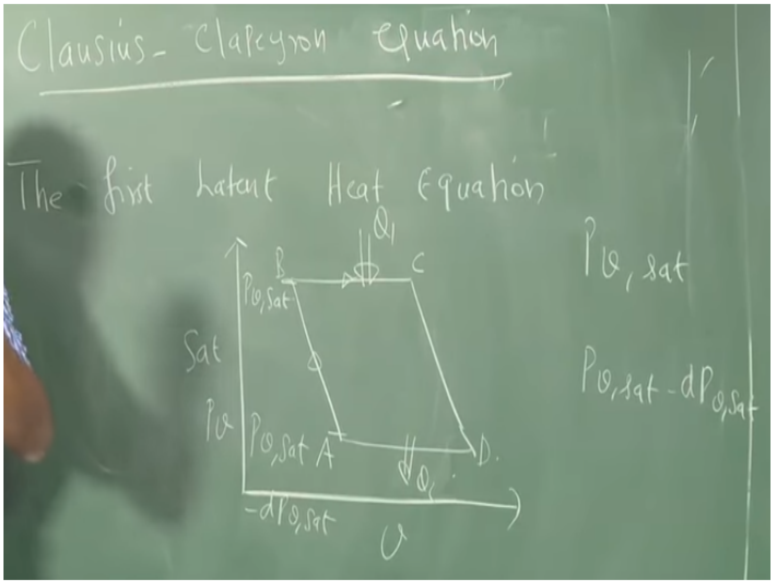

So again consider a, consider a Carnot cycle working between 2 small pressure differences right. Between 2 small pressure differences 2 small okay 2 pressure which have small difference okay. Now it will be like this. A why that this fellow became like this is there is a phase change which is taking place okay. This is Q 1. So here the pressure is P v, sat. Here the pressure is P v, sat - d P v, sat.

So it is a Carnot cycle operating between infinitesimal pressure difference and at this P v saturation what happens is at 100 degree centigrade for example one atmosphere water will change phase correct. So if this is T. This is T - d T. The pressure and temperature are one and the same within the saturation you know that right. Okay. Now we will a Carnot cycle is operating between these 2 pressures okay.

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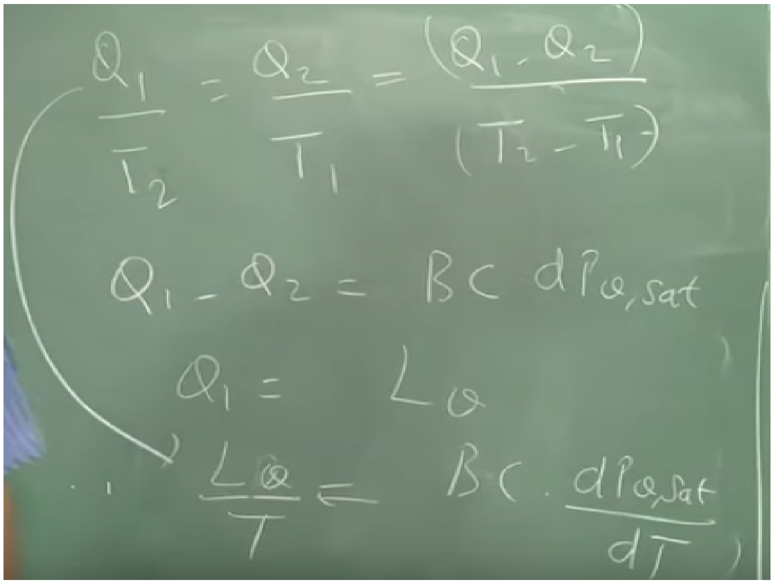

$$\frac{Q_1}{T_2} = \frac{Q_2}{T_1} = \frac{(Q_1 - Q_2)}{(T_2 - T_1)}$$

$$Q_1 - Q_2 = BC\, dP_{v,sat}$$

$$Q_1 = L_v$$

$$\therefore \frac{L_v}{T} = BC \cdot \frac{dP_{v,sat}}{dT}$$

So we know that Q 1 by T 1 equal to Q 2 by T 2. That we already seen right. Q 2 by Q 1 is no what did I write now. Now we again change it to T 1 and T 2 okay for the sake of continuity or I will, we will mess it up? What do you want to do tell me? Q 1 by T 2 equal to, it is okay. You want like this. So this is in line with what you have discussed. It is awkward but it is okay. So give anyway if you say this is fine. Now this is also equal to agreed?

If half is equal to 3 by 4 then 3 - 1 by 4 - 2 is also equal to half. That is called the dividendo componendo rule or the componendo dividendo rule. Some 3, does it ring a bell. Okay alright. So Q 1 by T 2 that is I do not like it man Q 1 by but anyway, it should be Q 1 by T 1, okay it does not matter. There is no logical error right. It is fine. So Q 1 by T 2 = Q 1 - Q 2 by this thing. So what is Q 1 - Q 2, area of the parallelogram, work done but evaluate it.

Line segment BC into d P v, sat correct? Alright. What is Q 1? Please tell me now. A saturated moist process water is changing into water vapour or water vapour is changing into water Q will be equal to latent heat into 1 kg L v. Okay. Therefore, L v by T = BC. Can I call T 2 - T 1 as d T? Of course, yes. Yes. Minus plus if there is a problem you have to take care alright. I am out of it. What is BC? From the figure. V 2 - V 1. Change in volume okay.

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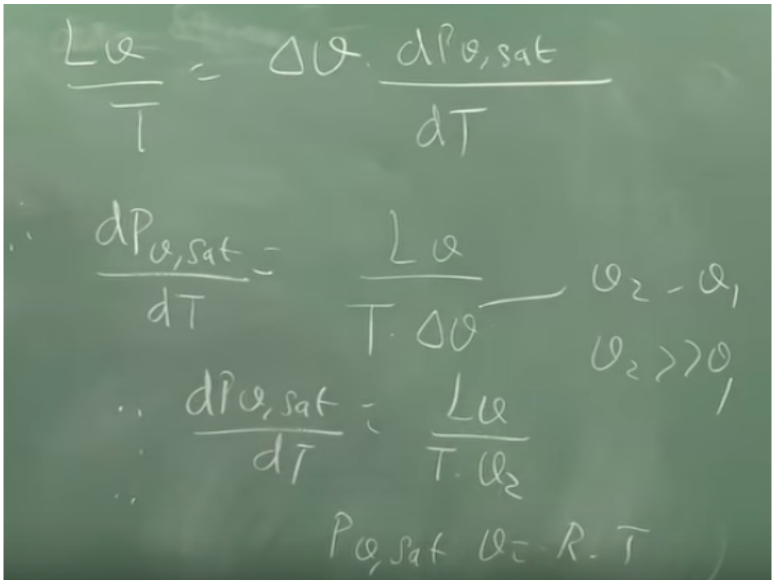

$$\frac{L_v}{T} = \Delta v \cdot \frac{dP_{v,sat}}{dT}$$

$$\therefore \frac{dP_{v,sat}}{dT} = \frac{L_v}{T \cdot \Delta v} \quad v_2 - v_1$$

$$v_2 >> v_1$$

$$\therefore \frac{dP_{v,sat}}{dT} = \frac{L_v}{T \cdot v_2}$$

$$P_{v,sat}\, v_2 = R \cdot T$$

BC del v okay. So let me call this v 2 and let me call this v 1. v 2 is the volume of the vapour and v 1 is the volume of the liquid. So this del v the specific volume v 2 is much greater than v 1 right? Liquid is changing to vapour. Specific volume is much larger correct. Therefore. But now when it has become vapour it follows the ideal gas correct. So correct. Now the water has become vapour.

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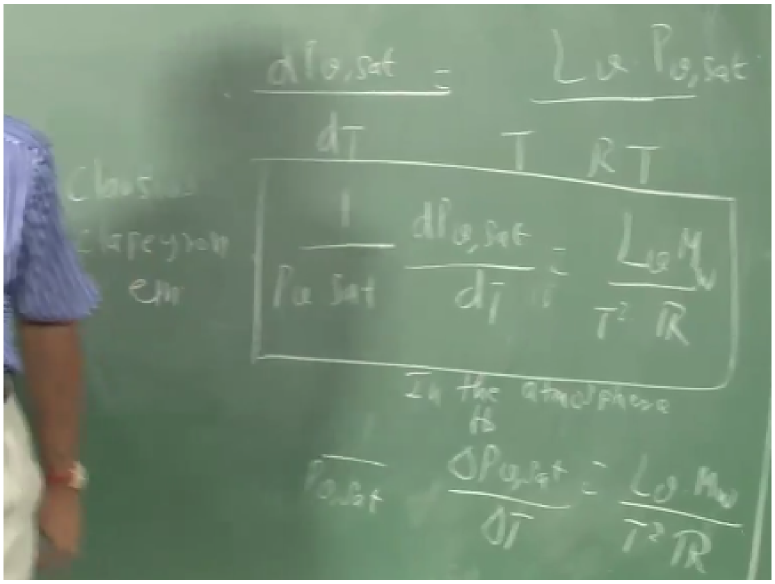

$$\frac{dP_{v,sat}}{dT} = \frac{L_v \cdot P_{v,sat}}{T \quad RT}$$

Clausius Clapeyron eqn

$$\boxed{\frac{1}{P_{v,sat}} \frac{dP_{v,sat}}{dT} = \frac{L_v M_w}{T^2 \bar{R}}}$$

In the atmosphere is

$$\frac{1}{P_{v,sat}} \frac{\Delta P_{v,sat}}{\Delta T} = \frac{L_v \cdot M_w}{T^2 \bar{R}}$$

Please correct me if I am making any mistake. Am I right? The R for the water vapour universal gas constant divided by the molecular weight of water vapour. So what I have indicated in that box is basically the Clausius Clapeyron equation. In the atmosphere this fellow can be simplified. In simple English if you give me the temperature and if you give me the latent heat at that temperature I can tell you how from a particular P v how the del P v will change.

From one saturated vapour pressure how the saturated vapour pressure will change with temperature. Okay if water boils at 100 degree centigrade for 1 bar at 1.2 bar what will be the temperature. You can get from the Clausius Clapeyron equation. Or for 110 degree centigrade what should be the pressure, either way okay. So the Clausius Clapeyron equation is very because latent heat process are all the time involved in the atmosphere this is widely used in atmospheric science calculation.

But in our course, it is the first course so I may ask you a simple question. Give me one vapour pressure and this thing and give one temperature and ask you to calculate what will be the vapour pressure for a different temperature or something or for the given temperature if the temperature is slightly changed what will be the vice versa. Is that okay. So we will stop now. Finally this brings us to the end of atmospheric thermodynamics. We are done with atmospheric thermodynamics. We will get on to RT that is radiative transfer.