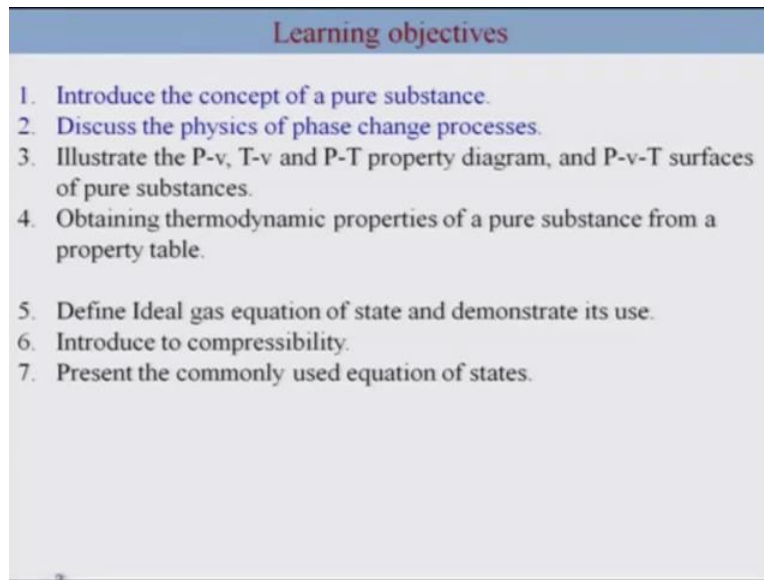


**Engineering Thermodynamics**  
**Professor Jayant K Singh**  
**Department of Chemical Engineering**  
**Indian Institute of Technology Kanpur**  
**Lecture 09**  
**Phase change of a pure substance**

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**Learning objectives**

1. Introduce the concept of a pure substance.
2. Discuss the physics of phase change processes.
3. Illustrate the P-v, T-v and P-T property diagram, and P-v-T surfaces of pure substances.
4. Obtaining thermodynamic properties of a pure substance from a property table.
5. Define Ideal gas equation of state and demonstrate its use.
6. Introduce to compressibility.
7. Present the commonly used equation of states.

So, welcome to the third chapter or the module of this course properties and this module we are going to cover the concept of pure substance and basic phased diagram, physics of phase change processes and in general how to obtained thermodynamic properties from there different tables which are usually given in the text box. So, we are going to make use of thermodynamic property tables to solve problems.

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**Pure substance**

- **Pure substance:** A substance that has a fixed chemical composition throughout.
- Air is a mixture of several gases, but it is considered to be a pure substance.

Nitrogen and gaseous air are pure substances.

(a)  $H_2O$

(b) AIR

A mixture of liquid and gaseous water is a pure substance, but a mixture of liquid and gaseous air is not.

3

So, later we are going to define ideal gas equation of state equation based property valuation and hopefully that will give a lot of understanding to thermodynamic systems. So, let us first start with a what is a pure substance. Pure substance is a substance that has a fixed composition. So, you can consider air which is composed of oxygen and nitrogen mainly and still it is a uniform in composition and hence it would be considered as a pure substance. Water can form in a liquid and vapor and as well as solid, but considering water in the form of let say liquid vapor form together can be considered as a pure system because composition is not changing.

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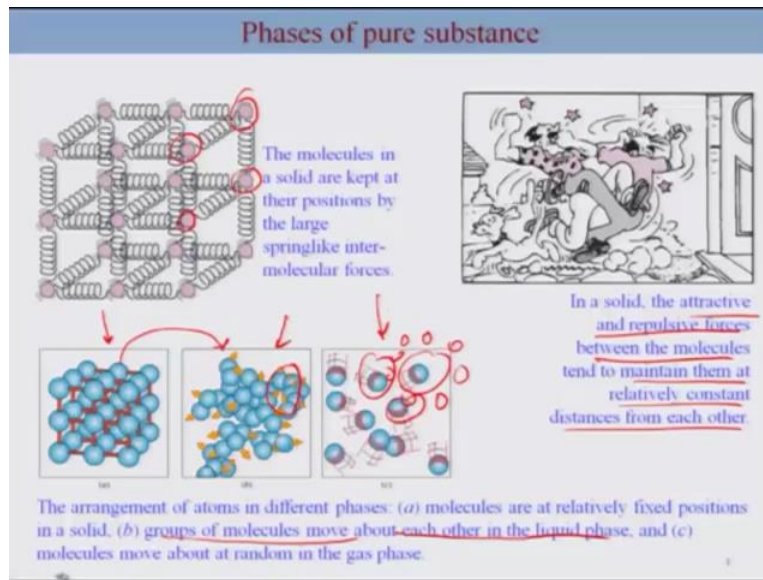
A mixture of liquid and gaseous water is a pure substance, but a mixture of liquid and gaseous air is not.

3

So, liquid composition is still the water only one space and as well as the vapor. So, this is an example here again, so nitrogen and the gaseous air are pure substances. Water, again as I was mentioning even though there are two phases vapor and liquid still considered to be pure phase, because it has uniform composition. On the other hand, if you considered air in liquid and vapor. They are not pure substance, because the vapor composition would be different from liquid composition, because of the different spaces involved in air.

So, thus this system is not a pure system. On the other hand a new formed the composition of air gas would be a pure system.

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Now a pure substance can be seen in different phases and what we call phase is what we observe let say in water, ice in a liquid water and as well as view water vapor. Now this is mainly because the substances are composed of atoms or molecules and they have relative different arrangements and different states.

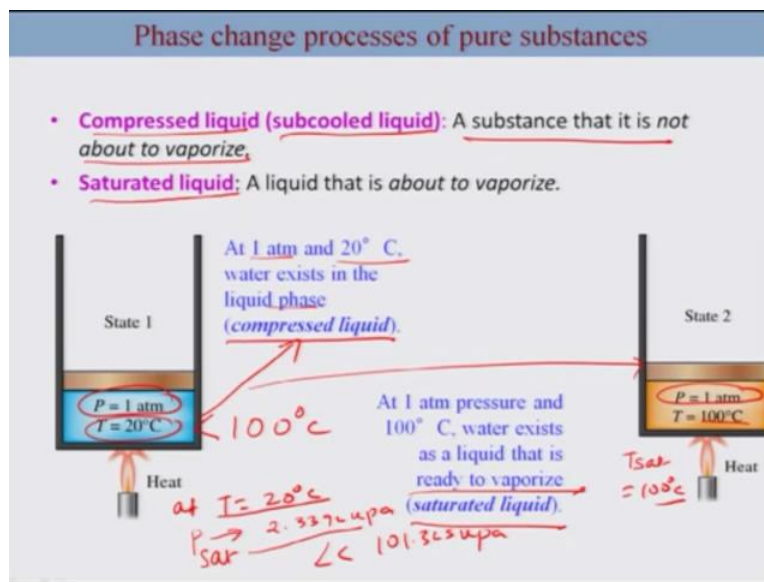
So, further case of solid they are placed the molecules are placed in a lattice and they oscillate at the lattice position. So, this is a let us lattice position they oscillate around this position and they are composed in such a fashion that all attractive and repulsive forces maintain, then are the relative constants distance from each other. So, this all perfectly balanced and they are at the lattice point but they oscillate around this lattice point but a heat up a little bit and they can change their forms.

So, for example they can change from a very ordered structure to something which is not so ordered like liquid, here the molecules intent to have more kinetic energy because it can now translate. It is not oscillating, it is around is this point it is own lattice point but is translating in the medium.

Beside that the each molecules do have some surrounding the atoms or molecule as it together and it has a certain structure. Solid has structure, liquid has structures but as you further the increase there temperature and make it a gaseous form they apparently move quite random okay.

There is no specific atom of molecule around each of them together. On the other hand there is a group of molecules in the liquid phase which move each other in the liquid phase. So, there is a specific structure here, there is a specific structure here, the structure get lost once it goes to the gas phase and because of the low density, they do not see too much each other and there is no weight can come together and form a local ordering such that they can form a group and moved together. So, it it has has a very low structure or structure less the gas. So, these are the different forms of the phases.

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Now I will take a example of how does the phase change during the process. You can heat up water and convert to a liquid. So, let us get little bit more technical about it, so let us considered a water at 1 atmosphere and 20 degree Celsius. Now in such case the water exist in the liquid phase. So, at room temperature in which you will see water as a liquid phase, it will not immediately vaporize. You need to heat it up at 1 atmosphere, you need to heat it up such that it goes to 100 degree okay and the here the state of the liquid is that it is ready to vaporized.

Now this particular state would be cause saturated liquid the reason being that, now this liquid is at equilibrium if it is own vapor it about to vaporize. So, the word saturation would be used for such a state or such a condition okay. So, it is something like liquid is saturated with his own vapor but this occurs at a specific condition for the case of 1atmosphere it occurs a 100 degree Celsius, for if you change the pressure the temperature would be change.

So, if this particular state where you considered the 1 atmosphere and 20 degree Celsius is sometimes also called compressed liquid. This is a liquid which is not going to vaporize okay at this condition. They are called compressed liquid, because at  $T$  equal to 20 degree Celsius. If you want to vaporize you need to reduce the pressure and this pressure which you want to reduce 2.3392 kilopascals. So, if you want to keep the temperature fixed and you still if you want to vaporize it then you need to reduce the pressure.

Pressure to such a conditions and at this point it will vaporize. So, this pressure at 1 atmosphere is much higher than this pressure. This is much higher than 101.325 kilopascals which is our 1 atmospheric condition, which essentially means this particular liquid is compressed, because you have increased the pressure at 20 degree Celsius. So, that is why it is also come compressed liquid.

So, essentially at 20 degree Celsius this  $P$  sat saturation pressure, at  $P$  equal to 1 atmosphere the saturation temperature is  $T$  sat is 100 degrees Celsius. This is also sometimes called sub cooled liquid, because the temperature to vaporized for 1atmosphere is 100 degree Celsius. So, this  $T$ , 20 degree Celsius is lower than 100 degrees Celsius is lower temperature than the saturation temperature and thus this is sub cooled a liquid.

So, let me again summarizes the compressed liquid is a substance that is not about to vaporize saturated liquid would be a liquid that is about to vaporize.

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**Phase change processes of pure substances**

- **Saturated vapor:** A vapor that is *about to condense*.
- **Saturated liquid-vapor mixture:** The state at which the liquid and vapor phases coexist in equilibrium.
- **Superheated vapor:** A vapor that is *not about to condense* (i.e., not a saturated vapor).

State 3:  $P = 1 \text{ atm}$ ,  $T = 100^\circ\text{C}$ . Saturated liquid and Saturated vapor coexist. As more heat is transferred, part of the saturated liquid vaporizes (saturated liquid-vapor mixture).

State 4:  $P = 1 \text{ atm}$ ,  $T = 100^\circ\text{C}$ . Saturated vapor. At 1 atm pressure, the temperature remains constant at  $100^\circ\text{C}$  until the last drop of liquid is vaporized (saturated vapor).

State 5:  $P = 1 \text{ atm}$ ,  $T = 300^\circ\text{C}$ . Superheated vapor. As more heat is transferred, the temperature of the vapor starts to rise (superheated vapor).

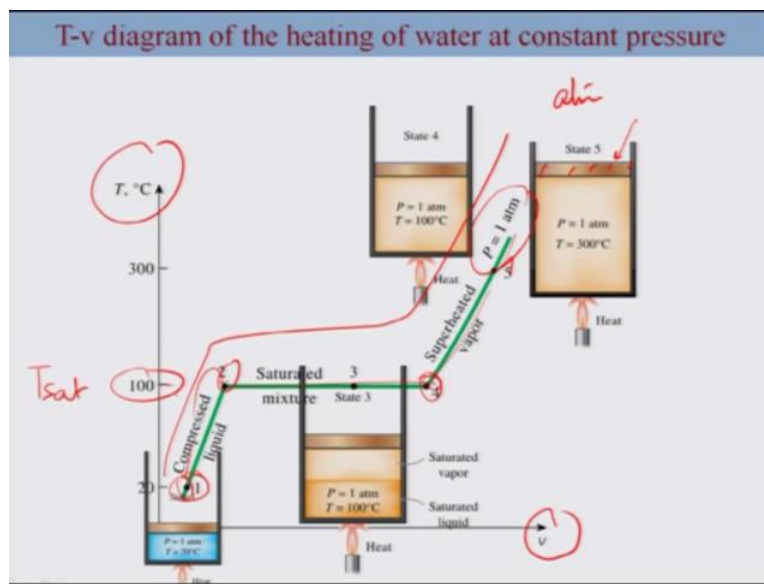
Okay what about the saturated vapor, a vapor that is about to condensed. So, instead of taking liquid if you have taking vapor and you change the variable temperature and pressure such that is about to condense, then it would be saturated vapor. So, will talk about this more illustratively, so now what was the state 1 was compressed liquid, state 2 was that liquid was ready to vaporized okay.

Now I am further heating up, now what happens that the certain amount certain molecules of the liquid is transferred to the vapor state. So, the liquid volume is also changing, this is a liquid volume, this is the vapor. So, the liquid volume is changing at this condition says this is one atmosphere. This is at equilibrium with this, this phase is at equilibrium with this phase, that is why it is called the saturated system, is saturated with a liquid and as well as vapor.

So, liquid and vapor are at equilibrium. So, this is a state 3, you further increase when all the liquid is converted to vapor completely. But at this point if you slightly reduce the change the variables then, then it can also convert that to liquid. So, this is the condition the temperature remains still constant. So, remember that temperature is constant heat here is being used to change the liquid to the vapor, once the complete vapor is formed then further the temperature will rise.

So, now you further heat it up you get a state which much higher temperature, which is 300 degree Celsius. So, as more heat is the transferred the temperature of the vapor starts rising. In this condition you have superheated vapor. So, you have a 3 states which we talked about, one is a saturated vapor a vapor that is about to condensed which is state 4. Saturated liquid vapor mixture the state at which liquid and vapor coexists which is of course this is state 3 and the superheated a vapor that is not about to condensed. So, superheated vapor is a vapor that is not about to condensed which is state 5.

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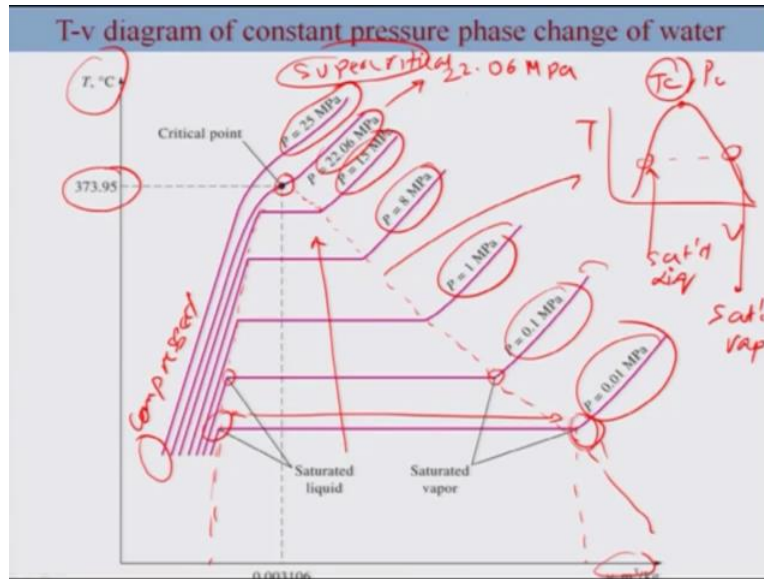
So, we can plot this in a temperature specific volume diagram and so let us go back again state 1 state 1 was compressed liquid. It was 20 degree Celsius at 1 atmosphere we keeping the pressure fixed. Now pressure is based on this weight here piston. So, the weight is fixed, so pressure is fixed, so you heat it up so you get from 1 to saturated liquid 2.

And then saturated liquid to saturated vapor here and the intermediate point are all saturated mixtures of different composition of liquid and vapor. And then after it reaches this saturated vapor the temperature goes up, okay. And the superheated vapor is achieved. Now you remember this flat region this flat region is where your temperature is fixed which is 100 degree Celsius.



So, this temperature is your  $T_{sat}$  is called saturated temperature corresponding to pressure  $P$  as of 1 atmosphere. So, if you change the pressure you are going to get different saturation temperature. So, if you increase the pressure you may get different one and this is something which we are going to talk or describe little more. So, this is how it is, so again going back to the values of the water.

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So, this is temperature or again this is a specific volume and earlier we talk about 1 atmosphere very closed to 0.1 mega Pascal. This was we were heating from compress liquid case to saturated liquid to then further to saturated vapor and then superheated vapor. Now if you change their pressure, so for example if you change the pressure to lower value such as this case  $P$  equal to 0.01 mega Pascal what you see you see that there is a positional change of saturated liquid and vapor.

So, saturated liquid is shifted to the left, saturated vapor is shifted to the right, the volume is shifted. So, you see the vapor volume is more the liquid is less right or in other word this deference is more at a lower pressure. And then this difference between this two pint is decreasing as you increased the pressure. And at certain point this two points coincide, the two points are the saturated liquid and saturated vapor and this particular point you cannot distinguish saturated vapor and a liquid.

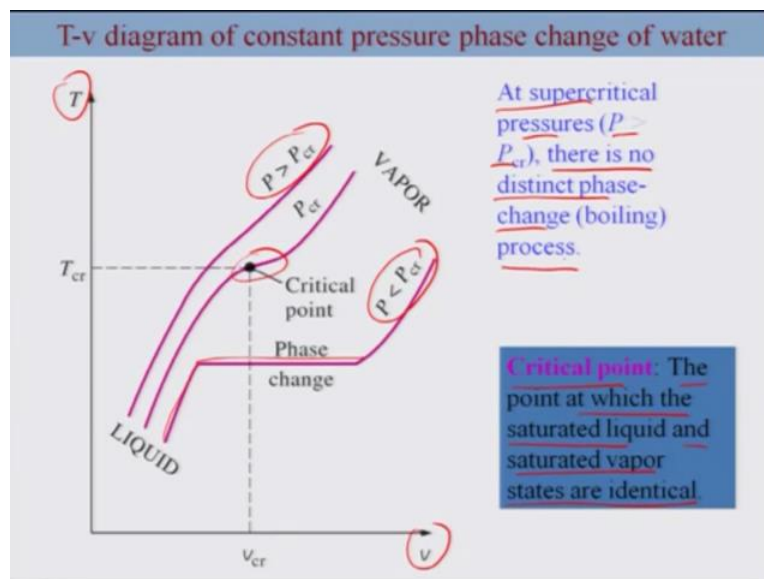
So, this is the point which we call it critical point, where there is no phase supuration, phases cannot be supparated, it is all homogeneous okay. So, this critical point is associated with all the systems, all the substances. So, for the case of water it is the critical point is 3739.95. And once you fixed this temperature the pressure is also fixed because it occurs at a specific point, here that pressure is 22.06 mega Pascal. You can connect this point like this and you can come up with a phase diagram.

So, this becomes the phase diagram, so in another word what you are doing is you are plotting this and you are generating this like kind of plot, where this each point corresponds to a specific saturated liquid and saturated vapor. So, this is your saturated liquid and this is your saturated vapor and this is your critical point so okay.

So, this has a specific critical point we are going to denote as  $T_c$  critical temperature and critical pressure okay. So, let us and what about the other state this one, for example the which here is a 25 mega Pascal where we do not do not see any phase change at all because this is a region of super critical point.

So, you are going from compressed this is a compressed liquid and this is a super critical region. This would be super, super critical region.

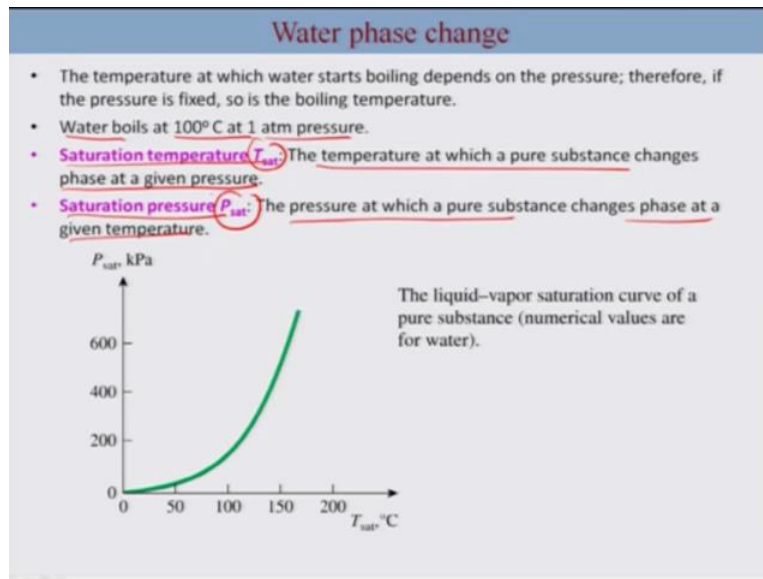
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So, this we can put it in the simpler form now, so you again this is a temperature and volume this is in general is not just a related to water now it is a general phenomenon that a liquid undergoes change. If the pressure is less than  $P$  critical and temperature is less than  $T$  critical and then at a certain point there is no further you cannot separate the phase that would be the critical point.

So, if  $P$  is greater than  $P$  critical, then there will be no phase change. There is a fraction point at  $T_c$  and  $P_c$ . So, the critical point is the point at which saturated liquid and saturated vapor states are identical, which means you cannot distinguish okay. So, at super critical pressure there is no distinct phase change process okay that means they cannot be a boiling at super critical process.

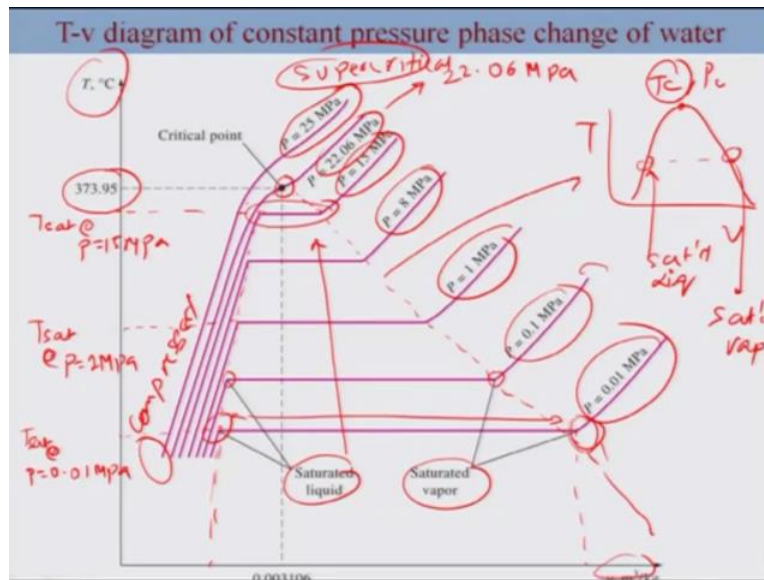
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Or such kind of phase change depends on pressure and temperature is already we can infer from the our discussion, for example your water boils at 100 degree Celsius at 1 atmosphere but water boils at a low temperature, when you go to mountain okay. So, why is that, so let us first look at it again thus what is the saturation temperature the temperature at which pure substance changes phase at a given pressure.

What is a saturation pressure, the pressure at which pure substance changes phase at a given temperature. So, can we find out this  $T_{\text{sat}}$  and  $P_{\text{sat}}$  for the case of water, let us go back.

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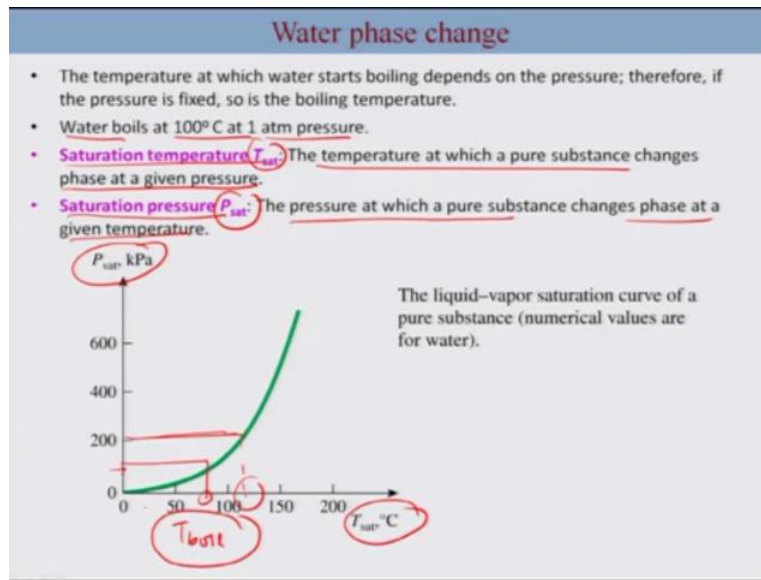


So, this line was a for  $P$  equal to point 0.01 mega Pascal, this was your  $T_{sat}$  at  $P$  equal to 0.01 mega Pascal. And similarly this would be your  $T_{sat}$  at  $P$  equal to 1 mega Pascal okay. And similarly it would be  $T_{sat}$  at  $P$  equal to 15 mega Pascal.

So, what we see we see that as you increase your pressure of the system, the saturation pressure increases. There is another thing which we should see this difference between this point the saturation liquid and the saturation vapor it is decreasing and we know that you need to provide energy to convert liquid to vapor. So, in the sense the vapor energy is larger than the liquid energy. So, difference between them is going to be latent heat of vaporization it is a change in the internal energy because latent heat is part of internal energy.

So, this is latent heat of vaporization latent heat of vaporization decreases as we increase the temperature and pressure you can clearly see because this differences are smaller okay.

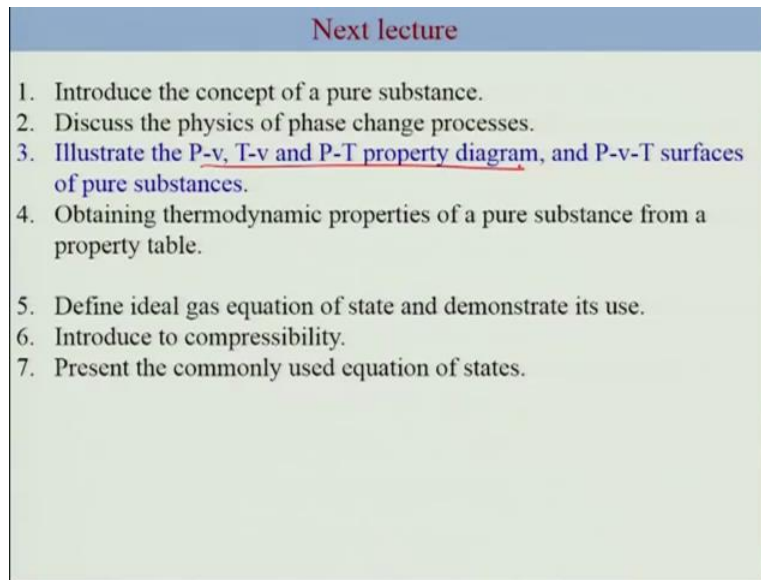
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So, based on this analysis you can clearly understand that the pressure as a function of  $T_{sat}$  should look like this and this is a region that if you reduced the pressure the temperature will be lower. So, if you reduced the pressure from 100 to somewhere here the corresponding pressure would be less, it will not be 100 degree Celsius for the case of water as in the case in the mountain.

So, as you say this if you fixed the pressure, this would be the temperature at which it will boil, you reduce the boiling temperature  $T_{boiling}$  temperature reduces okay. And that is a case what we see in the case, when you go to mountain and start heating up okay. That would be the end of this lecture, there we have introduced the concept of substances and discussed the phase change for pure substances. We have illustrated the  $P-v$  and  $T-v$  and some property diagram, we will continue with this discussion in the next lecture.

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Next lecture

1. Introduce the concept of a pure substance.
2. Discuss the physics of phase change processes.
3. Illustrate the P-v, T-v and P-T property diagram, and P-v-T surfaces of pure substances.
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Where we will discuss more that the property diagrams and particular we look into the P v T surface of pure substances. We will also introduce property tables and later on where we are going to use the tables to solve some relevant problems, later on in this particular module we will introduce equation of state and the commonly used equation of state. So, see you in the next lecture.