Thermodynamics of Fluid Phase Equilibria
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Lecture - 04
Review of the properties-part 1

Welcome back. So, we in this particular lecture, we are going to review properties of a pure fluid. So, we will start.

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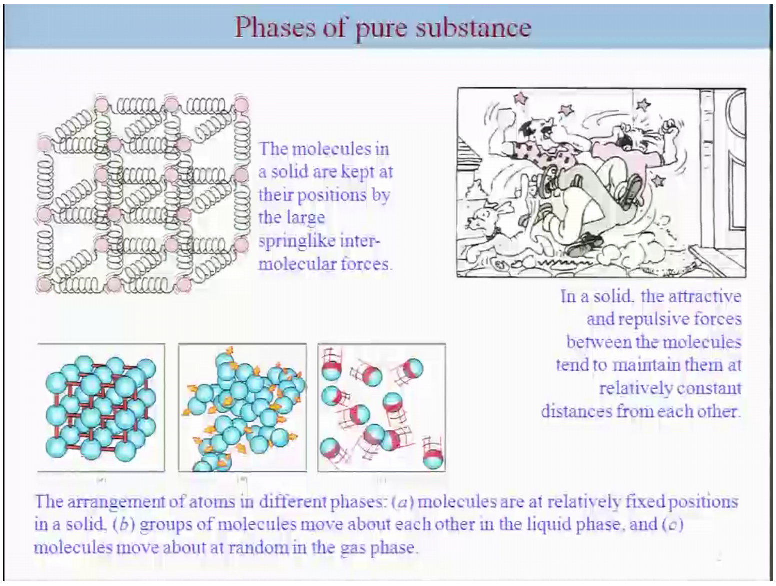

Phases of pure substance

The molecules in a solid are kept at their positions by the large springlike inter-molecular forces.

In a solid, the attractive and repulsive forces between the molecules tend to maintain them at relatively constant distances from each other.

The arrangement of atoms in different phases: (*a*) molecules are at relatively fixed positions in a solid, (*b*) groups of molecules move about each other in the liquid phase, and (*c*) molecules move about at random in the gas phase.

With the basic thing and that is the phases of a fluid we all know, molecules can exist in different phases such as, a solid where they are located the molecules are located in some lattice points, and they oscillate around that point our for that matter you have pretty much disordered structures such as, in liquid. But, there is a coordination around a single molecule; that means, they molecules preferred to stay around a certain molecule.

On the other hand, if you impart more heat they tend to have more kinetic energy, and essentially molecules are far apart, tending to behave like a gas. So, in general the simple phases are solid, liquid and gases. And mainly this is due to the attraction, and repulsion forces among the molecules. For liquid you certainly need a attractive force, but solid you can have phases just due to repulsive forces.

So, this is something which was around 1950, this particular aspect was cleared in terms of the necessity of a repulsive forces for solid phase.

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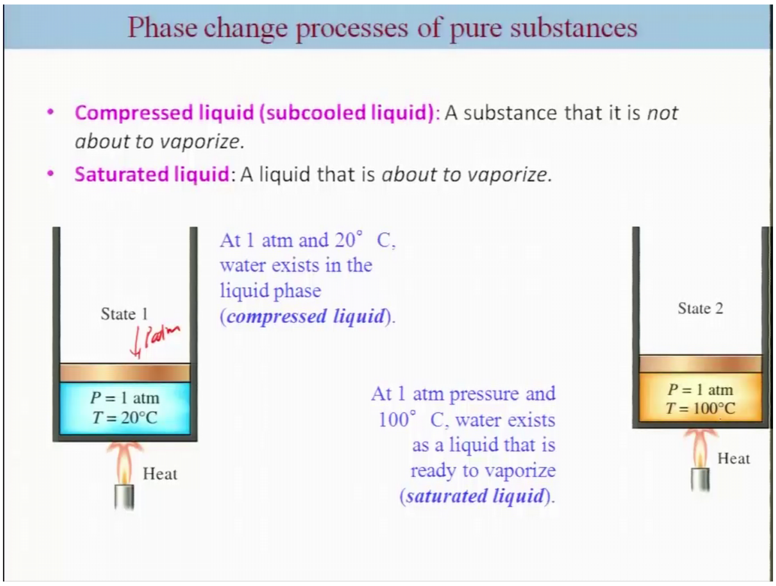

Phase change processes of pure substances

- **Compressed liquid (subcooled liquid)**: A substance that it is *not about to vaporize.*
- **Saturated liquid**: A liquid that is *about to vaporize.*

At 1 atm and 20° C, water exists in the liquid phase (***compressed liquid***).

At 1 atm pressure and 100° C, water exists as a liquid that is ready to vaporize (***saturated liquid***).

So, let me, just briefly talk about the phase change processes. So, I will just take an example of a compressed liquid, sub cooled liquid. To start with sub cooled liquid or compressed liquid is a substance that it is not about to vaporize, for example water at one atmosphere and 20-degree celsius or in general room conditions.

At this particular conditions water behave like, compressed liquid. Now, in order to vaporize, you need to heat it up. So, if you provide a heat, and this is an example of a piston cylinder. So, the we are keeping the piston mass in such a form, that the P atmosphere is that is the one atmosphere is kept constant in the system, and in this case when you heat it up in such a way, that the temperature rise to 100-degree celsius at this point, the first few draw bubble of vapor is formed, or that in other word the liquid starts to vaporize at this condition the liquid is saturated. And it continues to vaporize, until it completely vaporizes that is in state 4.

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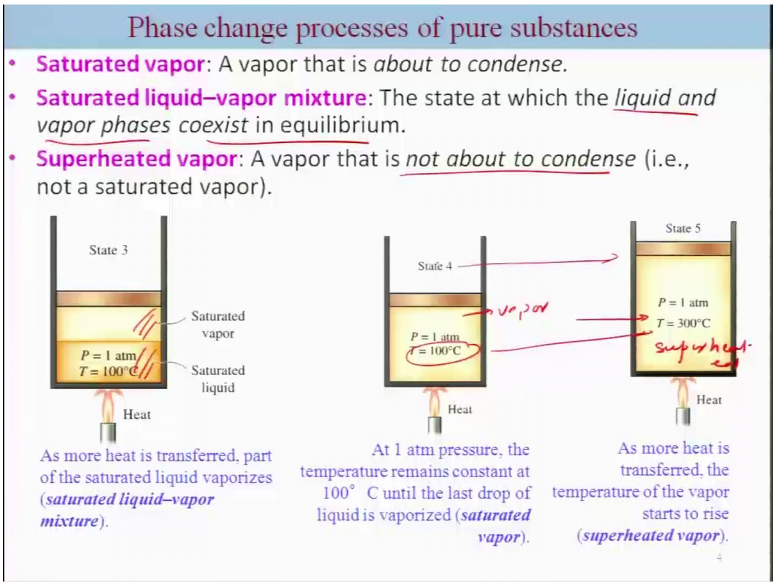

Phase change processes of pure substances

- **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).

As more heat is transferred, part of the saturated liquid vaporizes (***saturated liquid–vapor mixture***).

At 1 atm pressure, the temperature remains constant at 100° C until the last drop of liquid is vaporized (***saturated vapor***).

As more heat is transferred, the temperature of the vapor starts to rise (***superheated vapor***).

So, in other word, what is happening that at this point from state 2 to state 3, the temperature is constant. Because, for in the word for a given pressure the temperature remain constant, until all of the liquid gets converted to vapor, and that will be your state form.

So, at intermediate stage you have certain amount of vapor, and certain amount of liquid, and for the heating if you provide more heat, what happens that the temperature starts increasing because, now, this is vapor. So, this becomes superheated vapor, upon providing more heat. Now, the superheated vapor by definition is a vapor that is not about to condense, and saturated vapor liquid vapor mixture is the state at which the liquid, and vapor coexist in equilibrium, that is from state 2 to state 4. Now, you can present this particular graphical representation, or in terms of the process on a T-v diagram.

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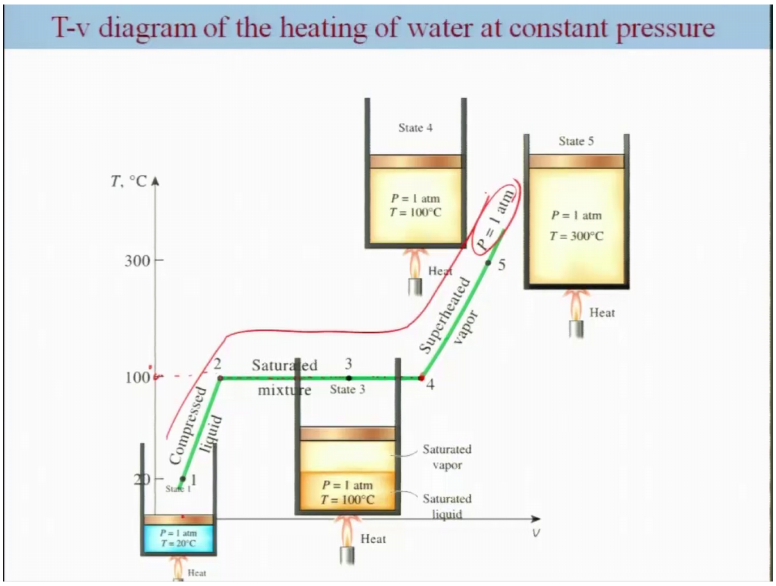

T-v diagram of the heating of water at constant pressure

So, we started from state one, which is basically compressed liquid for water at 20-degree celsius, and this is green line or the green curve represent pressure at 1 atmosphere. So, we started from here, around 20-degree celsius this condition the specific volume is very low, and upon heating we obtain a condition such that, at one atmosphere we got a boiling point here, 100 degrees celsius where it starts to boil, or start to vaporize.

And this it continues and in this point all these points, these are 2 phase mixture vapor and liquid, until the last drop of liquid gets vaporized. So, this becomes saturated vapor. So, this is compressed liquid, this point here, is saturated liquid, this point here, the drop point is saturated vapor, and upon further heating it up, we get superheated vapor. So, we can continue this exercise for different pressure also. So, for different pressure you will get of course, curves like this and so, forth.

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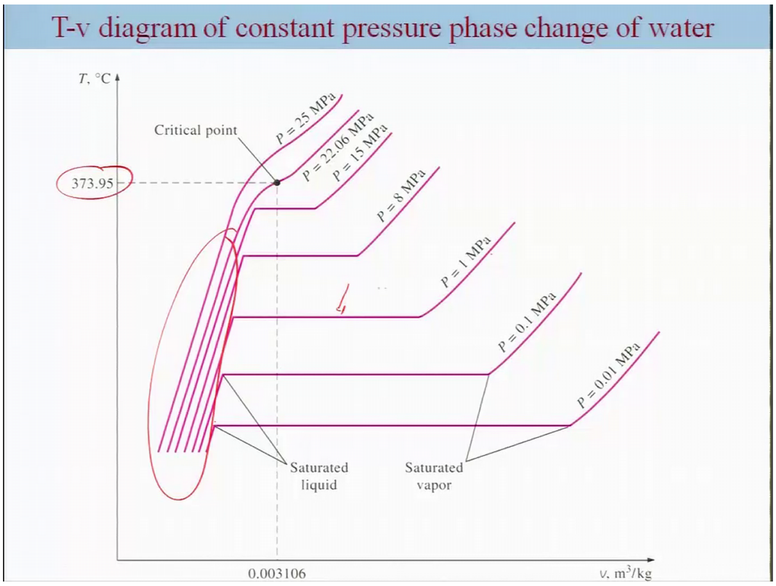

T-v diagram of constant pressure phase change of water

So, we can represent this in this plot, again is a T-v plot of a water, at a different pressure and what we observe is this is the compressed liquid region, and this is your saturated liquid vapor region, this is your superheated region. What you notice? Is that this point, from where from the point of a saturated liquid to saturated vapor the length, starts decreasing as we increase the pressure, and at certain point what we observe is that there is no specific horizontal range or the line here, which essentially means, at this point the liquid vapor is difficult to distinguish, and this is the point where the 2 phase may cease to exist and this is called critical point. And for the increase in the pressure, you do not use you do not see any phase change.

So, for water the critical pressure is 22.06, and the critical volume at this curve is point 0.0316-meter cube per kg, and the critical temperature is basically, 373.95. And this is nothing but inflection point; that means, the first derivative and second derivative of this curve are going to be 0, and this can be further explained here in the simpler form.

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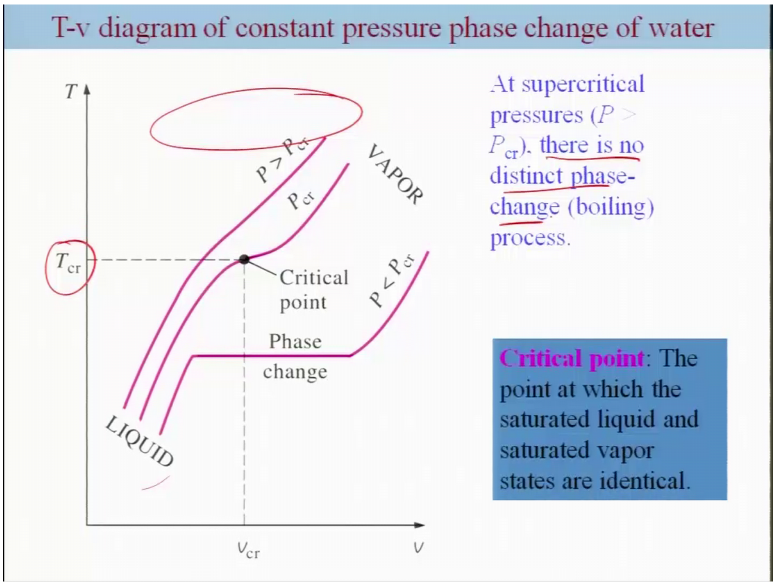

T-v diagram of constant pressure phase change of water

At supercritical pressures ($P > P_{cr}$), there is no distinct phase-change (boiling) process.

Critical point: The point at which the saturated liquid and saturated vapor states are identical.

So, for any pure fluid, need not be with just water it could be any other fluid, the behavior remains the same. So, you have at a certain temperature less than the Tc, you will observe a range where you will get a phase change, from liquid to vapor in this form, right? And so, this is what we call it a liquid, this is what we call this vapor, and above this is what we call it superheated gas or vapor.

So, this is a typical representation, at supercritical pressure there is no distinct phase change as we already mentioned.

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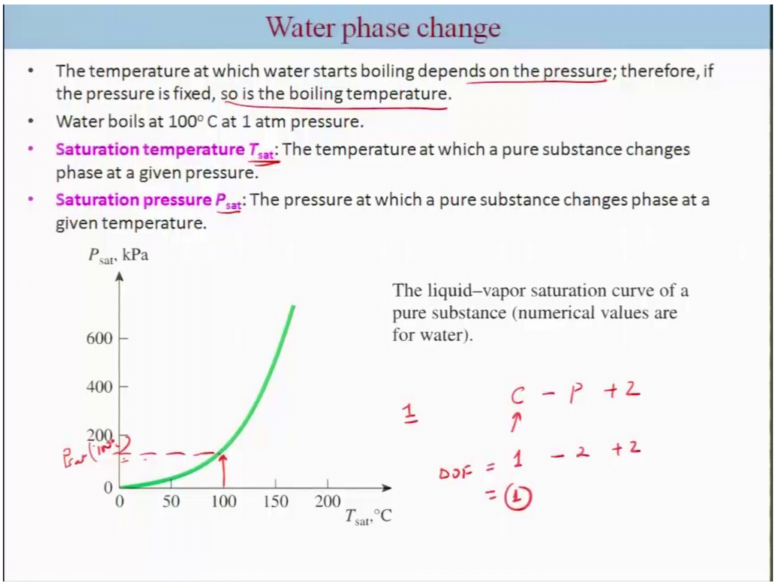

Water phase change

- The temperature at which water starts boiling depends on the pressure; therefore, if the pressure is fixed, so is the boiling temperature.
- Water boils at 100° C at 1 atm pressure.
- **Saturation temperature T_{sat}**: The temperature at which a pure substance changes phase at a given pressure.
- **Saturation pressure P_{sat}**: The pressure at which a pure substance changes phase at a given temperature.

The liquid–vapor saturation curve of a pure substance (numerical values are for water).

1

$C - P + 2$

$\uparrow$

$DOF = 1 - 2 + 2$

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So, what we observe here is the 2 things, one is the temperature at which water starts boiling depends on the pressure. So, let me, just go back again. The temperature here, at which the first liquid starts vaporizing, or it is boils, it depends on the pressure. The boiling point of course, is at 1 atmosphere is 100-degree celsius, that is what the normal boiling point. But, it does depends in general, the boiling point depends on the pressure here. So, that is what we say, that water starts boiling depends on the pressure therefore, if the pressure is fixed. So, is the boiling temperature, for 1 atmosphere the boiling temperature is 100-degree celsius.

Now, you can find out, temperature at which it boils for different pressure, and that we go also call it saturation temperature, we in a short, we call it Tsat the saturation temperature, and you can find out also corresponding piece and then, you can plot it. Now, what you can notice that once why fix the Tsat, the Psat is fixed. So, Psat is fixed for 100-degree celsius.

So, in other word, the degree of freedom for defining such a state is just 1. That is also you can obtain from the Gibbs phase rule. So, Gibbs phase rule says the following that, C is the number of component minus, P the number of phases plus 2, is the degree of freedom.

Now, C is the number of components pure is one, and in this case where you have a mixture, or to way of vapor and liquid, or in the word vapor liquid phase, there are 2 phases plus 2. So, in essentially, it also tells you the same thing, the degree of freedom you need one variables to fix, in order to find in order to specify the state.

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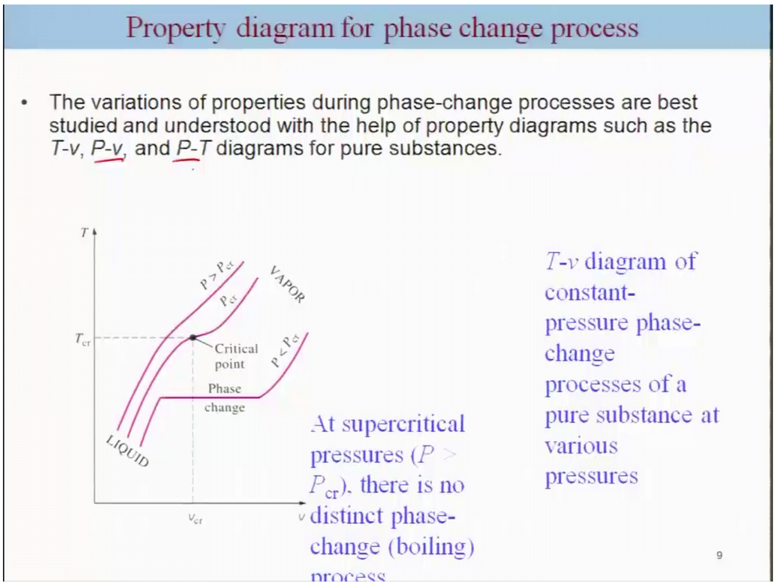

Property diagram for phase change process

- The variations of properties during phase-change processes are best studied and understood with the help of property diagrams such as the *T-v*, *P-v*, and *P-T* diagrams for pure substances.

At supercritical pressures ($P > P_{cr}$), there is no distinct phase-change (boiling) process

T-v diagram of constant-pressure phase-change processes of a pure substance at various pressures

So, the property diagram for the phase change and need not be just on a T-v diagram, you can use other process diagrams as well such as, P-v and P-T diagram.

So, the representation more or less is say, but it gives a different idea. So, I will just describe a bit more later. But, this is something extremely useful, in order to explain the behavior of the phase change on such diagrams.

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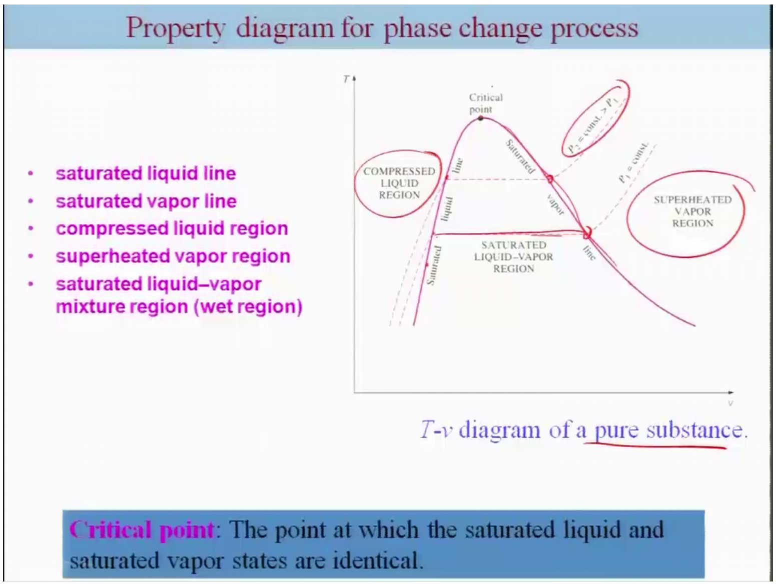

Property diagram for phase change process

- saturated liquid line
- saturated vapor line
- compressed liquid region
- superheated vapor region
- saturated liquid–vapor mixture region (wet region)

T-v diagram of a pure substance.

Critical point: The point at which the saturated liquid and saturated vapor states are identical.

So, let me, further point out here. So, let us again, take our T-v our diagram for pure substance just to summarize. So, what we have learned is the following that, if we change the pressure, the boiling temperature changes. So, in other word you have P1, and this is P2, and P2 is greater than P1. If we can joint all this points at which the liquid vaporizes, this curve will become saturated liquid line.

So, this would be from here, till the critical point, and the other point where you have a saturated vapor, where the first drop of liquid will form, if you are reducing the temperature on a constant pressure line then, that is what that will become your saturated vapor line. So, this is after joining this. This is your saturated vapor line, and this region is basically your saturated liquid vapor region, this is your superheated vapor region, this is your compressed liquid region and of course, this is your critical point.

So, this is a summary of that the later we will be talking about metastable, and other expects we will come back to this graph again. But, for simplicity we are just mentioning this for the sake of reviewing the earlier understanding of engineering thermodynamics. So, this was a T-v diagram now if it is a P-v diagram.

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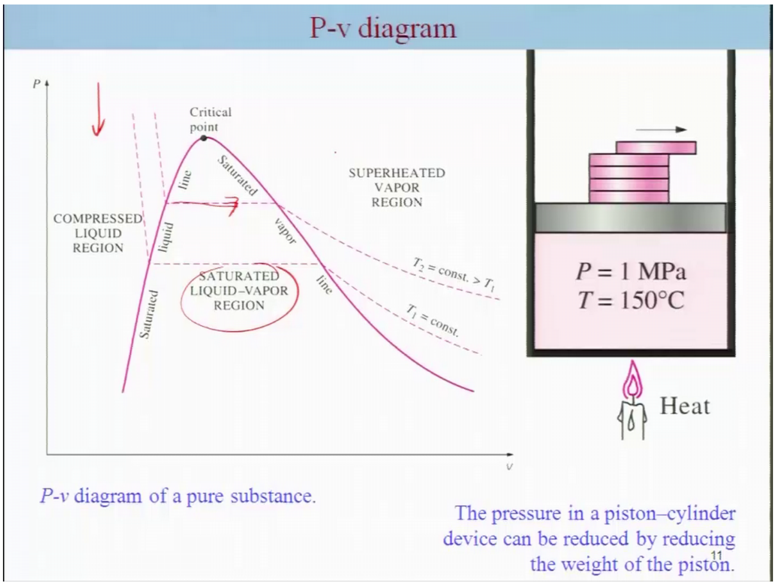

P-v diagram

P-v diagram of a pure substance.

The pressure in a piston–cylinder device can be reduced by reducing the weight of the piston.

So, the P-v diagram here, represents here, the same regions are same compressed liquid, super-heated vapor, saturated liquid and critical point; however, the isotherms the slopes are going to be different from the ones which we are using on T-v and isobars. So, the slopes are here, negative.

So, in other word, you can consider this representation. So, you are maintaining the temperature here, and if you are reducing the pressure if you are coming from here, reducing the pressure, what happens that the volume is going to expand. So, this is the representation and thus, it will start from here until it reaches the point, where it will start vaporizing. So, as we reduce the pressure, until it reaches a point where the liquid start reprising, it will remain in a compressed liquid region, and then it will reach to such a liquid vapor region until all the liquid gets vaporized and subsequently, you know that the volume keeps expanding, and thus the slope is negative, and it will be in the superheated region.

So, the rest of the definition of the region remains the same. So, this is the P-v diagram of a pure substance.

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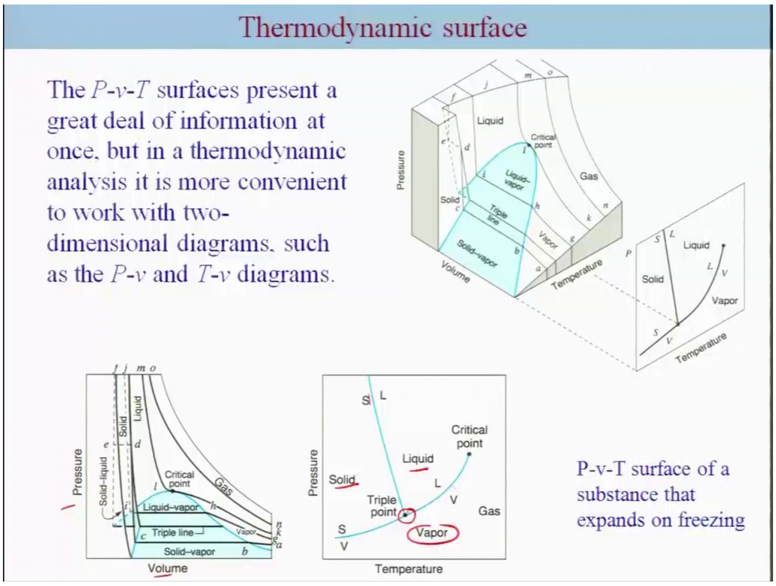

Thermodynamic surface

The *P-v-T* surfaces present a great deal of information at once, but in a thermodynamic analysis it is more convenient to work with two-dimensional diagrams, such as the *P-v* and *T-v* diagrams.

P-v-T surface of a substance that expands on freezing

Now, in general you have 3 variables the pressure, volume, and temperature and thus you can obtain the surfaces thermodynamic surface, and this is a representation of the 3d P-v-T services. So, which is more complicated in order to understand that and, this is the reason that we often work on a 2-dimensional diagram such as, P-v and T-v diagram. Just to take an example of this, this is a P-v-T service for substances, which expand on freezing.

So, the example are water, and that is due to the hydrogen bonding. So, this is a pressure, this is a volume, and this is the temperature. You have a liquid-solid vapor region then, you have a triple point line here, and then, you have this liquid-vapor region, and these are different isotherms, which has been drawn like b h. And so, forth and you can take the projection on a P-t diagram, or P-v diagram. Now, this is little interesting because, this region is broader in volume than this region that is what the expansions are.

So, one if you take a P-v diagram, it looks like this. This is the pressure and volume again, and as this is a little busy plot. So, again this is a critical point, this is the 2-phase region for the solid vapor, and this is a 2-phased region for the liquid vapor, and for solid. So, this is a liquid and this is basically, the region where the solid liquid coexist and of course, this is your solid region, and some volume of course cannot be accessible. So, this is much easier in this P-t diagram, and that is the reason that it is usually used in order to explain the phase transition for a pure substance.

So, you have this solid, and vapor. This is your sublimation line, this is your fusion line, this is your precision line, and this is your triple point where these 3 phases coexist. So, this is your triple point, and this is again solid, liquid and vapor. Now, this curve is basically, has a negative slope. Because, of the fact that, this is for substances which expand on freezing.

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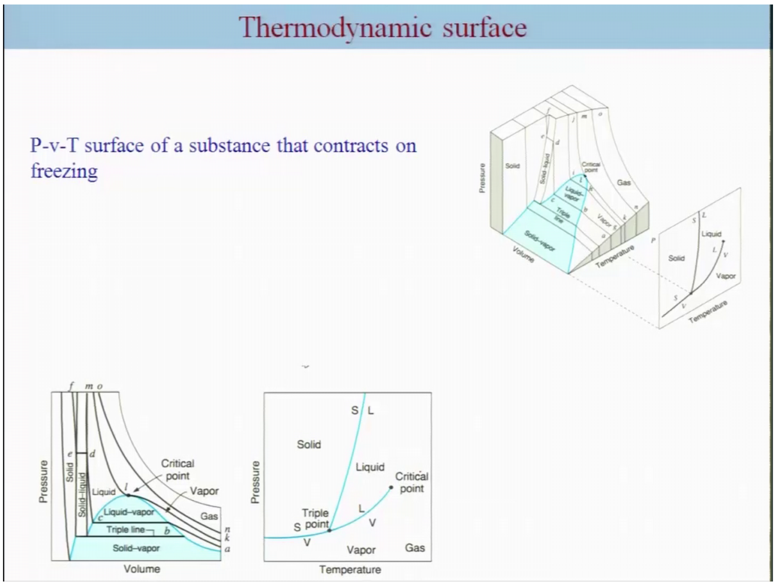

Thermodynamic surface

P-v-T surface of a substance that contracts on freezing

Now, for the case of substances which contract on freezing, this fusion line has a positive slope, and this is also evident in from the P-v diagram. If you look at it this goes more or like straight well, other case it has a little bit curve on the other side.

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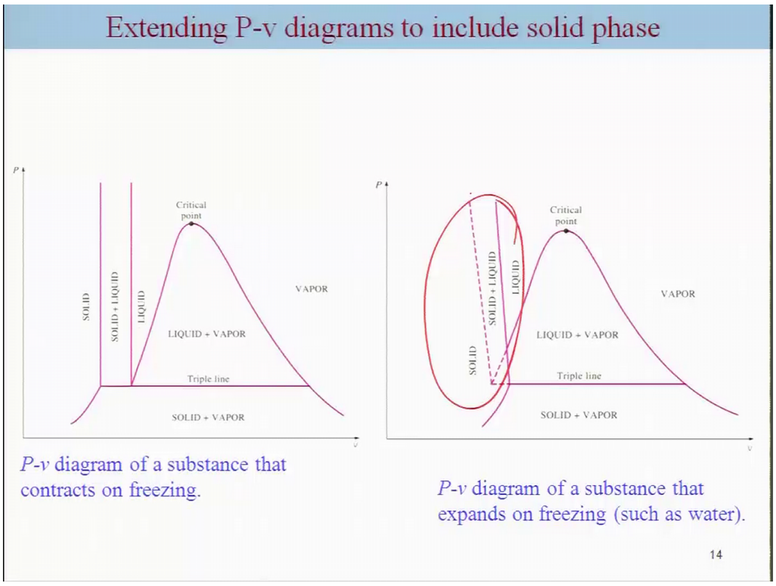

Extending P-v diagrams to include solid phase

P-v diagram of a substance that contracts on freezing.

P-v diagram of a substance that expands on freezing (such as water).

So, let me, summarize in this form. So, again this is a P-v diagram for substances contracts on freezing, and this is a P-v diagram which expands on freezing, and that is evident from this dash solid liquid lines.

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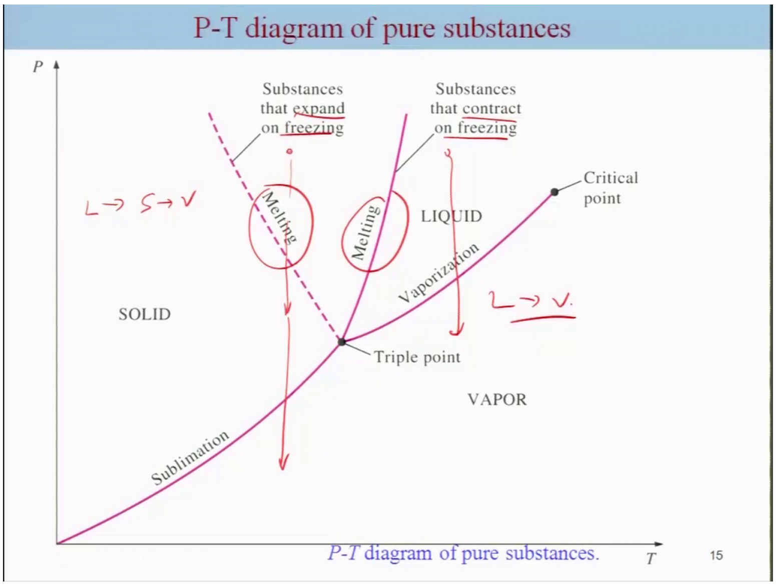

P-T diagram of pure substances

P-T diagram of pure substances.

So, on a P-t diagram, this is the melting and fusion curve, for substances expand on freezing, this is the melting fusion curve for substances contracts on freezing, represent vaporization curve and sublimation.

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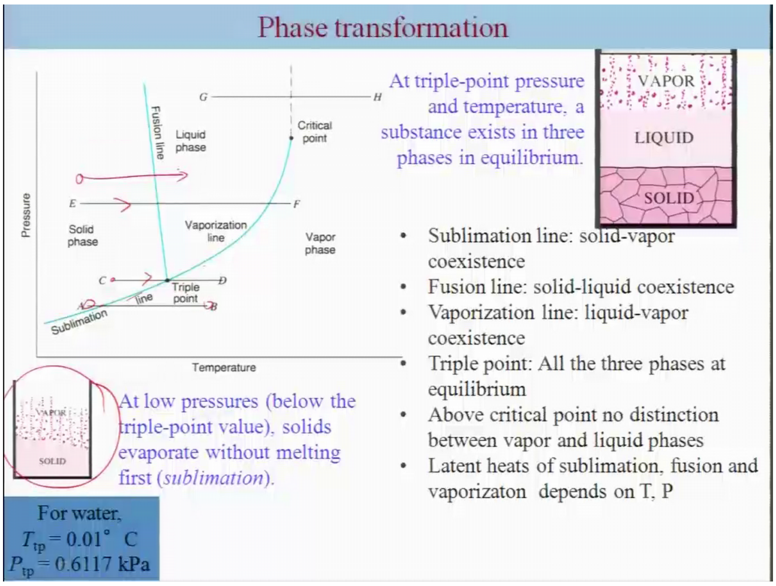

Phase transformation

At triple-point pressure and temperature, a substance exists in three phases in equilibrium.

- Sublimation line: solid-vapor coexistence
- Fusion line: solid-liquid coexistence
- Vaporization line: liquid-vapor coexistence
- Triple point: All the three phases at equilibrium
- Above critical point no distinction between vapor and liquid phases
- Latent heats of sublimation, fusion and vaporizaton depends on T, P

At low pressures (below the triple-point value), solids evaporate without melting first (*sublimation*).

For water,
$T_{tp} = 0.01°$ C
$P_{tp} = 0.6117$ kPa

Now, you can have phase transition along this various different regions. So, let me, just take an example of fusion line. So, you can have a phase transition if you are coming from let us say, E which is a solid phase, and if you increase the temperature and falling at a constant pressure, the first you are going to get a phase transition from solid to liquid, subsequently you will get a phase transition from liquid to vapor. On the other hand, here, from C you reach a triple point, where the all these phases coexist, and subsequently we jump directly to vapor. On a sublimation line, you will directly jump from A till this coexistence at point, where these 2 phases will coexist such as, in this case vapor and solid and subsequently, when the solid will vaporize directly to (Refer Time: 16:50).

So, of course, there will be certain heat which will be required in order to change the phase, and this latent heats, which is often called for sublimation, for fusion and vaporization will depend on temperature. So, for example, if temperature and pressure. For example, if you are coming from here, the value of the latent heat will be different, compared to for this case E to F. The phase transformation will be a little bit different, if you are let us say, coming from point from here, which is a case for substance that expands and freezing is a liquid phase, and if you are decreasing the pressure at a constant temperature, you will reach solid phase, and subsequently reach to a pure phase.

On the other hand, for the liquid in the case of substances for contract, which contracts and freezing, you get directly liquid to vapor. So, for them, for this case you have liquid to solid to vapor, but as in this case is simply liquid to vapor. So, the sequence of the phases, may vary depending on the type of the phase diagram which is a P-t diagram.

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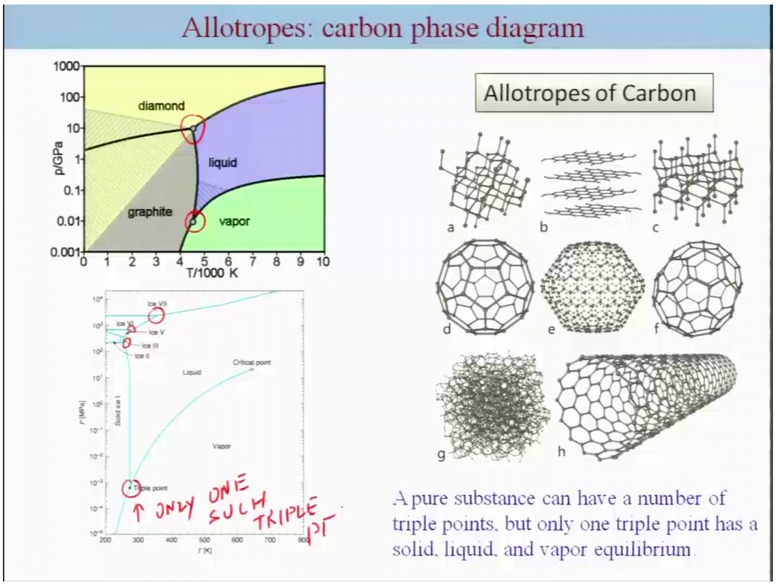

Allotropes: carbon phase diagram

Allotropes of Carbon

A pure substance can have a number of triple points, but only one triple point has a solid, liquid, and vapor equilibrium.

That they make there could be many solid phases which can exist, an example is basically other drops of carbon, or ice they have many different phases of that. So, the triple point which we defined is basically, for the point where basically the 3 phases coexist. For pure substance of course, the degree of freedom is 0. So, if you use the Gibbs phase rule, it will be just a 0. So, there is only one point such that, you have this 3 phases vapor, liquid and solid coexist. But, in addition you have many possibilities of other kind of triple point.

So, take an example of a carbon. So, you have pressure and temperature plot here, and of course, this is a triple point, where vapor, liquid and graphite coexist, the solid phase co-exists. But, there could be another triple point, where 2 solid phases coexist with liquid, and that is also known for you ice, for example this is, and this is one triple point, this is another triple point and so, forth. So, they could be many triple points, but there will be only one triple point, where a solid vapor and liquid coexist. So, there is the only one triple point, such triple point.

So, with this I will stop here, and we will continue our understanding of the properties in just like, it is like a review of the properties in the next lecture. So, see you in the next lecture.