Engineering Thermodynamics
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Lecture 10
Property diagrams of pure substances

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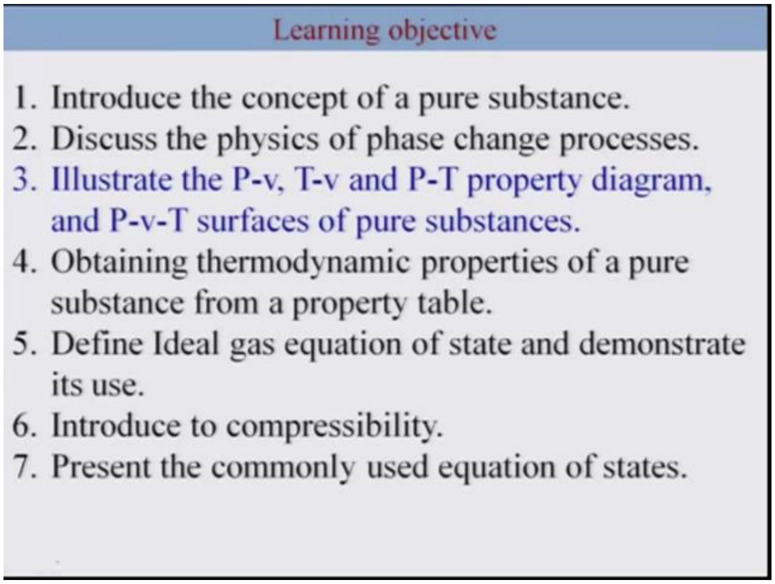

Learning objective

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.

This is the module on properties and so let us continue the discussing properties we have already looked into the introduction of concept of a pure substance, we have discussed the phase change processes and today we are going to illustrate some processes of phase change processes in the form of for property diagrams. And apparently this because very useful and diagrams to understand the phase change processes, they are many such property diagrams which you can illustrate in using a temperature specific volume, pressure specific volume and pressure temperature diagrams, for the pure case of pure substances.

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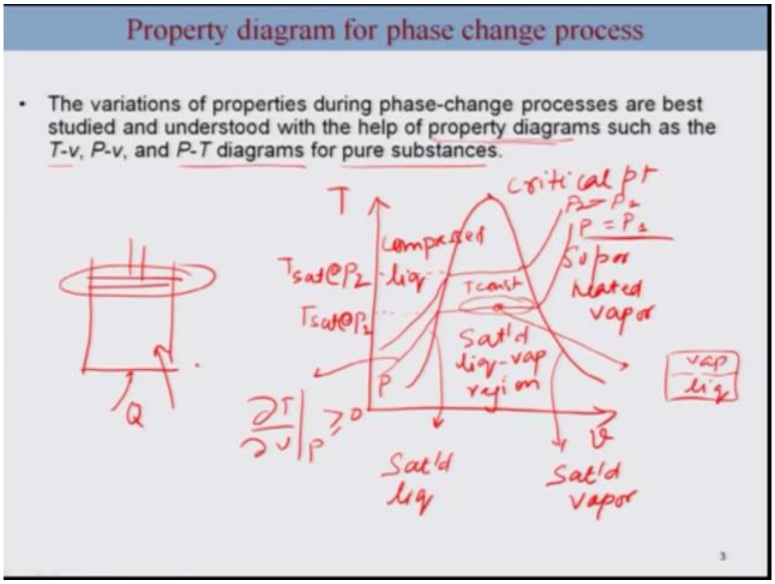

Property diagram for phase change process

- 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.

So, will going to just take example of pure substance is how does it look. The T v diagram, for example. So, I can draw it here, so this is your temperature and this is your specific volume okay. And this is how is going to look like for pure substance, this here is a critical point. Now the volume the lower side one is going to be a saturated liquid. So, this line is saturated liquid and this one is going to be a saturated vapor. And the intermediated range region is going to be saturated liquid, vapor region. This region is going to be a compressed liquid and this is going to be superheated vapor, okay.

So, this is a basic phase diagram of for the pure substance. Now you can consider a simple piston such that the piston mass is fixed and you provide heat to the fluid containing in the cylinders. So, this could be an example okay and then you are providing some heat here, so in such case the temperature is going to rise for the case of system. So, we can consider this operation in terms of phase change. So, let us say we started with a compressed liquid and we have already illustrated this example in the previous lecture.

So, this is the case for the continuous increase in the temperature as we provide heat but the pressure remains constant. And until the point it reaches a saturated liquid align it, it remains the compressed the liquid and here this point it starts vaporizing, until we reach saturated vapor aligh and then until this point the temperature remains constant. So, this is where the temperature remains constant, so t is constant okay. And for given P okay and then once it reaches saturated vapor and after the last drop of liquid gets converted to vapor it further, now complete in system is vaporized.

So, you have a vapor now the vapor temperature starts increasing okay. So, then is essentially takes this path. So, this is the case where some P is let say P 1 okay. You can do this operation by change in the pressure of your system at a higher pressure let us say. So, this would be the case of P 2 such that P 2 is greater than P 1. So, this is a simple phase change process, now you notice that the slopee of this line okay is positive.

So, essentially Del T by Del V at constant P is greater than or equal to zero right, because intermediate range is zero. So, here at this point at any intermediate point you have a system which consists of some vapor and some liquid. You can understand the same thing for if you change T v to pressure volume diagram or let me just point one more thing before going to the next slide, that for given pressure until it reaches the saturated liquid it starts changing the phase.

So, this temperature which remains constant would be it is saturated temperature at specific pressure, for example in this case this is P 1. Because we have already mentioned P 1 here and in this case this would be T sat at P 2.

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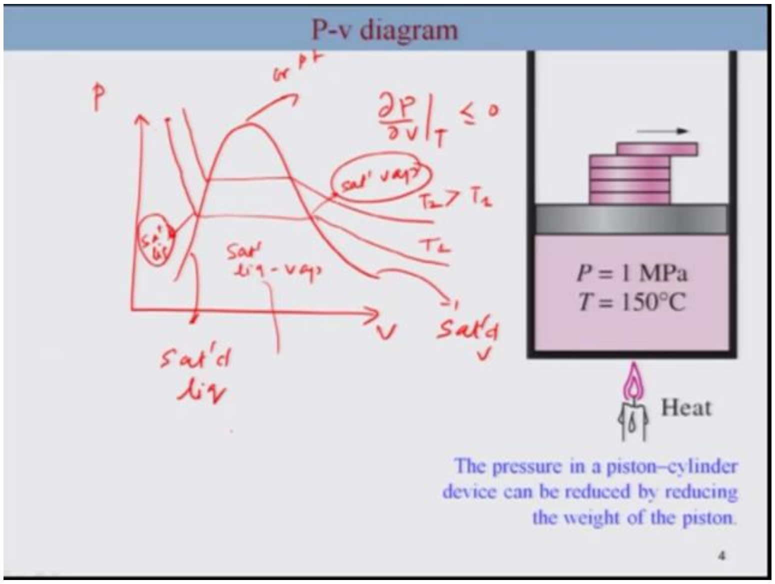
P-v diagram

P = 1 MPa
T = 150°C

Heat

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

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So, let us go to the next where we will go into change the pressure by keeping the temperature constant and in this case we have going to draw a P v diagram here okay. So, again here the lower volume range would be saturated liquid, so this is saturated liquid, this is saturated vapor this is again critical point okay.

And this is the saturated this region is going to be saturated liquid, vapor region this is your compressed liquid, this is your superheated vapor. So, in this case what we are going to do as is illustrated in this figure, that you maintain the temperature by providing heat, however the pressure you started with a very compressed liquid.

So, that we somewhere you are here and then you are decreasing the pressure by keeping the temperature constant. So, this is how is going to be you decreasing the pressure in this form keeping the temperature constant. This happens until, so you go continuously drop in the pressure until you reach the saturated liquid line. And here again the phase change is to vapor and further the pressure will drop as you crosses the saturated vapor line, again this is a saturated vapor line and this is going to be saturated liquid.

So, this is about to vaporized this is about to condensed this this points represents in that form. So, this is at certain temperature and this is at let say T 1, you can do the same operation at a higher temperature and this is going to T 2, T 2 is going to be greater than greater than T 1. The note this slope here the slope in this case is negative. So, that means Del P by Del V at constant temperature is less than equal to zero. So, this is the case of P v diagram for the case of pure substance okay.

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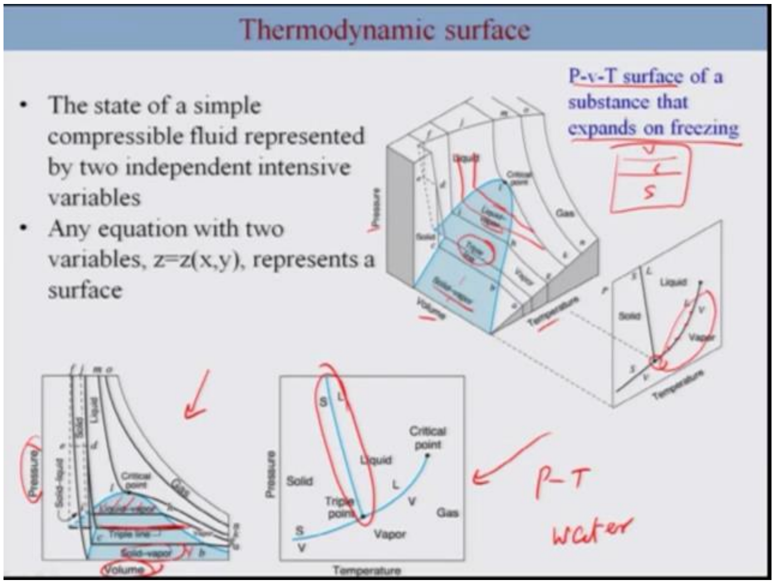

Thermodynamic surface

- The state of a simple compressible fluid represented by two independent intensive variables
- Any equation with two variables, z=z(x,y), represents a surface

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

Now we are aware of the fact that a state of a simple compressible fluid is represented by 2 intensive variables like temperature and pressure right and so any mathematical function which you represent in terms of 2 variables can be represented by a surface . So, thus a P v T surface of a substance would be more complicated diagram as shown in this case.

So, pressure, volume, temperature and here, for example you can clearly see there are many regions are there, there is solid liquid region, there is vapor liquid region the same thing which we have illustrated in P v diagram or T v diagram. You can take orthogonal projection and you can obtain this P temperature diagram as in the case of this okay.

So, this is your P t diagram okay. And so what you see here is, for example the vapor liquid line here in this region there could be many vapor liquid line and each of them would point as would represented by a simple point here in P t diagram and so we know that vapor liquid region is the case where your system consist of some part in vapor and some part in liquid. And similarly you have other case where is a triple line where you have three phases at coexistence.

So, that would be the case for your vapor, liquid and solid okay. They can change their volume percentage all the composition okay. That and based on that you can have a different volume here and thus when you take a projection it is just one single point here. So, because there is a only 1 line here okay. On the other hand you have a region of a vapor liquid and that why it X here as a complete line. So, this line would be projection line and I will talk about this in the subsequent part of this lecture okay.

So, this is a orthogonal projection and for the case of substance which expends what you see is this negative slope of pressure and temperature this region particularly for solid or so because it expands on freezing. So, this is something like example would be water and this is another projection which is a P v a diagram, where you do see liquid vapor region as we have already seen for our case in T v and P v diagram and as well as this solid vapor region if it is a solid case and then you have a triple line okay where the three phases coexist.

So, but this is very complicated particularly when you look into the P v T surface at thus many times or usually we do not go for three dimensional diagrams or rather we prefer two dimensional diagrams.

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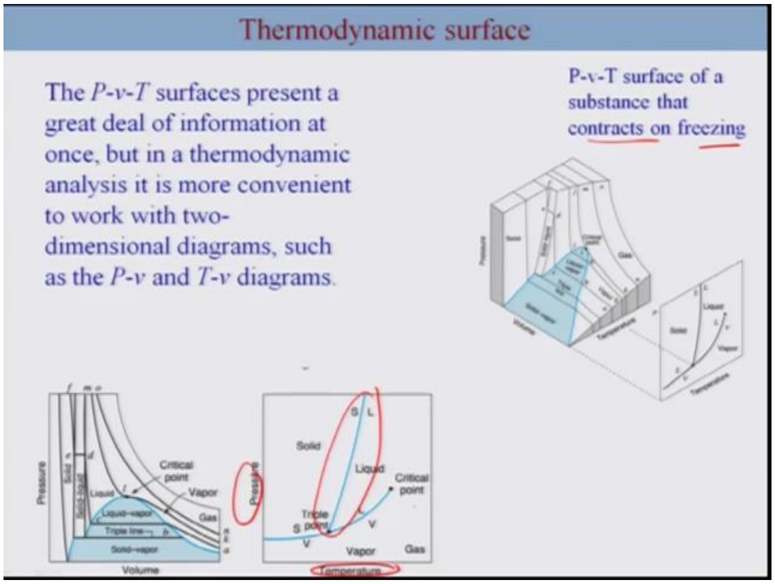

Thermodynamic surface

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 contracts on freezing

You can also use a same thing for substances which contracts on freezing which is more easily you can understand from the P t diagram, where the slope here for the case of solid liquid coexistence line is positive. So, let us look at now only the two dimensional plots the such as P v diagram.

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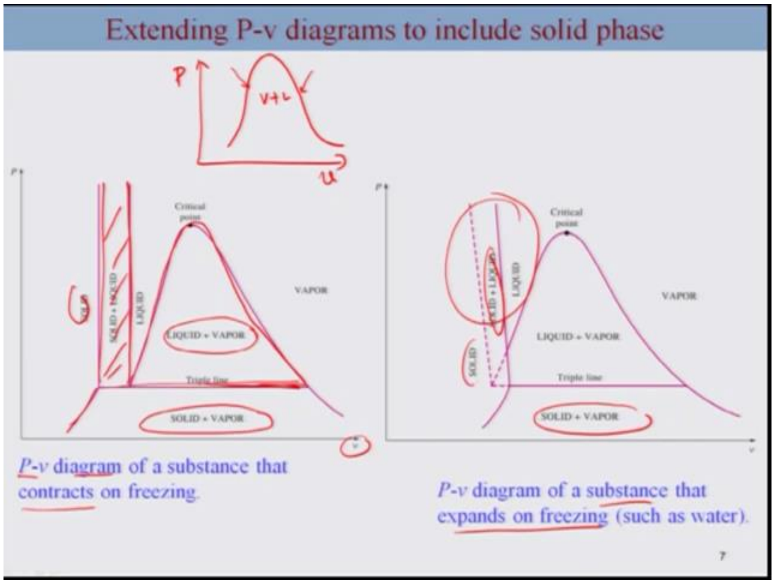

Extending P-v diagrams to include solid phase

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

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

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So, earlier we mentioned that well you have a P v diagram in this form okay. And I drew in this kind of phase diagram. So, this was always vapor plus liquid, this was saturated vapor, this was saturated liquid right. So, this is a same plot, when you include the solid phase or an as well as the solid liquid then essentially you get this kind of region.

Similar to liquid vapor region you have solid, liquid region and then the solid region is at lower volume up till higher pressure okay. And then you have another region which is solid plus vapor means that means this is the region where solid and vapor coexist and then you have this triple line, okay. Triple line, which means the three phases solid, vapor and liquid coexist in this of different volume, so volume can change.

So, this is the case where you have a substance which contracts which is usually, this fluid system by and this is a case where you have different slope for the case of substance expand, but now we have also included the solid vapor regions okay.

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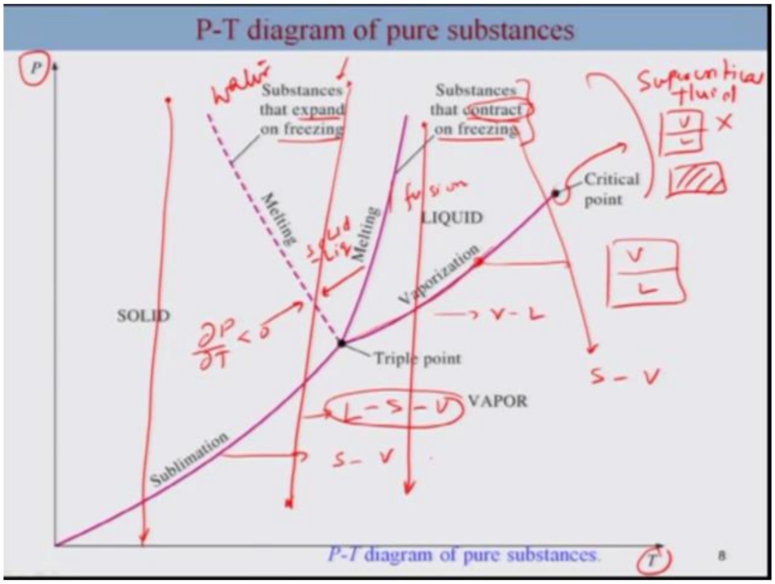

P-T diagram of pure substances

P-T diagram of pure substances.

So, now you going to understand for the case of same phase transition for the case of P t diagram it is much easier compare to other cases. So, here you see this different lines are there, this is a pressure again the temperature pressure temperature plot and this is your sublimation, this is your melting of fusion line.

This is a case where for the substance that contracts on freezing okay. So, and this is a case where it expends on freezing such as water okay. Now this is your negative slope, so that means your del T by del T is negative and this is your positive slope and these are the different line these are the line which represent coexistence.

So, this line each point here represent that you have a system containing vapor and liquid and at this point you cannot distinguish vapor and liquid. So, you cannot do that, because here this is there is a homogeneous system is difficult to distinguish and this is the region it is this is here is a super critical and we will talk about super critical fluid later in this course okay.

So, this is a vaporization line which means the vapor and liquid are at equilibrium. This is the sublimation line which means solid and vapor are at equilibrium this is your melting of fusion line. So, fusion which means is a solid liquid at equilibrium.

Now you can see that how this two different cases where the one is at substance which expands on freezing and another case is you substances which contract on freezing they behave differently. For example you can start with a case where you have start with let say solid phase and then you can change the pressure keeping the temperature constant. The way it transition or the path of transition or the phase transition and it undergoes it is quite different.

So, take an example for example here. If you are taking a solid phase okay far in the left side and you keep the temperature constant and you drop the pressure you undergo solid to vapor transition, so this is the solid to vapor transition. So, this would be true for both the cases but now you take a case somewhere here, for the case of substances which expands you have because for the case of let say water this would be solid, this would be liquid.

So, you undergo liquid to solid to vapor okay but for the other case which is the case of a contracts on freezing. So, this would be your solid to vapor, okay. And if you go from here, than it will be completely different because you are starting from liquid to vapor okay.

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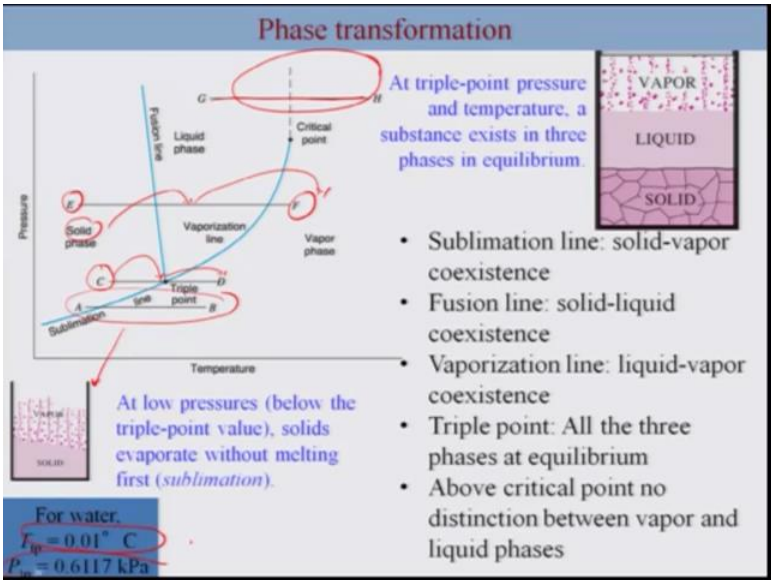

Phase transformation

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

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

For water,
$T_{tp} = 0.01^\circ$ C
$P_{tp} = 0.6117$ kPa

So, already we have gone through some of the examples. Now keeping the temperature constant here this is an example of where you kept the pressure constant. So, this is where you change from A to B that means change from solid to liquid in the case of a transition from C to D you undergo transition from solid then to the case where you pass through triple point which means you have solid, liquid and vapor and then finally to the vapor phase.

Now in the case of E to F, you undergo from solid to liquid to vapor phase okay. And then you have a state or where you do not have any phase transition because your super critical region. So, if there is continuous it okay.

So I already mentioned the sublimation part which is illustrated in this particular picture okay. For the case of the water the triple point is given here is 0.01 degree Celsius and this kilopascals okay.

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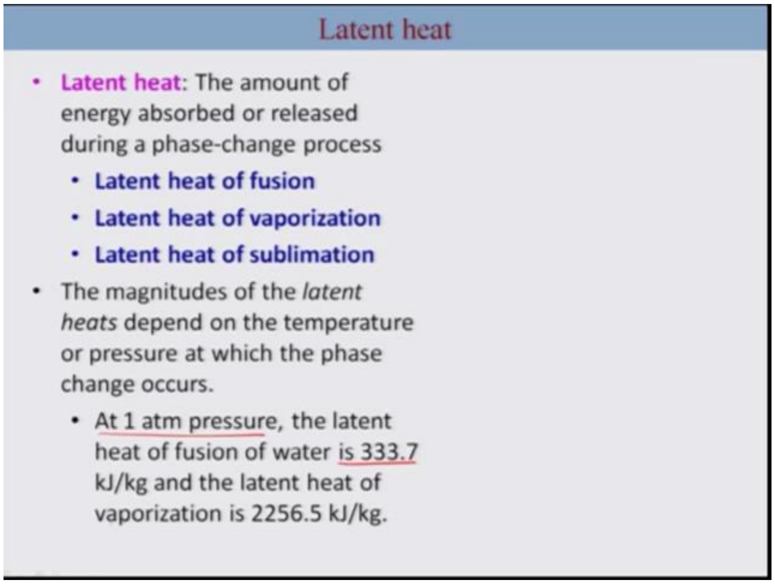

Latent heat

- **Latent heat**: The amount of energy absorbed or released during a phase-change process
  - **Latent heat of fusion**
  - **Latent heat of vaporization**
  - **Latent heat of sublimation**
- The magnitudes of the *latent heats* depend on the temperature or pressure at which the phase change occurs.
  - At 1 atm pressure, the latent heat of fusion of water is 333.7 kJ/kg and the latent heat of vaporization is 2256.5 kJ/kg.

So, when you undergo phase transition there is the energy change effectively is represented by latent heat. So, this is the amount of energy absorbed or released during the phase change process.

So, you will have latent heat of fusion, you will have latent heat of vaporization. So, in the case of solid liquid and in the case of vapor liquid and then in the case of solid vapor you have a latent heat of sublimation okay. And this magnitude of this latent heat depends on the temperature and pressure because it depends on what kind of phase transition you are or the system is undergoing. So, for example at 1 atmosphere the latent heat of fusion and water is 333.7 kilojoules per kg and for the case vaporization much higher.

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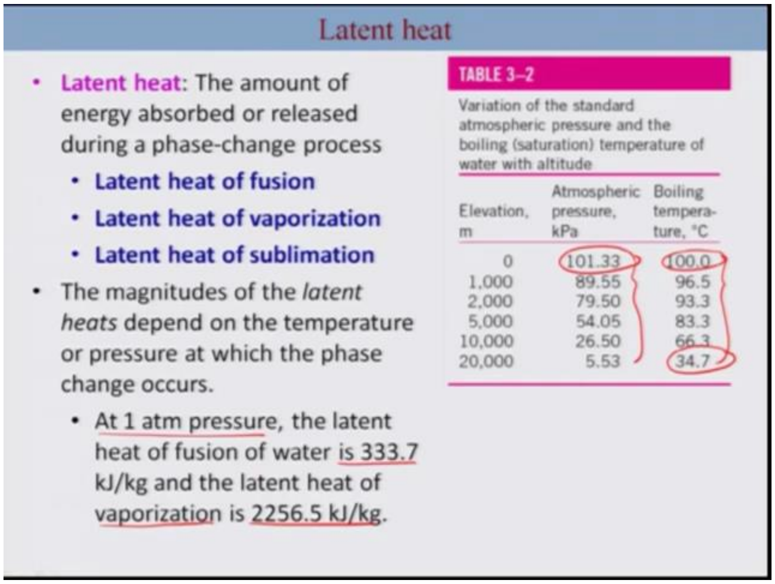

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TABLE 3–2

Variation of the standard atmospheric pressure and the boiling (saturation) temperature of water with altitude

Elevation, m	Atmospheric pressure, kPa	Boiling temperature, °C
0	101.33	100.0
1,000	89.55	96.5
2,000	79.50	93.3
5,000	54.05	83.3
10,000	26.50	66.3
20,000	5.53	34.7

So, this is the case of water which boils at different temperature, when it has a different pressure, for example at the normal conditions so normal atmosphere it boils at 100 but at high elevation the boiling temperature decreases and hence you have difficult in cooking it went (())(16:41) by looking at latent heat and as well as the conditions of the boiling.

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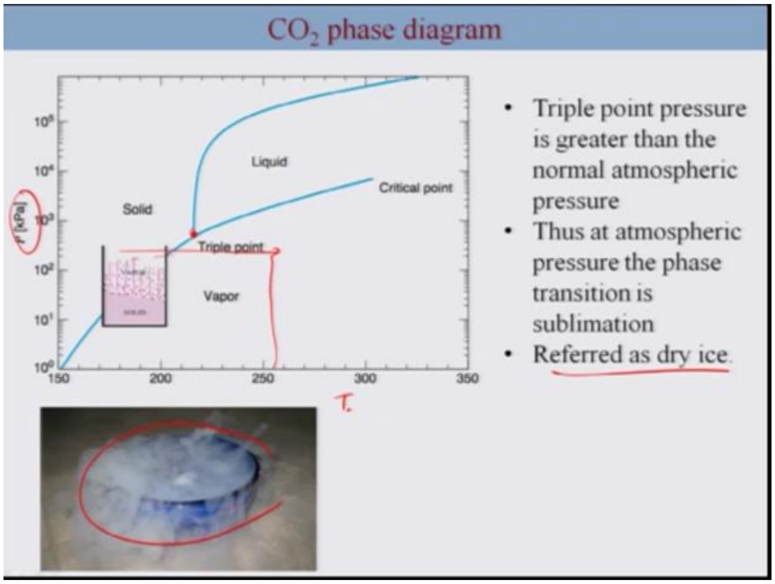

- Triple point pressure is greater than the normal atmospheric pressure
- Thus at atmospheric pressure the phase transition is sublimation
- Referred as dry ice.

Let us take some examples of the phase diagram this is the example of CO2 phase diagram, so you have a pressure again a temperature. Now in this case what is interesting is, so this is a

(()(17:00) kelvin. So, what is interesting is this triple point, this is a triple point where the solid vapor and liquid are at equilibrium, triple point is much greater than the normal atmospheric pressure.

So, you know it is hundred and one point something we should be somewhere here okay. So, this triple point is much greater. So, at normal condition if you take the solid CO2 at room temperature what happens it immediately vaporize, why because you can see it is more stable at this condition let say 273. It immediately jumps from a low temperature to vaporize and that is why it is called as a dry ice and this is illustration which you can see that it vaporize and you can clearly see the conversion from solid to vapor.

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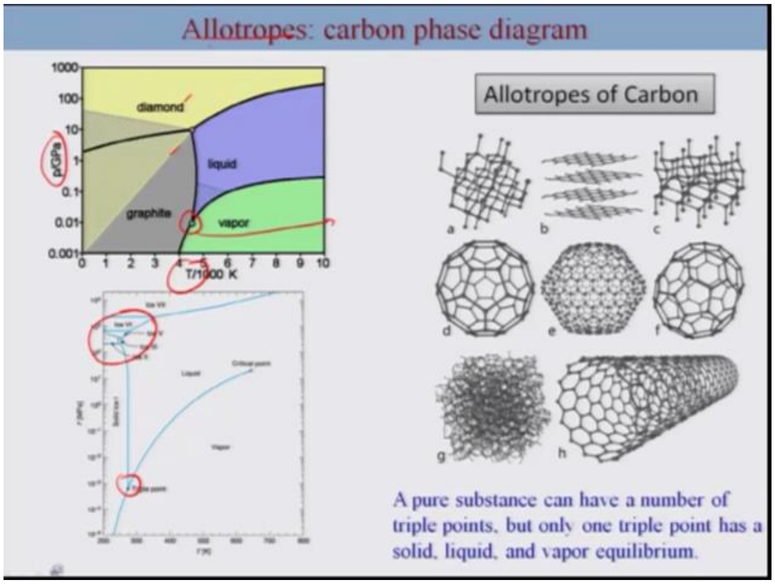

Allotropes: carbon phase diagram

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.

Now there are many other phases which we see, it is not just a solid, liquid and vapor. The solid can have many different forms and that is also referred as Allotropes, you can you aware of different forms of carbon , you can put this in terms of phase diagram and this is your P and temperature for carbon and you can see this is of course your triple point, but then there are other points as well where different phases coexists.

So, triple point will be one for system vapor, liquid and solid coexist but they could be other triple point where you can have 2 solid coexisting with liquid or 3 particular solid phases at coexistence okay. So, this is just an example of graphite, diamond and the carbon liquid at very high temperature for that matter. The other example would be your ice. So, ice has various different forms and which is represented into 1, 2, 3, 4 and so forth, it has a triple point one but it has many other triple point as well.

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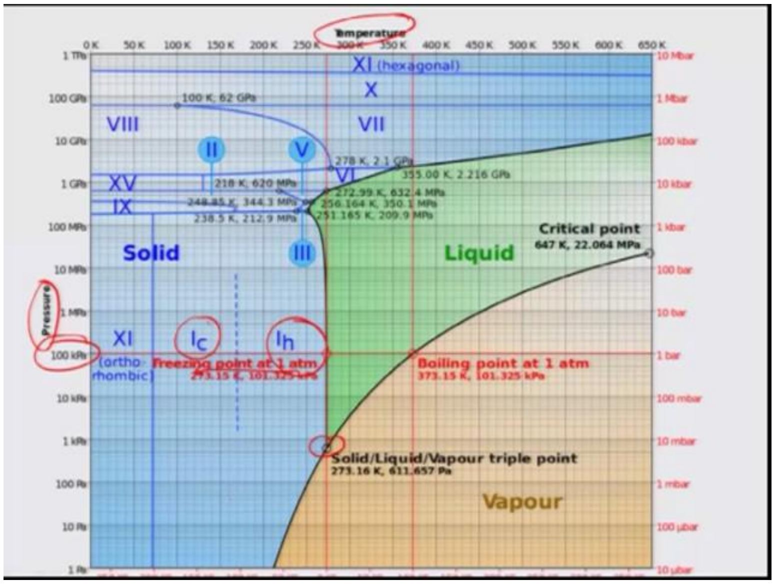

So, let me just pay little more attention to this and explain this is more complex diagram pressure and temperature this is again your triple point okay. So, at normal condition for the case of ice what you see is something calls hexagonal form of ice okay. So, that is closed to that is almost zero degrees Celsius at normal pressure. If you decrease the temperature to around 37 minus 37 degree Celsius and it is argued and it is a debate that the ice the water changes is structure form hexagonal form to something of cubic structure, okay.

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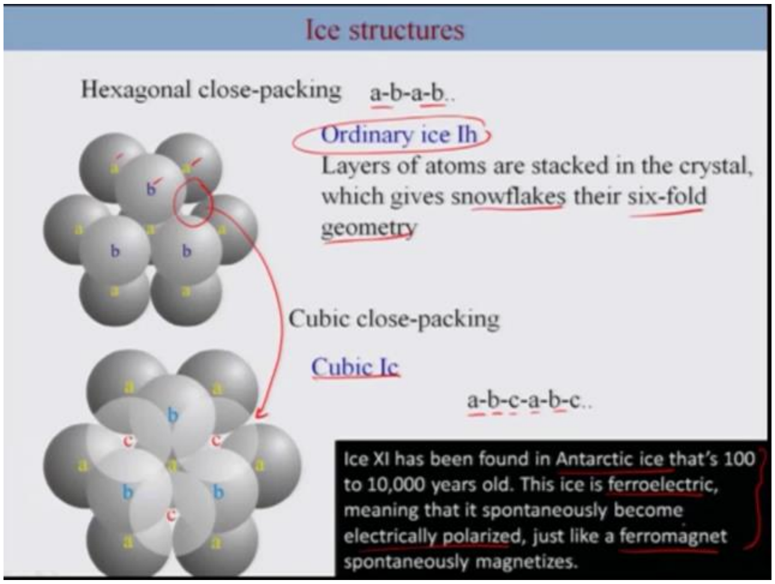

Ice structures

Hexagonal close-packing a-b-a-b..

Ordinary ice Ih

Layers of atoms are stacked in the crystal, which gives snowflakes their six-fold geometry

Cubic close-packing

Cubic Ic

a-b-c-a-b-c..

Ice XI has been found in Antarctic ice that's 100 to 10,000 years old. This ice is ferroelectric, meaning that it spontaneously become electrically polarized, just like a ferromagnet spontaneously magnetizes.

So, let us look at what is hexagonal well this is a simple hexagonal close packing where the water molecules fills up the positions represented here is A first as a first layer and B in the second layer. So, that becomes AB-AB kind of pattern and that is what the ordinary ice which Ih form and it may what is you see those kind of structure in a snowflakes and giving their six-fold geometry. But another case which we call a cubic, the third layer, the first two layers are the same but the third layer occupies this particular position here as shown in this particular picture and thus the sequence becomes ABC-ABC oaky.

Now apparently this is not argue the this is not very stable it does not stay for long time, is also argued that in normal conditions also you can see cubic phase and hence it is a quite a debate of discussion or this intense research area in this direction. Now if we further decrease the temperature from minus 37, it actually turns to something called 11 orthorhombic structures.

Now this orthorhombic structure apparently is found in Antarctica ice and it has a interesting property it is called ferroelectric kind of properties which essentially electrically polarized just like for example of a ferromagnet which spontaneously magnetize. So, you can see that phase transition can interestingly change many different properties and thus it is of quite interesting subject of research okay.

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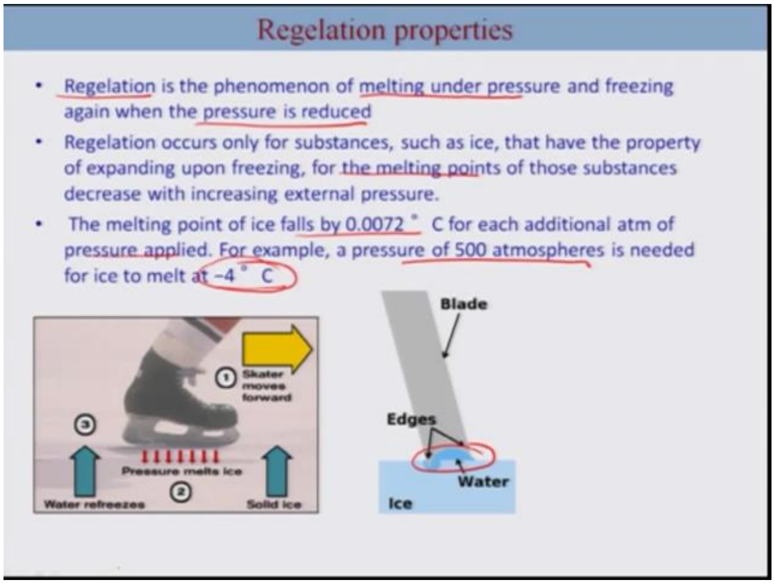

Regelation properties

- Regelation is the phenomenon of melting under pressure and freezing again when the pressure is reduced
- Regelation occurs only for substances, such as ice, that have the property of expanding upon freezing, for the melting points of those substances decrease with increasing external pressure.
- The melting point of ice falls by 0.0072 ° C for each additional atm of pressure applied. For example, a pressure of 500 atmospheres is needed for ice to melt at −4 ° C

So, I will in a kind of wrap up this particular lecture by just looking at this property of ice and it is called Regelation property. Well this is a phenomena which is the case of melting under pressure and freezing again when the pressure is reduced. So, essentially the water or the ice, for example it has a property to expend upon freezing, okay for the case of melting it compresses.

So, essentially this is a interesting material okay. For example the melting point of ice falls by 0.0072 degree Celsius for each additional atmosphere pressure applied and this is be argued that since you applied pressure, you you melt the ice and by melting an ice you have a thin layer of fluid and hence you can ice skate on it. But let us look at it whether this is feasible at all or not, okay. But because as we see from the phase diagram that for a small change, for example you want to melt ice at minus 4 degree Celsius you need to apply 500 atmosphere pressure.

Now let us look at it how it is possible that you can ice skate, okay. So, this is again Regelation phenomena is nothing but the phenomena of melting under pressure. So, occurs for the substances such as ice okay.

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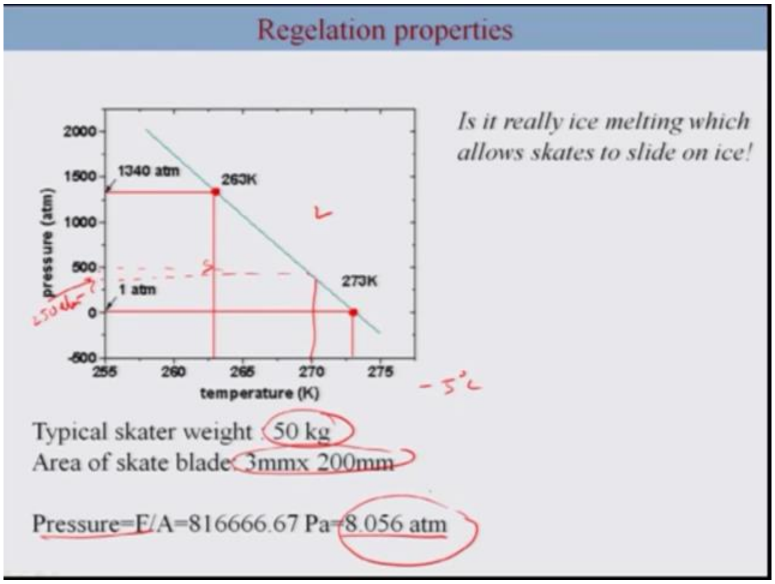

Regelation properties

Is it really ice melting which allows skates to slide on ice!

Typical skater weight : 50 kg
Area of skate blade: 3mmx 200mm

Pressure=F/A=816666.67 Pa=8.056 atm

So, this is the zoomed pressured temperature diagram for the water case and now you can take an example of a ice skate person, let say a typical weight of a skater would be 50kg, the area of the skate blade could be 3 millimeter into multiplied by 200 millimeter. You can calculate the pressure due to the weight and apply to the thin skate blade, the pressure comes out to be 8 atmosphere. And thus 8 atmospheres is it suitable, I mean is it sufficient to melt the ice for to give you a sufficient lubrication in order to reduce the friction and you can ice skate .

Now you can clearly see eve even if it is a minus let say if 5 degree okay atmospheric condition. The amount of pressure you need this is your solid, this is your liquid okay, for the case of water, amount of pressure you need would be much more many many times. So, I mean it should be more than 10, 20 of almost like may be with respect to scale it could be something like 250 atmosphere. Okay.

So, certainly the applied pressure is much lower. So, there is more complex phenomena going in this and hence this is an also a debate.

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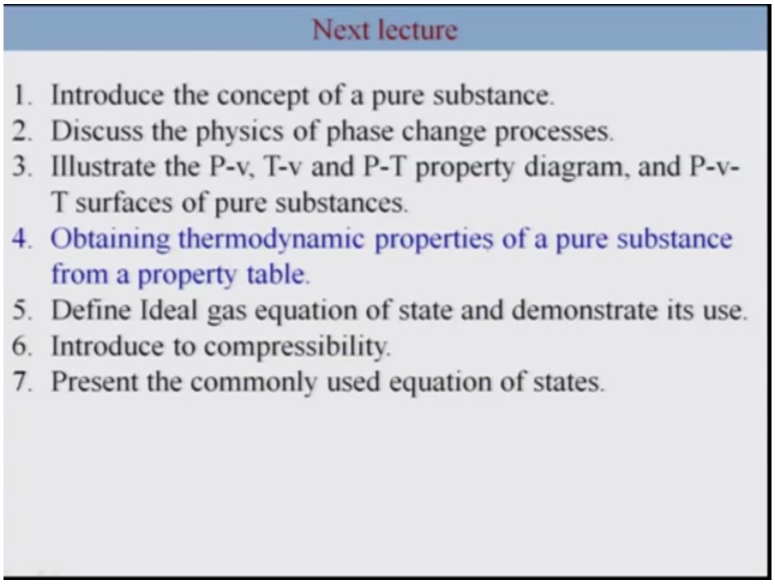

Next lecture

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So, that would be the end of this lecture, next we are going to study thermodynamic property you may have from a property tables. So, we will introduce the property table and we will discuss about that.