Applied Thermodynamics for Engineers

Prof Dipankar N Basu
Department of Mechanical Engineering
Indian Institute of Technology - Guwahati

Lecture – 08

Liquid-Vapor Phase-Change Process

Hello friends, so we are into the week number three where our topic of discussion is properties of pure substance. Now in the previous week, we have discussed about the development of generalized equations for the change in some of the most important thermodynamic properties like the specific internal energy, specific enthalpy, specific Gibbs free energy and specific Helmholtz free energy.

From using their definitions, we have developed generalized relations for changes in all these properties and of course I should not miss the changes in specific entropy and specific heats. We developed the Maxwell's relations and using the Maxwell's relations we got all those generalized equations. Now those equations are applicable to any kind of thermodynamic system, whether we are talking about a single-phase system or multiphase system. Whether we are talking about a system involving chemical reactions or not, those equations are always applicable maybe with additional terms etc. And the most important observation that we have made there, that to understand or to calculate the changes in any kind of thermodynamic potentials or maybe the changes in specific entropy or any other relevant parameters. We primarily need to know the PvT relationship and some auxiliary relation maybe the variation of specific heat with temperature or those kinds of relations. But always you must know the PvT relationship i.e., the relationship between the primary variables, primary variables: pressure, temperature, and specific volume something which is conventionally called the equation of state. So once we know the equation of state, we generally in a position to calculate the changes in all these thermodynamic properties or at least those which are of major importance to us. But problem is that, as long as we are dealing with a very simple form of equation of state something like, $Pv = RT$ that is fine. We can easily perform all those mathematical manipulation like differentiation or integration and we can easily established corresponding relation in changes in thermodynamic potentials, or any other equational state like, in the previous week we have solved problems involving the Van der Waals equation of state or I gave you another assignment involving helium as a working fluid where your relation was slight modification of the ideal gas equation that is:

$$P\,(v-a) = RT$$

So those form of equations are quite easy to deal with. But, in several thermodynamic systems we can encounter equation of states which can be extremely complicated.

They may involve higher order terms, higher order exponents of temperature or pressure making them quite difficult to deal with in terms of mathematical point of view. Say, for example, if we considered a very simple thermodynamic system. Say, we have a fixed container, a rigid container housing a particular mass of water. Now this is a close system, also with fixed wall non-movable wall therefore no moving boundary work involved.

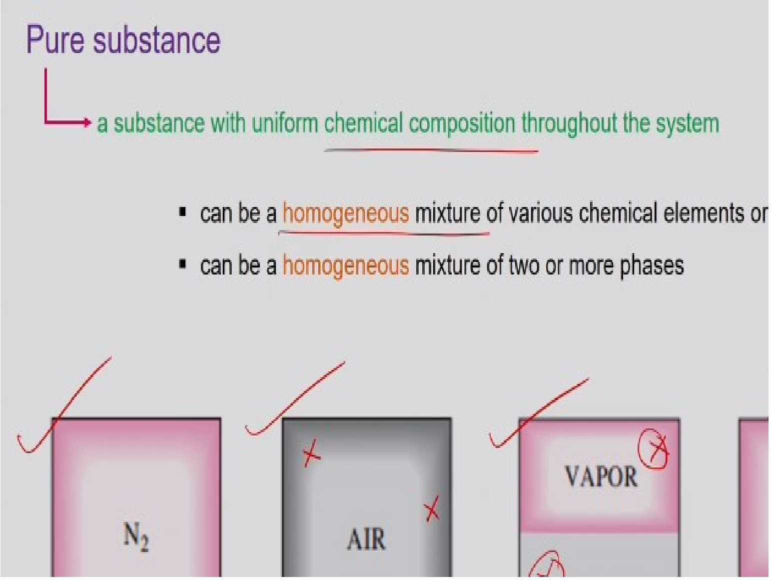
Now if we are adding heat externally to that particular system, then it is being subjected to energy interaction in the form of heat transfer between system and surrounding. There is no work transfer, but there is heat transfer into a system and because of that heat transfer from first law we can easily say that there will be a change in the total energy content of the system primarily in the internal energy of the system, which will be manifested in the form of changes in temperature of the system. This is an example of a sensible heat addition, i.e., the amount of heat that is getting added that is directly getting manifested in the form of changes in temperature of the thermodynamic system. So it is a very simple thermodynamic example, its practical application you can see in several cases.

Just for making a cup of tea at your house, we have to boil water or we have to heat some liquid up to a certain temperature. But even in such situations also, the equation of state can be a quite complicated one. Like, as we have seen if we are dealing with an ideal incompressible substance then, we get very easy form of equation of state: $\mathrm{d}v = C_v \mathrm{d}t$, $\mathrm{d}h = C_p \mathrm{d}t$, $C_p - C_v = R$ etc**.,** but truly speaking no real substances are perfectly incompressible. Whatever small maybe but there is still some effect of pressure.

And therefore to correctly encounter that particular effect of pressure we often have to deal with very large orders like 20th order, 25th order exponential or polynomials in terms of both temperature and pressure. And when we have to deal with such complicated equation of states even in a single-phase application, then you can just imagine what will happen in a multiphase application or when we are encountering a phase change process.

It is extremely difficult to define proper equation of state for phase change processes, almost impossible in most of the situations. And even if we can define one in such equation that will be very much situations restricted. And therefore, though it seems very attractive that the knowledge of PvT relationship allows you to calculate the changes in all properties, but in several cases because of the complicated form of equation of state that we get we may have to restrict ourselves on some thermodynamic tables., Tables, where the data for a given thermodynamic state has already been given either through some kind of detailed mathematical manipulation, maybe something done using high performance computers or sometimes just experimentally measured data values. And that is precisely what we are going to learn in this particular module here, where we are going to talk about the pure substances particularly the phase change processes associated with the pure substances. And then we shall be seeing how to make use of the data tables to get the properties of those pure substances during a phase change process or maybe during single-phase operation. But, to start with we first have to define what do we mean by a pure substance?

(Refer Slide Time: 06:43)



Pure substance

a substance with uniform chemical composition throughout the system

- can be a homogeneous mixture of various chemical elements or
- can be a homogeneous mixture of two or more phases

If pure substance refers to a substance which is having a uniform chemical composition throughout the thermodynamic system, i.e., the chemical composition has to be uniform and that is a very important term to have. We are not talking about difference in terms of its physical shape, difference in terms of its phase, but we are talking about difference in terms of chemical composition or I should say uniformity in terms of chemical composition.

Say, for example, the uniform chemical composition we can still get even when we are dealing with a homogeneous mixture of various chemical elements or compounds, like this particular one. Here we have two boxes, one completely filled with nitrogen. Now, nitrogen is having a uniform chemical composition. So, throughout the box or from wherever you may take a sample you are going to get the same chemical composition.

Then what about air? So, this particular one is definitely a pure substance. But, what about air? Air is not a single substance rather its a mixture, its a mixture of various gases, various common gases primarily nitrogen and oxygen, but there also may be small quantity of carbon dioxide, water vapor and several other gases. So, it is a mixture of gases. Then should we call it a pure substance?

That is where the second line comes into play, where we are talking about a homogeneous mixture means everywhere, we should have the same mixture composition. And that means if we take a sample say somewhere from here and another sample from here and another sample from here for this particular box, we are most likely to get the identical chemical composition or identical mixture composition from each of these sample data points.

And similarly, we can collect data from any point anywhere in this particular system and we should get the same mixture composition. Then we can call this one also a pure substance because the chemical composition is not varying. Despite it being a mixture, the chemical composition is not varying with space whatever chemical composition or mixture composition you are having at one particular point the same prevails throughout the domain.

There can be another scenario when we are talking about a homogeneous mixture of two or more phases. Like this example, look at the first situation here; here we are having a mixture of liquid water and water vapor. Something like again we have a closed container and, in this container, we are having liquid water which is being heated to produce water vapor. So partially this container is filled with the liquid phase and partially with the vapor phase.

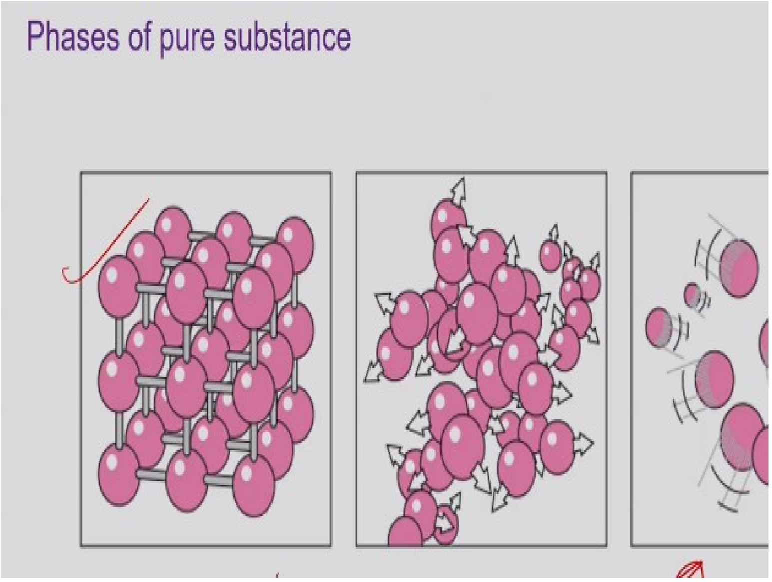
So, they are having different phases and physically they look different. If you take a sample say somewhere from here you are going to get liquid water and if you take another sample from here you are going to get the water vapor. However, what about their chemical composition? Their chemical composition is same because we are talking about the same H_2O molecules only. So from this particular position, whatever chemical composition or whatever molecular structure that you are going to get, you are going to get the same molecular composition there are as well. So, this one also qualifies as a pure substance. So pure substance can be a homogeneous mixture of various chemical constituents or can be a homogeneous mixture of two or more phases of the same substance. The same thing can prevail when we are talking about a mixture of say liquid, water and ice in a closed container maybe inside an insulating container. Here again despite being having different physical phases, we have the same chemical composition and so that mixture of water and ice can also be treated as a pure substance. Then what about this one? It is a mixture of liquid air and air in vapor or gaseous state.

Now how we can visualize this? Let us take a sample of air under atmospheric condition and that fixed quantity of air is enclosed inside a container. Now we are reducing the temperature inside the container. If I keep on reducing the temperature of this container then what will happen? If we do the same experiment with water vapor and constantly reduce the temperature then at some point the water vapor starts changing its phase.

The same thing should happen with air. But problem with air is it is a mixture and all these constituents does not have the same temperature as which should mark the phase change. The boiling point of oxygen, the boiling point of nitrogen they are not same. Oxygen will start to condense much earlier despite nitrogen remaining the vapor phase. And therefore when we are having this mixture of liquid air and air vapor, if we collect a samples from somewhere here, you are going likely to get a mixture of both oxygen and nitrogen whereas if you collect a samples from somewhere here you may get only liquid oxygen and not nitrogen. Because nitrogen the boiling point of nitrogen is still not been reached and so nitrogen remaining as a vapor phase. Now between this point and this point the chemical composition is not same.

The mixture composition is also not same so this is not an example of a pure substance. So, we have to be very careful about the definition of a pure substance when you are talking about a single chemical composition, we can blindly identify that as a pure substance. However, when there is multiple chemical composition then we have to judicially think whether it just a homogeneous mixture or not.

(Refer Slide Time: 12:06)



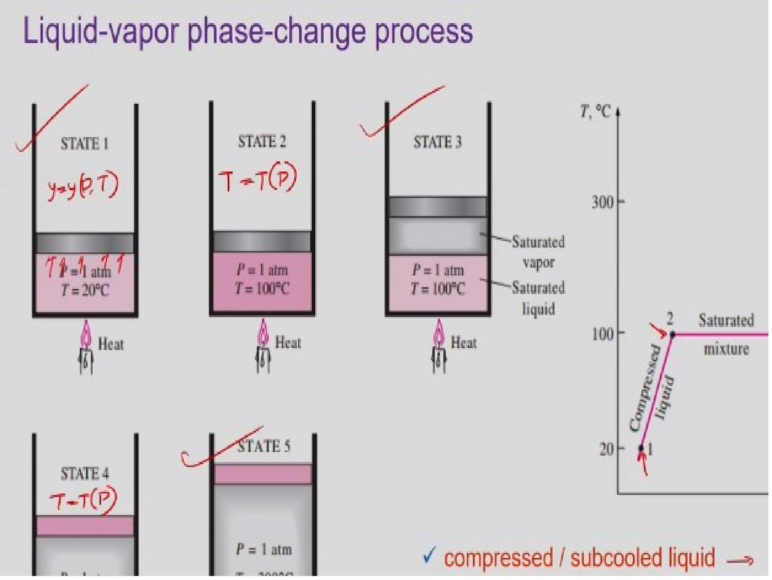
Pure substances can exist in commonly three different phases as we all know solid, liquid and gases. In solid, we generally have fixed lattice structure where all the molecules are bound in a ties lattice unit with maintaining a constant average distance between the neighbouring molecules these molecules can vibrate with respect to their own position but they cannot have translational motion.

Whereas in case of liquid we generally have groups of molecules floating almost freely with respect to the other groups. Intermolecular attraction is extremely strong in case of solid, it is much lesser in case of liquid. But still some kind of intermolecular attraction exist because of which we may get such groups of molecules, but not all molecules together. And intermolecular attraction is even lower in case of gases where almost all molecules are free to do whatever they want to do. They are free to move over the entire domain available to them because of their random movement they often keep on colliding with each other, they are going causing some exchange of energies but they are hardly get bound back to a common structure. So, the intermolecular attraction is the highest in case of a solid, the lowest in case of a gaseous medium.

And a pure substance can undergo phase change processes as well, i.e., its phase can change from solid to liquid or vice versa. Similarly, liquid to vapor or vice versa or in certain special cases it can also change directly from solid to vapor or vice versa. We shall be shortly be seeing the condition for which we get this. So all these three kinds of or I should say 6 kinds of exchange process are possible.

But out of which the liquid to vapor phase change or vapor back to liquid phase change is the most common one that you can find in industrial engineering applications. And that is why we shall primarily be defining the characteristics of a phase change process of a pure substance in the light of liquid-vapor or vapor to liquid phase change. But whatever we are discussing that is equally applicable to solid liquid or solid vapor phase change processes.

(Refer Slide Time: 14:08)



Liquid-vapor phase-change process

✓ compressed / subcooled liquid →

To understand the liquid-vapor phase-change process, we shall be talking about a simple experiment. In this experiment we have a piston cylinder arrangement, the piston is allowed to move such that it inside the atmospheric pressure is always maintained. So, to start with outside the piston it is open to atmosphere inside we have 1 atmospheric pressure and 20 ^{0}C temperature.

At this point, we are starting to supply heat to the system because of supply of heat we shall be seeing a sensible heat addition i.e., the temperature of the system will start to increase but there is no change of phase as long as the pressure is maintained to be 1 atmosphere. Because the heat addition the temperature increases and because of that the volume of the liquid water that wants to expand thereby forcing the piston in the outward direction in order to maintain that 1 atmospheric pressure.

But that is again I repeat there is no phase change process so whatever heat addition is taking place is entirely sensible heat addition. This particular phase of liquid water is called compressed liquid or subcooled liquid. Here the term subcooled refers to it is still will below certain kind of threshold. Here despite addition of heat the liquid molecules are not able to become free to reach that gaseous stage.

You can think about this way the 1 atmospheric pressure that the piston is imposing on the water here, inside the cylinder, that is, actually imposing the outward motion of the molecules. And the molecules not having sufficient amount of energy so that it can push the piston in the outward direction. The temperature of the molecules is quite low only 20 ^{0}C as the temperature keeps on increasing the force exerted by the molecules on the lower surface of this piston that also keeps on increasing. Accordingly, the piston tries to move in the outward direction in an effort to maintain the constant temperature inside. And then we reached the second situation state 2, where the temperature is reached to a threshold value of 100 ^{0}C. For water under atmospheric condition this threshold temperature that we are talking about is 100 ^{0}C, but for other substances the temperature will be different.

Even for water also if change in pressure this temperature will be different. But for a given pressure and given substance we have a unique threshold temperature. At this temperature, or till this temperature there has only been sensible heating that is the addition of heat has caused a rise in the temperature of the fluid. However, if we add even the smallest possible amount of heat to the system at this particular condition the phase change will get initiated.

So, this particular state is called saturated liquid state. The subcooled liquid refers to the state where the fluid is not going to vaporize, the fluid is not looking to vaporize at least immediately but when it reaches the saturated liquid state it is about to vaporize. So, the compressed or subcooled liquid state here expands from that 20 ^{0}C the starting temperature to that 100 ^{0}C, the threshold.

However, saturated liquid we are talking about only at this particular point, where we have the atmospheric pressure at 100 ^{0}C temperature. Then with further addition of heat, the phase change starts and if we monitor carefully then after sometime you may find that we have two distinct layers one like a layer of liquid and another layer of vapor. But the pressure and temperature that remains constant during this particular process.

Of course, liquid and vapor have different properties but the temperature and pressure will not change and this particular state we call the saturated liquid-vapor mixture. Because here we have liquid and here, we have a vapor and we are getting this mixture at a constant pressure and temperature. The pressure and temperature which it attained at the point of saturated liquid so it is a saturated liquid-vapor mixture.

As we keep on adding the heat the fraction of vapor in the mixture keeps on increasing and then we shall be reaching a state which is just opposite to state number 4 where the entire system is filled up with vapor at 1 atmospheric pressure and 100 ^{0}C, this particular state is called saturated vapor. So saturated vapor refers to the state where the liquid gets 100% converted to vapor.

Or if we see from the other point of view a saturated vapor is the one from where if we take even smallest amount of heat out then it will lead to a condensation process. So saturated vapor means something which is about to condense. So, a saturated liquid refers to the liquid which is about to vaporize that with small addition of heat it will initiate a phase change process. Similarly, a saturated vapor refers to the vapor which is about to condense with small amount of heat removal from the system it will lead to the condensation process. And from saturated vapor, then if we move forward in terms of heating then it is again single-phase heating during which pressure if pressure is maintained constant during the experiment the temperature will keep on increasing continuously. This state is called superheated vapor state. So superheated vapor state refers to the state beyond this critical temperature or beyond I should say the threshold temperature. So when we are talking about the saturated liquid that is in our state number 2, in this case, with addition of heat temperature keeps on increasing and while the pressure is maintained at 1 atmosphere. And therefore if we are talking about any general property y here, the y will be a function of pressure and temperature and generally can be represent as a function of pressure and temperature.

Or instead of writing this I should write it here any general property y is a function of pressure and temperature for the compressed subcooled liquid, i.e.,

$$y = y(P,T)$$

The similar scenario is attained in case of superheated vapor which is not going to condense on removal of heat. So, in this case again the y is a function of pressure and temperature. But the saturated liquid state that we are talking about for a given pressure value there is only a single temperature, like, it is 100 ^{0}C for water under atmospheric pressure. So, as we are talking about a single temperature for a given pressure. And therefore, this temperature that we are talking about is a function of the pressure in case of a saturated liquid.

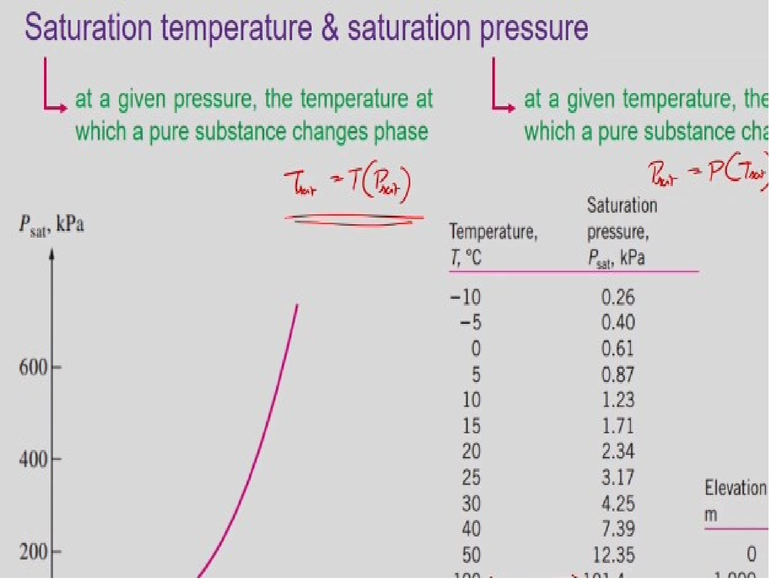
$$T = T(P)$$

Then same applies for the saturated vapor because here again it is just the opposite scenario of the saturated liquid and inside the mixture both temperature and pressure remain constant.

So, we can combine all these five situations into a *Tv* diagram where *T* in the vertical axis and *v* in the horizontal axis. This is the point, state number 1, from where we are starting our experiment as the temperature of the subsystem that keeps on increasing it passes to the compressed liquid level with continuous raise in its temperature and specific volume to reach this state number 2. In state number 2, it reaches the saturated liquid state.

From there we have the state 3, which is a saturated mixture state and ending up at state number 4, which is a saturated vapor state. With further addition of heat further increase of temperature the saturated at vapor state gives rise to the superheated vapor state. So, these are the five different stages that we can identify during the liquid to vapor phase change process or you may say that there are three primary stages: the compressed liquid stage, the saturated liquid for mixture stage and superheated vapor stage. The saturated liquid state is the state which signifies the end of state 1 and beginning of state 3. Similarly the saturated vapor state that is stage 4 indicates the end of state 3 and starting of state number 5.

(Refer Slide Time: 22:32)



Saturation temperature & saturation pressure

at a given pressure, the temperature at which a pure substance changes phase

at a given temperature, the which a pure substance cha

$T_{sat} = T(P_{sat})$

$P_{sat} = P(T_{sat}$

Temperature, T, °C	Saturation pressure, P_{sat}, kPa
−10	0.26
−5	0.40
0	0.61
5	0.87
10	1.23
15	1.71
20	2.34
25	3.17
30	4.25
40	7.39
50	12.35

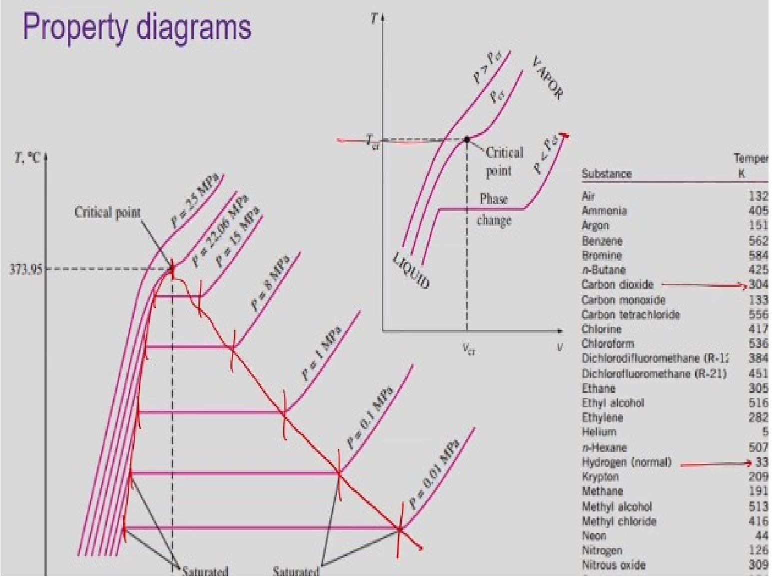
And in this context, we get the definition of saturation temperature and saturation pressure. Saturation temperature refers to the threshold temperature that we are talking about for a given pressure. So, at a given pressure the temperature at which a pure substance changes phases that is called the saturation temperature. But we can also get it corresponding to pressure, that is by maintaining the temperature constant if we vary the pressure we can get the similar effect and that pressure is called the saturation pressure. So, at a given temperature the pressure at which a pure substance changes phase we call that a saturation pressure. This saturation temperature and saturation pressure are functions of each other that is for a given pressure, saturation temperature of a substance is fixed. Like, we have seen for water under atmospheric condition saturation temperature is 100 ^{0}C.

So, the saturation temperature can be written to a function of the saturation pressure alone or conversely, we can write the saturation pressure is a function of the saturation temperature alone. So, they can be represented by a line like this where with increase in saturation temperature saturation pressure also keeps on increasing. Saturation temperature, of course, a strong function of pressure is a table for water, as you can see for 100 ^{0}C, the saturation pressure is 101.4 kPa which is basically the atmospheric pressure. In fact, the idea or the scale was defined using the value of this particular value itself where, the saturation temperature of water under atmospheric pressure was marked as 100. Whereas the saturation temperature corresponding to the melting point corresponding the atmospheric pressure was marked as 0 degrees.

You can see the pressure keeps on increasing saturation temperature also keeps on increasing. Like if your pressure is 8.5 MPa, the saturation temperature can be as high as 300 ^{0}C. Similarly, any factor which leads to an exchange in the saturation pressure can cause a change in the saturation temperature. Like for example, here I have a table which signifies or which lists the change in atmospheric pressure with elevation, correspondingly the saturation temperature also keeps on changing. This particular information that is saturation pressure and saturation temperature functions of each other is very important in practical application point of view. In fact, whenever two phases are existing together, we can easily say that they are not saturated condition and therefore as long as the phase change process will go on, both the temperature and pressure will not change.

Therefore, if we have to maintain a constant temperature at a particular surface the easiest way to do that applying some kind of phase change process which suits this particular kind of application.

(Refer Slide Time: 25:31)



Property diagrams

Substance	Temper K
Air	132
Ammonia	405
Argon	151
Benzene	562
Bromine	584
n-Butane	425
Carbon dioxide	304
Carbon monoxide	133
Carbon tetrachloride	556
Chlorine	417
Chloroform	536
Dichlorodifluoromethane (R-1	384
Dichlorofluoromethane (R-21)	451
Ethane	305
Ethyl alcohol	516
Ethylene	282
Helium	5
n-Hexane	507
Hydrogen (normal)	33
Krypton	209
Methane	191
Methyl alcohol	513
Methyl chloride	416
Neon	44
Nitrogen	126
Nitrous oxide	309

Now earlier we have drawn the *Tv* diagram only for a single case which was for atmospheric pressure are 0.1 MPa and here we have seen that initially we have a compressed liquid zone during which temperature increases rapidly along with the specific volume and then we reach the saturation temperature. So, this is the saturation temperature from this point we have the phase change process going on, till with this point where we have the saturated vapor zone and then we have the superheated vapor zone. But if we change the pressure and do the experiment or repeat the experiment for some other pressures, we will get the similar trend. Like if we increase the pressure to 1 Mpa, then you will can find that there is the same trend. However, the distance between the saturated liquid point and saturated vapor point has decreased significantly.

Or if we mark that v_1 as the specific volume corresponding to saturated liquid and v_2 as a saturated vapor specific volume then the difference i.e.,

$$v_{12} = v_2 - v_1$$

that keeps on reducing with increase in pressure. Similarly, if we go to 8 MPa, there you can see it is even shorter the distinction between these two phases that keeps on coming down. On the contrary if we decrease the pressure to this level, you can see the saturated liquid point the saturated vapor point the length of the line has increased so the phase changes taking more energy and it's a slower process. And this particular trend keeps on continuing till we reach this particular scenario, a pressure of 22.06 MPa. So, as we are moving in the higher-pressure zone, the distance between the liquid and vapor is reducing signifying that the distinction between liquid and vapor is gradually diminishing.

And at this particular point, which we are marking as a critical point, the distinction with liquid and vapor is non-existent, i.e., both liquid phase and vapor phase are identical to each other. And if we do the experiment now for a pressure higher than critical pressure then there will be no phase change at all. So, for a pressure lower than critical pressure we can see there is a distinct phase change during which there is change in all the property values.

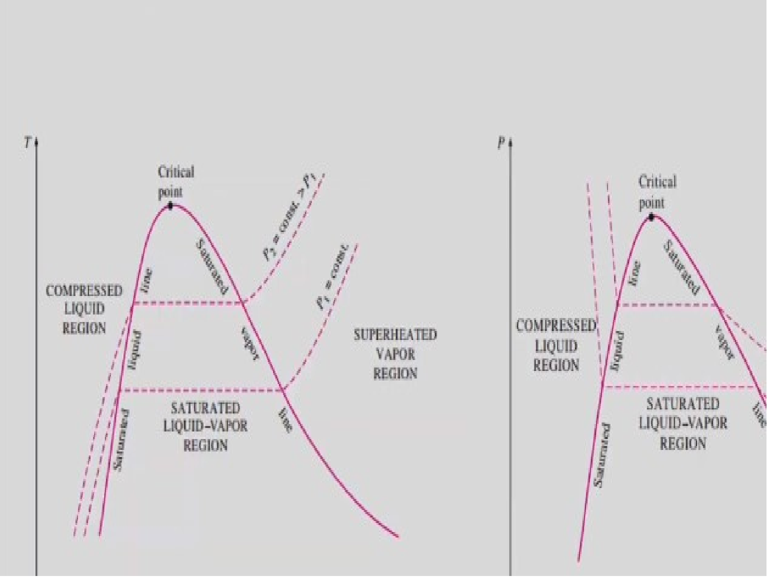
However, when we reach the critical pressure level, then the distinction between vapor and liquid vanishes or that reduces to a single point. And if we increase the pressure even further, then there is no phase change process just temperature or energy content of a system keeps on increasing continuously. So critical point is a very important point, in a way to identify the nature of a system.

Just take the example of this particular pressure level, where the pressure is lower than critical pressure. Your initial system is at this particular point and now slowly you are moving heat from this, then what path it will follow? It will come like this, then it will reach saturated vapor phase here, saturated temperature is there then it will go through the phase change process during which the vapor will get converted to liquid till it reaches saturated liquid point and then we have single phase liquid cooling. However, if the same process we are starting at this point and moving again allowing a constant pressure line, then what will happen? Here the temperature of the substance keeps on reducing in this direction, but there is no exclusive phase change it just continues in this way. So, this scenario i.e., $P > P_{cr}$ we call it as super critical pressure level.

At super critical pressure level there is no distinction between liquid and vapor phase. However as long as we are working under for a pressure below critical pressure, we shall be having a distinct phase change process. So, this is an interesting chart which lists the critical pressure for several substances. Just if for water, that critical temperature 647.1 K, critical pressure is 22.06 MPa, which is quite high, we have extremely high pressure and temperature for water, to add the critical point and therefore under normal atmospheric condition, normal atmospheric pressure levels water goes through the phase change process. However, if we are talking about a substance example for hydrogen. So where is hydrogen in the list? this is the hydrogen so for hydrogen you can find the critical point temperature is only 33 K, but pressure is reasonably high 1.3 MPa. So, its temperature is being so low under normal atmospheric condition it always remains as a super critical condition at least in terms of its temperature. And when a substance is in supercritical condition then it cannot undergo any phase change and therefore this critical point quite often serves as an important guideline or critical temperature serves as an important guideline on about which one, we should call as vapor and which one we should call gas. If we are talking about a substance at a temperature higher than the critical point, then just by compressing this one we cannot convert it to liquid. Whereas if it is lower than the critical pressure we can easily compressing to liquid. A very interesting case you may get for carbon dioxide; carbon dioxide has a critical temperature of 304.2 K which is just about 31 ^{0}C.

Its critical pressure however is quite high about 7.4 MPa. So, under normal atmospheric condition, carbon dioxide may; will be remaining as a vapor state because as long as the surrounding temperature is lower than 30 ^{0}C we can treat this to be a vapor.

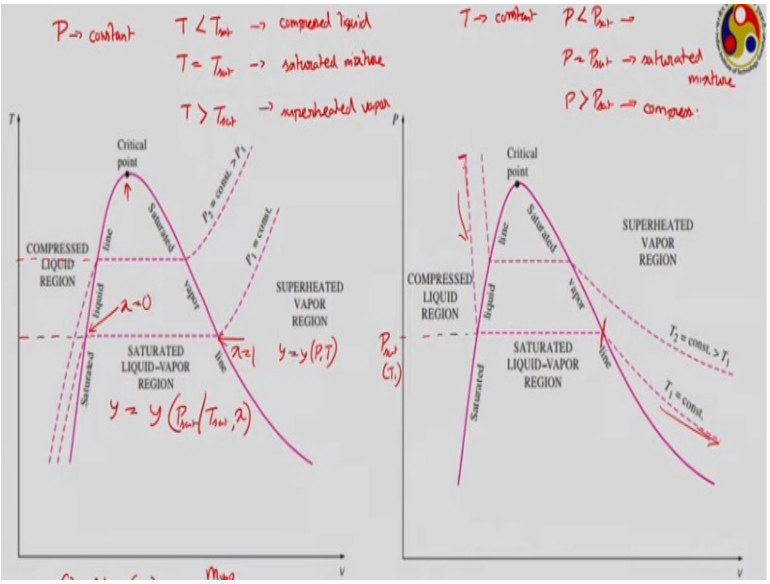
(Refer Slide Time: 31:46)



So, these are the two common property diagrams where we generally plot the phase change processes. If I just go back, you can see for each of the pressure levels now you are getting a saturated liquid point and a saturated vapor point. So, if we join all the saturated liquid points, till the critical point then we should be getting a line which is called the saturated liquid line.

Similarly, if we join all the saturated vapor points till the critical point then we shall be getting another line which is called the saturated vapor line. So, this will be your saturated liquid line, this will be your saturated vapor line.

(Refer Slide Time: 32:34)



And that is exactly what we have here, we have a saturated liquid line which is exactly the locus of all the saturated liquid state. We have a saturated vapor line which is the locus of all the saturated vapor state and they are connected at the critical point. On the left-hand side of this dome like structure we call it compressed liquid, on the right-hand side we call it the superheated vapor and inside we have a saturated liquid-vapor mixture.

Now, in the compressed liquid zone as I have mentioned, the property of any substance can be mentioned as a function of pressure and temperature. Similarly, superheated vapor zone it can be a function of pressure and temperature. Then what about the mixture zone? In this zone we know that for a given pressure, the temperature is constant and vice versa. And therefore, pressure and temperature both are not independent of each other.

However as per the phase rule, we need to identify two independent intensive properties and therefore we should not take both pressure and temperature here for defining the properties of saturated liquid-vapor region. If we say y is one of the properties, then it will be a function of either the saturation pressure or saturation temperature, because specifying one of them is symbolizes specification of the other.

But we need a second property now. So, what can be a second property, second property is called quality generally denoted by x. Quality refers to the mass of the vapor phase in the mass of the mixture. So, in this liquid-vapor we have mixture zone we shall be using this quality as the second independent intensive properties. At this particular point, we have 100% liquid so this is called $x = 0$. At this particular point, we have 100% vapor we call it $x = 1$ or 100%.

There is another diagram which is again very common is the Pv diagram. In case of a Pv diagram, here we follow a constant temperature line, it starts from this point onwards and maintain the temperature constant. So, at this point, if we keep on reducing the pressure of the substance continuously then what will happen?

As the pressure reduces, the substance will expand in its volume. So, moving in this direction gradually until it reaches the saturated liquid state. Then with further reduction in pressure actually pressure will remain constant and we should go through a liquid-vapor or saturated mixture region till we reach the saturated vapor point and then with further reduction in pressure we moving this particular direction T_1 where the T_1 is constant.

So, from a given state, we can identify or we can achieve the phase change process by varying either pressure or temperature. And then how can we define a common criterion for that? When we are having pressure constant then, when temperature is less than saturation temperature, we call it compressed liquid. Like, if we look at the first diagram this for this given pressure this is the saturated saturation temperature.

Similarly, for the second pressure P_2 level this is the saturation pressure. Saturation temperature, when temperature is equal to saturation temperature then where are we? We are in a mixture zone or I should write the saturated mixture zone. Now we can still be at $x = 0$ that is saturated liquid or $x = 1$ the saturated vapor state, but these two end points are also part of the saturated mixture. And when temperature is greater than saturation temperature corresponding to the pressure, then what we shall be having? We are into this super-heated vapor zone. Then what about in terms of pressure? That is when temperature is constant, then what we can say we can have again three scenarios: pressure less than saturation pressure, pressure equal to the saturation pressure or pressure greater than the saturation pressure. So, when pressure is equal to saturation pressure, we know that, that is saturated mixture.

Now, which one is compressed liquid and which one is superheated vapor among these two? Just a look at the *Pv* diagram for this given temperature T_1 this is your saturation pressure P_{sat} corresponding to T_1. So in the compressed liquid zone what about the pressure it is higher than saturation pressure or lower than saturation pressure? It is higher so when pressure greater the saturation pressure we are into the compressed liquid zone.

Whereas when the pressure is less than saturation pressure, we are here, i.e., we are in the super-heated vapor zone. So just from the knowledge of pressure and temperature values and by getting either saturation temperature or saturation pressure we can easily identify each of the three states. Like, for example, suppose I give you your data that I am giving you some quantity of water under 10 bar pressure and a 250 ^{0}C temperature. This is the state point pressure and temperature given and you have to identify exactly where it lies. So, what should you do is to get the saturation temperature corresponding to this pressure corresponding to this 10 bar, the graph that I have shown you there are standard tables which you shall be discussing in the next lecture. But some sample examples I have given you the previous slide itself.

If we can form some tables etc, if we can get the value of the saturation temperature corresponding with this pressure, then we have to use these criteria. That is if this 250 ^{0}C is greater than this then we know it is super-heated vapor, if it is less than this, it is compressed liquid or subcooled liquid and if it is equal to these 250 ^{0}C, saturation temperature then we are in the mixture zone, i.e., saturated liquid-vapor mixture region and we may be having a phase change process going on. Now, I would also like to mention here why you are calling it compressed liquid than on sub-cooled is quite logical which refers to temperature lower than saturation temperature. But compressed actually is referred to this particular condition, pressure greater than saturation pressure.

Here the system is being subjected to pressure greater than his saturation pressure and that is why you call it a compressed liquid. Whereas in the super-heated vapor zone there is nothing called expanded vapor kind of term. But here the pressure is lower than the saturation pressure. So these are the two most common diagrams that we use to represent the liquid-vapor phase-change processes either liquid to vapor or vapor to liquid.

And now we know that from the knowledge of pressure and temperature how we can identify the state in any one of the three regions and also have been introduced to this concept of this quality, as the second intensive property to characterize the mixture zone. Use of this quality we shall be learning in this next lecture.

(Refer Slide Time: 40:59)

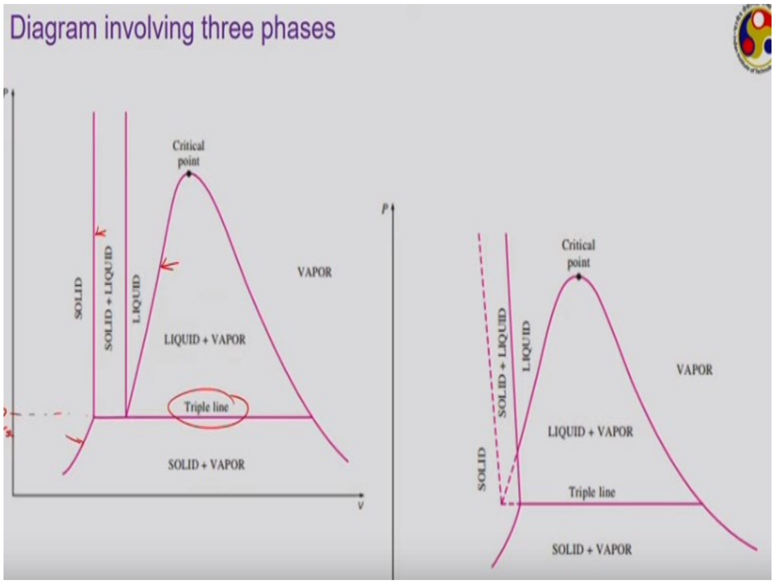


Diagram involving three phases

Now, we have so far talked about the liquid and vapor phases but quite often we may have to encounter the three phases simultaneously. And then we can expand our diagrams, *Pv* or *T*v diagrams we incorporate the solid phase as well here I have put only the solid *Pv* diagram. Let us say, we start at a point like this and move along a constant pressure line. So, if we are moving in this direction starting from super-heated vapor state, then as the energy is taken out of the system its volume will reduce till it reaches this particular situation what we call this the super-heated vapor zone. We started superheated vapor and now we reached the point which is the saturated vapor. Then with further removal of energy to go through the phase change process vapor getting condensed back to liquid till we get to 100 % liquid point. So, what do you call this state? It is called the saturated liquid state. Now, with further remove removal of energy there will be further reduction in the specific volume and we are into the sub-cooled or compressed liquid state and this will continue till we attain the melting point temperature. Here one thing is important to know that, here the for the vapor phase we are having this much of changes specific volume whereas for liquid we are having only this much.

But the corresponding change in temperature may not be or it is not that the change in temperature for the vapor case is much larger compared to the liquid rather it can completely opposite. But liquid is mostly incompressible and therefore the change in its volume because of the change in temperature is quite small. Now once we attain the melting point, they need to go through a phase change process again during the change in the temperature and pressure, both remains constant this is a point where we reach the 100 % solid point. So, this particular point can be identified as a 100 % liquid because in terms of the solid-liquid phase change. Similarly, this point is 100 % solid where the phase change is completed, we can define equality in like the like the previous case here as well. Where quality can be just a fraction of liquid in that total mixture or mass fraction of liquid in a total mixture. Then we thought the removal of energy we have temperature going down for the solid phase. So, this is the way we can plot the diagram involving all the three phases. But as we keep on reducing the pressure, we may reach a situation like this where along a particular line all the three phases can coexist in equilibrium. That particular line is called triple line.

Above the triple line like we can see the liquidity of phase change is going on maybe if you are having somewhere here at this particular specific volume and pressure level. At this particular state point, we have liquid-vapor existing in equilibrium and also solid-vapor mixture existing in equilibrium. So triple line refers to the line along which all three phases can simultaneously exist in equilibrium.

Like, if we talk about this particular line liquid and vapor can coexist in equilibrium under saturation. If we talk about say this particular line along this line solid and liquid can exist in equilibrium. Similarly, if we talk about say this particular line solid and vapor can coexist in equilibrium. But along the triple line all three phases can coexist in equilibrium. This triple line therefore is an important concept.

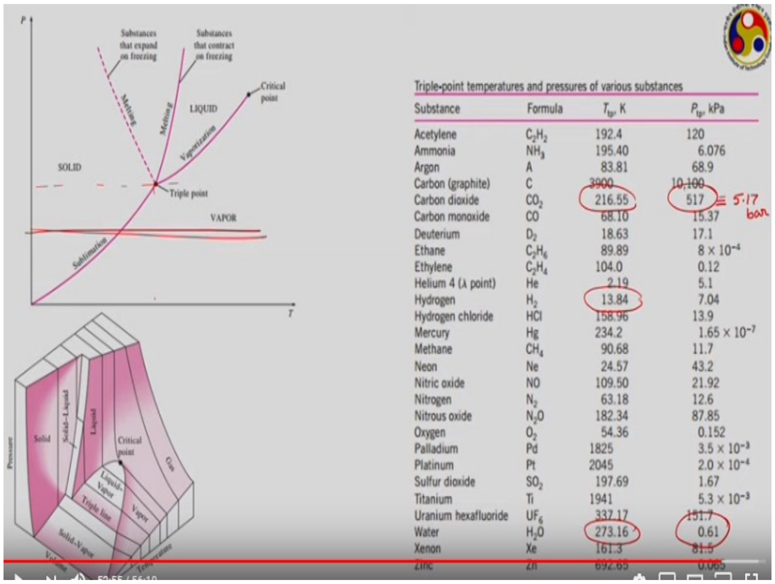
We can see that the solid to vapor phase change is possible only when your pressure is below the pressure corresponding the triple line. Therefore, when we are at a pressure level above this triple line level, like if we extend this particular pressure often called that triple point pressure or triple pressure. So, once we are at a pressure above the triple pressure then we can have solid to vapor conversion only through liquid.

That is a solid has to convert and get converted to liquid first and then that liquid will get converted to vapor. However, when we are below that triple point pressure, then solid can directly get converted to vapor and liquid is non-existent, liquid state cannot exist below the triple point. So, this is the common diagram common *Pv* diagram involving all the three phases. But there are certain exceptions also. For substances which expands on freezing, commonly we know that for all substances as it freezes the volume reduces i.e., volume of solid is lesser than the volume of corresponding liquid. Or conversely, we can say that the density of solid is higher than the density of corresponding liquid. But that is not true for certain common kind of substances for which density of solid actually is lower than density of corresponding liquid.

Can you think about any common example? Definitely, water has his highest density at 4 ^{0}C as smallest specific volume. Now, as the water temperature reduces from 4 ^{0}C to 0 ^{0}C, actually its density keeps on decreasing a specific volume keeps on increasing. And once it gets converted to ice then the specific volume is even higher and therefore liquid water at 4 ^{0}C is having a higher density compared to solid.

And hence for water, the solid contracts on freezing and leading to this kind of modification in the corresponding diagram. Mind you that such kind of anomalous expansion though very uncommon but it is not only a new unique characteristic of water, there are several other substances also, which can show us kind of anomalous expansion substances like Bismuth, Antimony, Germanium, Gallium and Silicon okay acetic acid can be another good organic example. These all generally give certain kind of anomalous expansion i.e., their solid is lighter than the corresponding liquid. But for most of the common substances this diagram itself is sufficient. Quite often instead of plotting in *Pv* or *Tv* plane, we just plot the profile for pressure and temperature. This allows us to represent all the three phases and their corresponding transition lines easily.

(Refer Slide Time: 47:23)



Triple-point temperatures and pressures of various substances

Substance	Formula	T_{tp}, K	P_{tp}, kPa
Acetylene	C_2H_2	192.4	120
Ammonia	NH_3	195.40	6.076
Argon	A	83.81	68.9
Carbon (graphite)	C	3900	10,100
Carbon dioxide	CO_2	216.55	517 = 5.17 bar
Carbon monoxide	CO	68.10	15.37
Deuterium	D_2	18.63	17.1
Ethane	C_2H_6	89.89	8×10^{-4}
Ethylene	C_2H_4	104.0	0.12
Helium 4 (λ point)	He	2.19	5.1
Hydrogen	H_2	13.84	7.04
Hydrogen chloride	HCl	158.96	13.9
Mercury	Hg	234.2	1.65×10^{-7}
Methane	CH_4	90.68	11.7
Neon	Ne	24.57	43.2
Nitric oxide	NO	109.50	21.92
Nitrogen	N_2	63.18	12.6
Nitrous oxide	N_2O	182.34	87.85
Oxygen	O_2	54.36	0.152
Palladium	Pd	1825	3.5×10^{-3}
Platinum	Pt	2045	2.0×10^{-4}
Sulfur dioxide	SO_2	197.69	1.67
Titanium	Ti	1941	5.3×10^{-3}
Uranium hexafluoride	UF_6	337.17	151.7
Water	H_2O	273.16	0.61
Xenon	Xe	161.3	81.5
Zinc	Zn	692.65	0.065

So, you can clearly see on this *PT* plane that three phases solid, liquid and vapor. And on the such *PT* diagram the triple line contracts to a single point which is called a triple point. It is again a unique characteristic of any system quite similar to that critical point.

Like critical point is unique for a given substance same as the triple point. Critical point, the importance is above the critical point we generally call it gas and below we call it a vapor. Because a substance which is above critical point, we cannot change its phase very easily. Similarly, for triple point you can clearly see, if as we have drawn from the previous diagram the same thing.

Below triple point we can have only solid and vapor phase but no liquid phase whereas, above the triple point, we have above the triple point pressure I should say we can have all the three phases. If we see in terms of temperature, then for common substances which contracts and freezing below triple point temperature also we cannot have liquid.

We can have only the solid or vapor phases below the triple point temperature. But the exception on substances like water, which expands on freezing their corresponding melting line is this dotted one that is the solid to liquid phase change. So, for that substances we can still have a liquid existing below the triple point temperature. Like for water under normal atmospheric condition water freezes at 0 ^{0}C. However, if we go to very high-pressure levels say at 200 MPa, we can still have water liquid state at − 20 ^{0}C, that is because of this anomalous expansion. So, in this diagram we have the dotted line for the substance that expand on freezing and for common substances this is a melting line which represents that change in phase from solid to liquid or liquid to solid.

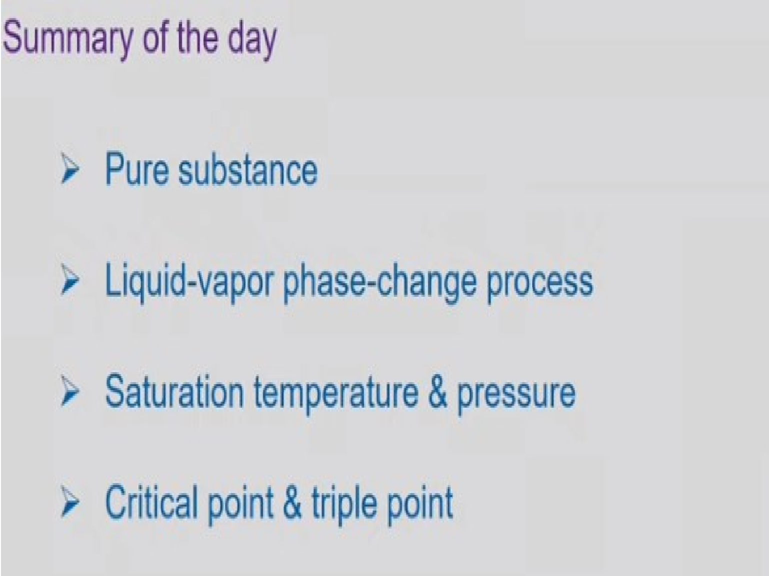
This is the vaporization line which represents the transition from liquid to vapor or vapor to liquid. See the vaporization line finishes at critical point which is not applicable for a melting point line. Melting line can be extended up to infinity but beyond the critical point there is no distinction between liquid and vapor and therefore vaporization line stops there. And this is sublimation line sublimation refers to the process of digital conversion from solid to vapor or vice versa vapor to solid. Actually, sublimation is a solid to vapor conversion vapor to solid often we call it solidification or vapor solidification. So, this line is the corresponding characteristic. These are the triple point temperature and pressure values for certain common substances for water, the triple point temperature is 273.16 K or 0.01 ^{0}C.
Till very recently, this one used to be the reference temperature based on which all the thermodynamic temperature states used to be defined, but that has recently changed. So, its critical is triple point is a quite low and its triple point pressure is extremely that is 0.61 kPa that I should say or, 611 Pa only. Certain substances can have a quite interesting triple point temperature value. Like if we say again for substances like hydrogen, for hydrogen the triple point temperature is 13.84 K. So, hydrogen cannot exist in liquid phase below this temperature. Another excellent example can be carbon dioxide which has a triple point of 216 K which is less than 0 ^{0}C.

That is under common atmospheric condition, carbon dioxide is a substance which is the like normal substances it expands on freezing. So, if we see often normal atmospheric condition say carbon dioxide at a temperature of atmospheric say, 300 K, then exactly where the carbon dioxide will be located? So, 300 K triple point temperature for carbon dioxide is 216.55 K, so it will be somewhere here maybe somewhere along this line.

And what about its critical triple point pressure? Its triple point pressure is 517 kPa or we can write this one as 5.17 bar, i.e., it is 5 times atmospheric pressure. So, under normal atmospheric pressure, this is the triple point pressure. Under normal atmospheric pressure carbon dioxide maybe located somewhere along this line and that is why carbon dioxide cannot be liquid state under normal atmospheric condition. It can remain either in a solid state or vapor state, but not in liquid state, simply because of the high triple point pressure. Quite often instead of drawing separate *Pv*, *Tv* and *PT* diagrams, we present them in a three-dimension plot like this. This is a plot for common substances that contracts on freezing whereas this is for exceptional substances showing anomalous expansion which expand on freezing.

The *Pv*, *Tv* or *PT* diagrams can be thought about as the three projections of this particular thing. If we talk about this particular one, if you take the front view, we are going to get the *Pv* diagram. Whereas if we take the side view from this side then you are going to get the *Tv* diagram and this way we can get the projection for each of these diagrams and to each of these three-dimensional representations to plot all the three i.e., *Pv*, *Tv* or *PT* planes.

(Refer Slide Time: 53:32)



Summary of the day

- Pure substance
- Liquid-vapor phase-change process
- Saturation temperature & pressure
- Critical point & triple point

So that takes us to the end of our discussion for the day. We have actually tried to review the thermodynamic terms associated with a phase change process, quite quickly we defined the pure substance and then talked about the liquidity for phase change process in detail defining the concept of saturation pressure and saturation temperature, then leading to the concept of critical point triple and a triple point.

We introduced the diagrams that is *Pv, Tv* diagrams and even the *PT* diagrams also. The critical point is a very important criteria I keep on repeating which allows us to identify a substance which whether that can be condensed on applying pressure or not. If required I can discuss a bit more on the importance of critical point in the next lecture. Triple point is something that is associated with the simultaneous existence in equilibrium for all the three phases.

And triple point for common substances allows us to understand whether we can have a liquid state or not. Like common substances like carbon dioxide which has a high triple point pressure cannot be in liquid state and along with atmospheric condition that is because of its triple point value. We have also discussed about the property diagrams, three diagrams and also their combination in terms of a three-dimensional projections.

So that takes us to the end of todays discussion I would like to thank you for the attention but I have gone through very quickly through today's topic. Because I hope in your basic thermodynamics we have already been introduced to these terms. But in the next lecture, I would like to spend a bit more time to understand about how to calculate the properties of pure substances in each of these regimes.

Like when it is in the super-heated vapor regime or compressed liquid regime or most importantly when it is in the mixture regime. How to calculate all the properties? How to use the property diagrams? And maybe a little bit more on the importance of a critical point. So, till then be patient and review your literature review the lecture and wait for the next one. Thank you.