

Basics of Mechanical Engineering-3

Prof. J. Ramkumar

Prof. Amandeep Singh Oberoi

Department of Mechanical Engineering

Indian Institute of Technology, Kanpur

Week 04

Lecture 16: Pure Substances, Phase and Phase Change

Welcome to the next lecture on Pure Substance, Phase, and Phase Change. You know very well that matter can exist in solid form, liquid form, or gas form. In thermodynamics, you also know there are only three parameters: P, V, and T. Now the question is, how do I link these with all three forms? That is what will be the prime focus of this lecture. So, a solid can undergo a phase change and become a liquid.

A liquid can undergo a phase change and become a gas. When we apply temperature during a phase change, the volume expands. When temperature is applied, the volume expands. When the volume expands, the pressure drops. Now, what you can do is try to control the pressure or try to control the volume.

Then observe what happens to the temperature and what happens to the pressure. So, you can try to control any one of them and find out their relationship. That is what will be covered in this lecture. When we talk about gas, there is gas, and generally, we also use water. So, it becomes steam.

Now, in steam, there is a limit. So, that is called a saturation limit. So, how much steam can water take? So, that is what is going to be there. So, with this understanding, we will try to venture into this lecture. Very simple, and it is very fundamental.

Contents



- Pure Substance
- Phase of a Pure Substance
- T-v Diagram for a Pure Substance
- P-v Diagram for a Pure Substance
- P-T Diagram for a Pure Substance

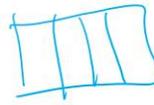


So, the content of this lecture is going to be pure substance. Friends, pure substance is again a theoretical one. Whenever it is converted into an engineering application, it becomes an alloy or a mixture. So, you add some more material. Just for discussion's sake, we always take pure substance.

Then you can ask, why are you doing so? See, I cannot bring all the different phases in my modeling. The modeling becomes tougher. So, that is point number one. The second thing is, when I try to take the predominant presence, for example, 80% of X is there, 20% of Y is there.

Now, the overall behavior will be dictated by that AT in a large condition. So, that is why we are always happy with the Pure Substance. Then, Phase of a Pure Substance. We will try to see the Temperature-Volume Diagram for Pure Substance, then the Pressure-Volume Diagram for Pure Substance, then the Pressure-Temperature Diagram for a Pure Substance. Then, from there, we will try to move on and see what the PVT Surface is. Then, Properties of Pure Substances: Volume, Enthalpy, and Internal Energy. Saturation Temperature, Saturation Pressure, then Quality. Then, finally, we will try to see Supercritical Fluid Behaviors.

Pure Substance



- A pure substance is defined as a substance with a uniform chemical composition and consistent physical properties throughout its entire mass, regardless of the phase it is in.
- It can exist as a solid, liquid or vapor—or a combination of these phases—but remains chemically homogeneous.
- This concept is fundamental in thermodynamic analysis, as it allows the use of property tables, phase diagrams, and equations of state to describe the behavior of the substance during processes such as heating, cooling, compression, and expansion.



Pure Substance: A Pure Substance is defined as a substance with a uniform chemical composition and consistent physical properties throughout the entire mass, regardless of the phase in it. The definition is very clear. A Pure Substance is defined as a substance with uniform chemical composition. I try to take a section anywhere.

Cut it, and the composition will be uniform and have consistent physical properties, right? From anywhere you take, it will have consistent physical properties throughout the mass, regardless of its phase, and is called a Pure Substance. What are phases? Solid, liquid, gas. It can exist in solid, liquid, or vapor—the phase I am referring to.

Or it can also exist in a combination of phases, but remains chemically homogeneous, right? So what it means is: I can have a semi-solid. So it can be 50% solid, it can be 50% liquid. Where is it used? Predominantly in polymers.

When we do injection molding, we always take it to a semi-solid state or a viscoelastic state. It is in between. So that's what a combination of these phases is. You can have a liquid and a vapor phase also. This concept is fundamental in thermodynamic analysis, as it allows us to use the property tables, phase diagrams, and the equations of state to describe the behavior of the substance during the process of heating, cooling, compression, and expansion.

So this is very important because I can derive it. There are tables available. We will see some of the tables in the next lecture. So there are property tables. From there, I can bring out all those things.

So you can see here, made of two or more different types of atoms chemically bonded together in a fixed ratio is water. You can have salt. You can have carbon dioxide. These are all combinations.

Pure Substance in Thermodynamics



- Water, refrigerants, and steam are common examples of pure substances extensively used in thermodynamic systems like power plants, refrigeration units, and engines.
- The study of pure substances provides the foundation for understanding phase change phenomena, energy transfer and thermodynamic cycle efficiency.
- **For example, water is a pure substance whether it is in the form of ice, liquid, or steam.**
- In thermodynamics, pure substances are crucial because they allow for simplified analysis of energy and phase changes, as their properties are consistent and well-documented.
- The study of pure substances helps engineers and scientists to understand phase diagrams, analyze thermodynamic cycles and **predict the behavior of systems during heating, cooling and phase transitions.**



Water, refrigerant, and steam are common examples of Pure Substance extensively used in thermodynamics because we always use water in boilers, in steam turbines, in pressure cooker, we use water, right?

Refrigerant when there is a heat extraction to be done in a closed volume or heat dumping it into that, so we try to always use the refrigerant. Then Steam is used for driving and generating work out of it. As systems, they are used in thermodynamic systems like power plant, refrigeration unit and engines. The study of these Pure Substances provide a foundation for the understanding of phase change phenomena, energy transfer and thermodynamic cycle efficiency. We will later see when there is a cycle coming into existence, we always have to find out the efficiency of the cycle. Why efficiency?

Because this tries to talk about the input I give and the output I extract. So it is thermodynamic cycle efficiency. For example, water is a pure substance, whether it is in

the form of ice, liquid, or steam. In thermodynamics, the pure substances are crucial because they allow to simplify analysis. This is what I was trying to say.

It will allow us to perform simplified analysis so that you can quickly derive the first principle. You can try to find out what is going on. They allow for simplified analysis of energy and phase change as their properties are consistent and well documented. For that reason, we always try to use a pure substance. The study of pure substances helps engineers and scientists understand phase diagrams, analyze thermodynamic cycles, and predict system behavior during heating, cooling, and phase transitions.

So this is very important. So it helps engineers and scientists understand phase diagrams, analyze thermodynamic cycles, and predict system behavior during heating, cooling, and phase transitions.

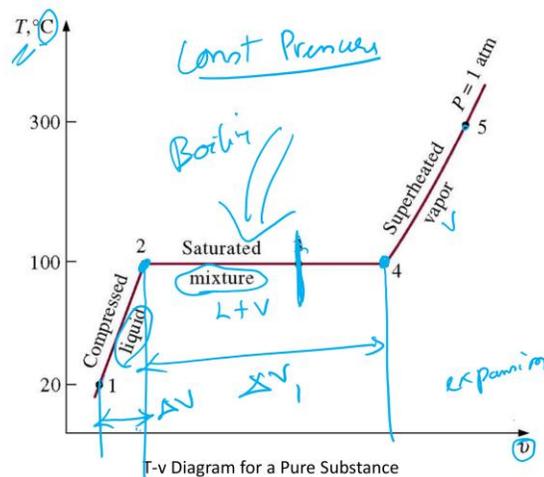
T – v Diagram of a Pure Substance



T-v diagram for a pure substance is a graphical representation of relationship between its **Temperature** and **specific Volume**, often used to visualize phase changes and other thermodynamic processes.

It visually conveys how heat addition affects the phase and specific volume of a substance at constant pressure.

The horizontal axis (v) denotes the specific volume, and the vertical axis (T) indicates temperature in degrees Celsius.



T-v Diagram for a Pure Substance

<https://www.tesistat.org/en/pure-substance-and-features.html>



So this is a simple diagram, a T-V diagram (Temperature versus Volume diagram). This is the graphical representation of it. So whatever volume comes, you can also try to convert it into specific volume.

Specific volume is per unit. So that becomes specific volume. The graphical representation of the relationship between temperature and specific volume is often used

to visualize phase changes. Other thermodynamic properties are also very important. So, if you try to see, this exists in a liquid phase.

When you compress it, it gets saturated. There is a mixture of liquid and vapor. Then, after point number 4, it becomes superheated. So, it gets into a vapor phase. So, a liquid, when you heat it, gets a mixture of L plus V, and then here it is going to be V. So, it visually conveys how heat addition affects the phase and the specific volume change of the substance at a constant pressure.

I write it as constant pressure because what happens to pressure that is also a variable. For example, inside a pressure cooker, you fill it with water, put rice in it, and then heat it. You keep on heating it. The volume is restricted inside a pressure cooker. What happens to the pressure?

It keeps changing, right? So, but here in this diagram, I try to keep the pressure constant. Why is this important? When we try to do a phase formation or a mixing of two phases in metallurgy, or heat treatment, or in cooking, or any other process where heat is involved. So then this becomes handy.

At what temperature should we try to mix the other substance such that we can get what we want? For example, mixing something at this phase between 2, 3, and 4 is going to be easy. 2 is the end of compression of the liquid phase. 4 is the end of the mixture phase, and 5 is the end of the superheated phase. So, the horizontal axis V denotes specific volume, and the vertical axis represents the temperature change. And friends, I have already told you that degree units are very important.

T – v Diagram of a Pure Substance



- The curve begins at point 1, which represents the subcooled or compressed liquid state.
- **At this point, the liquid is at a temperature below its saturation temperature for the given pressure.**
- As the substance is heated from point 1 to point 2, the temperature increases with only a slight change in volume, remaining in the compressed liquid region.
- At point 2, the liquid reaches the saturation temperature (100°C at 1 atm), becoming a saturated liquid.
- From point 2 to point 4, the substance exists as a saturated mixture, transitioning from saturated liquid to saturated vapor.
- **During this phase change, known as boiling or vaporization, the temperature remains constant while the specific volume increases significantly.**



The curve begins at point 1, which represents a sub-cooled or compressed liquid state. Normal. At this point, the liquid is at a temperature below its saturation temperature for a given pressure. Friends, please note down the terminology called saturation temperature.

Because later, you will always try to understand what saturated heat is. All these things will be there. So, saturated temperature. At this point, the liquid is at a temperature below its saturation temperature for a given pressure. As the substance is heated from 0.1 to 0.2, you are moving from 20 degrees Celsius to 100 degrees Celsius with only a slight change in volume.

So you can see here, the volume does not change to a large extent. This is ΔV . The ΔV is not very high. So the temperature increases with only a slight change in volume, remaining in the compressed liquid region. At point 2, the liquid reaches the saturation temperature.

What is saturation temperature? It is at 1 atmosphere. You try to reach the saturation temperature, becoming a saturated liquid. From 0.2 to 0.4, the substance exists as a saturated mixture, transitioning from saturated liquid to saturated vapour. So saturation temperature, saturated liquid, saturated vapour. During this phase, known as boiling or vaporization.

During this phase, 2 to 4 is known as boiling or vaporization. So when we talk about thermal power plants or some of the cycles, we always say boiling. So boiling means there is a phase change between liquid and gas without a change in temperature. The temperature remains constant while the specific volume increases significantly. From here to here, you see the ΔV is larger. Friends, it looks very fundamental, but this is going to be very useful for you when we start looking into the cycles.

T – v Diagram of a Pure Substance



- Point 3 represents a state within this mixture where both liquid and vapor phases coexist.
- At point 4, the substance becomes a saturated vapor, meaning all the liquid has vaporized.
- Further heating from point 4 to point 5 leads to the superheated vapor region.
- **In this phase, the vapor's temperature rises beyond the saturation temperature and it behaves increasingly like an ideal gas.**
- The curve from point 4 to point 5 shows that specific volume increases substantially as temperature rises.
- **This T-v diagram is crucial for understanding the thermodynamic behavior of pure substances, especially in applications involving phase change processes such as boiling, condensation and steam power generation.**

Point 3 represents a state within this mixture where both liquid and vapor phases coexist. Where is point number 3? The temperature is constant, the volume is expanding, you are taking a midpoint or offset of a midpoint, and here what we are trying to see is where there is a mixture of liquid and vapor phases coexisting. So, sometimes it is tricky when liquid and vapor phases coexist. Suppose you are trying to remove all the vapor from that phase; it is going to be a little tougher.

It is going to be a little tougher. So, we will try to see the liquid and vapor phases. At point 4, the substance becomes a saturated vapor. At point 4, it becomes completely vapor, meaning all the liquid has vaporized. Now you see there is not much of a ΔV change as you saw between 2 and 4.

Volume change, specific volume change. So, at point number 4, the substance becomes a saturated vapor, meaning all the liquid has vaporized. Further heating from point 4 to

point 5 leads to the superheated vapor region. So now, the heat, whatever vapor is there, is going to be completely in the vapor phase only. So, in this phase, the vapor temperature rises beyond the saturation temperature, and it behaves increasingly like an ideal gas.

So, in this phase, the vapor temperature rises beyond the saturation temperature, and it behaves increasingly like an ideal gas. The curve from 0.4 to 5 shows that the specific volume increases substantially as the temperature rises. So, what happens is we are going from this phase, right? So, when the temperature increases, the volume also increases. So, here the curve from 0.4 to 5 shows the specific volume increases substantially due to the temperature rise.

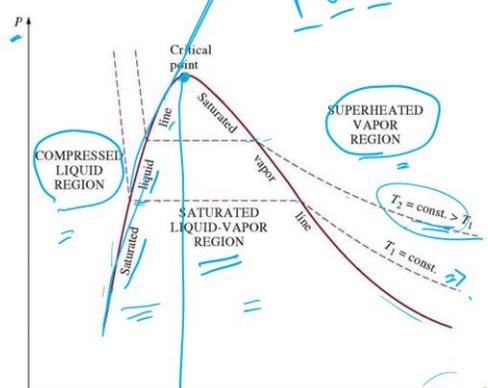
This TV diagram is crucial for understanding the thermodynamic behavior of pure substances, especially in applications involving phase change processes such as boiling, condensation, and steam power generation. So now you know, where does boiling happen? Where is the expansion happening, the volume expansion? So it is specific volume expansion, by the way. Till now, what we saw was the Temperature-Volume Diagram.

P-v Diagram of a Pure Substance

A P-V diagram for a pure substance is a graphical representation of the relationship between its **Pressure** and **Volume** as it undergoes various thermodynamic processes, showcasing the different phases and phase transitions.

It is a foundational tool in thermodynamics for understanding how substances behave under different pressure and volume conditions.

It prominently features the dome-shaped saturation region, which is bounded by the saturated liquid line on the left and the saturated vapor line on the right.



P-v diagram of a pure substance.

Now let us try to see the Pressure-Volume Diagram. The relationship of Pressure-Volume. Because, as I told you, there are only three parameters. P, V, T. First, we saw temperature and volume. Now, we are trying to see pressure and volume.

The P-V diagram of a pure substance graphically represents the relationship between pressure and volume. It undergoes a thermodynamic process, showing the different phases and phase transitions. So, you have this line, where you try to talk about the saturated liquid line. And this is the saturated vapor line. This is the liquid line, and this is the vapor line.

When you compress it, it is in the liquid region. When it is supersaturated, it is in the vapor region. So, in between these two, there is a transition region called the saturated liquid-vapor region. So, this is how it is, right? So, you have a saturated liquid line and then a saturated vapor line.

So, you can try to; if here it is liquid, here it is vapor. So, now, if you want to do anything—say, for example, boiling—if I want to do it, I have to go for superheated boiling. So, then I will have to get into this vapor phase. If boiling happens here, but here, if I go, it is completely vapor. So, when it is completely vapor, I will get better performance.

Liquid is expansion. So, from vapor to liquid is expansion. From here liquid to vapor, you can try to saturation mixed, you can try to do by boiling phase. So, this diagram tries to tell that the top most point is called as a critical point, where there is a change in the phase from liquid to vapor. So this is for a constant T and this is for a T which is greater than constant T1 for a temperature change. So now you can try to understand little bit more.

This curve is very important because later when you see the cycles, what you will do is you will try to move in the compression stage, you will try to move in the expansion stage. So when you try to do it, what happens to the liquid is the understanding. It is a foundation tool in thermodynamics for understanding how substances behave under different pressure and different volume in different phases. It predominantly features the dome shape. This dome shape will come which is a dome-shaped saturated region.

It is bound by the saturated liquid line on the left side and the saturated vapor line on the right side. So, this is the critical point. So, below this critical point, you will have liquid, and after this, you will have vapor, but inside the dome, you will have a liquid-vapor

mixture region. But once you get out of this dome, you will have a vapor or you will have a liquid.

P – v Diagram of a Pure Substance



- The area under the dome represents the saturated liquid-vapor mixture region, where both liquid and vapor coexist in equilibrium.
- The left region of the dome is known as the compressed (or subcooled) liquid region, where the substance exists purely in the liquid phase at a pressure higher than the saturation pressure corresponding to its temperature.
- The right region of the dome is the superheated vapor region, where the substance exists entirely in the vapor phase at a temperature higher than the saturation temperature for the given pressure.
- At the top of the dome lies the critical point, a unique condition where the saturated liquid and saturated vapor lines meet.
- Beyond this point, the distinction between liquid and vapor phases ceases to exist and the substance becomes a supercritical fluid.



The area under the dome represents the saturated liquid-vapor mixture region, where both liquid and vapor coexist in equilibrium. This is what we say: coexists. The left region of the dome is known as the compressed liquid region, where the substance exists purely in liquid form. For example, if I put the pressure cooker on the burner and assume a constant temperature, when I try to adjust the pressure and volume, I keep increasing the pressure. The liquid gets converted into the saturated liquid line region, then into a liquid-vapor mixture, and then it exits. So, the pressure keeps increasing.

So, I am increasing the pressure along this region. An idealistic case, right? And volume; when pressure increases, volume also increases. It need not be the case. Here, in this particular region, when the pressure increases, the volume increases—this is the response we observe from the working fluid. So, the right region of the dome is the superheated vapor region, where the substance exists entirely in the vapor phase at a temperature higher than the saturated temperature for a given pressure. The top of the dome lies the critical point, a unique condition where the saturated liquid and saturated vapor lines meet.

Saturated liquid and vapor lines meet. Beyond this point, the distinction between liquid and vapor ceases to exist, and it becomes a supercritical fluid. So, what happens in a

supercritical fluid? You will have more energy. So, more can be done, but it is very difficult to reach the supercritical fluid state easily because temperature is always a restriction.

P – v Diagram of a Pure Substance



- Within the dome, the horizontal line connecting the saturated liquid and saturated vapor lines at a constant pressure is known as the isobaric line, and the pressure remains constant during the phase change.
- The two dashed curves labeled $T_1 = \text{const.}$ and $T_2 = \text{const.}$ $> T_1$ represent isotherms (constant temperature lines). These curves help visualize how pressure and specific volume vary at constant temperatures, with higher temperatures resulting in higher isotherms.
- **It is especially critical in analyzing systems involving phase changes, such as boilers, condensers and refrigeration cycles.**
- The regions and lines on this diagram help to identify the phase of the substance (liquid, vapor, or mixture) and predict how it will respond to changes in pressure, temperature or volume.



Within the dome, the horizontal line connects the saturated liquid. Now, we are getting within this. Within the dome, the horizontal line connecting the saturated liquid and the saturated vapor lines is the constant pressure line, which is known as an isobaric line. Now, we are trying to get into these dotted lines. Isobaric lines are constant pressure lines at a given constant pressure. So, now when the temperature increases, you can see what happens.

The volume increases, pressure is constant, temperature lines. Within the dome, the horizontal line connects the saturated. So, one side is liquid, one side is vapor, constant pressure. At a constant pressure, it is known as an isobaric line, and the pressure remains constant during this phase change. The two dashed curves labeled $T_1 = \text{constant}$ and $T_2 = \text{constant}$, which is $> T_1$, represent isotherms. So, where are they?

They are here. They are here, isotherms, right? Temperature. Because we are trying to bring in the relationship of temperature with respect to the volume and pressure. Isotherms.

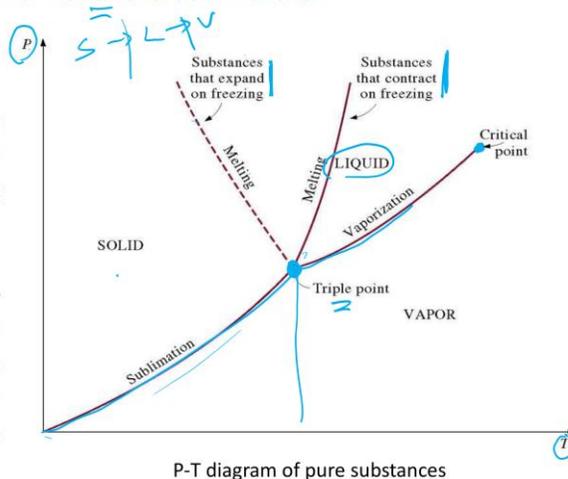
These curves help visualize how pressure and specific volume vary at constant temperature, with higher temperatures resulting in higher isotherms. It is especially critical in analyzing systems involving phase changes, such as boilers, condensers, and refrigeration cycles. These lines are very important. The regions and lines on this diagram help to identify the phase of a substance, whether it is liquid, vapor, or a mixture, and predict how it responds to changes in temperature, pressure, and volume.

P – T Diagram of Pure Substances



A P-T diagram (also known as a **phase diagram**) for a pure substance is a graphical representation that shows the phase boundaries (solid, liquid, and gas) of a substance at different **Pressure** and **Temperature** conditions.

The diagram shown is a Pressure–Temperature (P–T) phase diagram for a pure substance, illustrating the regions of stability for the solid, liquid and vapor phases and the boundaries between them.



P-T diagram of pure substances



So now, let us try to draw a Pressure-Temperature diagram for a pure substance. So this is pressure, this is temperature. So, for a pure substance, how does it look? So you can try to have an increase. Say, for example, as the pressure increases, the temperature—so this portion is called sublimation. And at sublimation, you will try to have melting at two portions.

One is a substance that expands on freezing, then a substance that contracts on freezing. So, you will have melting happening in this region, melting happening in this region, and here it will be a liquid. And the third line, which goes from here, is the vaporization line. So, the point here is called the critical point. So what was the critical point here?

See you saw the critical point here. Now we are trying to bring in the relationship. So critical point is here. So this diagram is otherwise called as triple point diagram. So wherein which we draw for a pure substance between pressure and temperature.

So a PT diagram for a pure substance is graphically represented that shows the phase boundaries of solid, liquid and gas of a substance at pressure and temperature conditions. The diagram shown is a Pressure-Temperature Phase Diagram for a pure substance illustrating the regions of stability of solid, liquid and vapor phase and the boundaries between them. So, why is it important? Solid, liquid and gas you know or vapor you know, but where is the boundary that is what is important to know. So, that is what is shown here. The stability of the solid, liquid and vapor phase and the boundaries between solid. You see solid melt, you will see that. So, this is expansion, and this is contraction.

So, friends, I would like to request you to just look at an assignment and see: when does the substance expand while freezing? When does contraction happen? You can try to see some examples.

P – T Diagram of Pure Substances



- These boundaries represent the conditions under which two phases coexist in equilibrium, and the diagram is instrumental in understanding the phase behavior of materials.
- **The curves separating these regions are known as the Sublimation, Melting and Vaporization curves.**
- The **sublimation** curve divides the solid and vapor phases and represents the conditions where sublimation (solid to vapor) or deposition (vapor to solid) occurs.
- The **melting** curve separates the solid and liquid phases and denotes the fusion (melting) or solidification process.
- The **vaporization** curve separates the liquid and vapor phases and defines the conditions for boiling or condensation.
- At intersection of all three phase boundaries lies **triple point**, a unique condition where the substance exists simultaneously in solid, liquid and vapor - in equilibrium. It is highly specific and occurs at a precise pressure and temperature for each substance.

These boundaries represent the conditions under which two phases coexist in equilibrium. The diagram is instrumental in understanding the phase behavior of the material. So the curve separating these regions is known as sublimation, melting, and vaporization curves. Sublimation is solid to vapor, melting is solid to liquid, and vaporization is liquid to

vapor. The sublimation curve divides the solid and vapor phase and represents the condition where sublimation or deposition occurs.

When you move towards real-time applications, there are several coating techniques wherein the solid will be bombarded or heated by a source, and then the metal melts, vaporizes, and gets deposited on the workpiece. So, the sublimation curve divides the solid and vapor phase and represents the condition where sublimation or deposition occurs.

The melting curve separates the solid and liquid phase and denotes the fusion or solidification process in metallurgy. When we studied metallurgy or the casting process, we saw fusion and solidification processes. When vaporization comes into existence, it is always between the liquid and vapor phase and defines the condition of boiling or condensation, right? And fusion and solidification are opposites. Sublimation, what is sublimation?

You deposit vaporization. So these things are very important. So now, in engineering terms, what we do is use these processes. And then we have material. Now we have to know what temperature and pressure we should apply such that we get into these processes, so we can try to achieve the required output.

At the intersection of all these three phases' boundaries lies a triple point, a unique condition where the substance coexists simultaneously in solid, liquid, and gaseous phases. So just at that point, it can coexist in any of those phases. So we are more interested in the triple point. A unique condition where the substance coexists in solid, liquid, and vapor in equilibrium. It is highly specific and occurs at a precise pressure and temperature for each substance.

So this point is a very critical point. A very critical point, and it is very sensitive. It is highly specific and occurs at a precise pressure and temperature for each substance. It can happen that when you heat it, it can jump over this and go. You have to moderate and find out this triple point.

P – T Diagram of Pure Substances

- Beyond the end of vaporization curve is the **critical point**, where the distinction between the liquid and vapor phases vanishes, and the substance exists as a **supercritical fluid**.
- At this point, the properties of liquid and vapor merge, and phase boundaries cease to exist.
- **On P-v or T-v diagrams** → **Triple line**
- **On P-T or T-v diagrams** → **Triple point**
- An important aspect highlighted in this diagram is the **slope of the melting curve**, which differs for substances depending on their behavior during freezing.
- For most substances, the melting curve slopes **positively**, indicating that they **contract on freezing**—that is, the solid phase is denser than the liquid.
- However, some substances, like water, **expand on freezing**, and for these, the melting curve slopes **negatively**.



Beyond the end of the vaporization curve is the critical point, where the distinction between the liquid and vapor phases vanishes, and the substance exists in a supercritical fluid form. So if you go back to the T and volume diagram, you saw this, right? So here is the critical point. So in the triple point diagram, you can see the critical point is here. So why is this point important?

Beyond this point, the substance exists in a supercritical fluid form. At this point, the properties of the liquid and vapor merge, and the phase boundaries cease to exist. At this point, because here, if you see in the diagram, we had a liquid here and a vapor, so at this point. So, at this point, the properties of the liquid and vapor merge, and the phase boundary ceases to exist. So, on a PV or TV diagram, we saw a triple line, and on PT and TV diagrams, we saw a triple point.

So, you can see here, this is the triple point. In a PV or PVT diagram, you see a triple line. An important aspect highlighted in this diagram is the slope of melting. That is very important. Why is the slope of melting important?

Because it will determine the rate at which you have to heat it, melt it, or whatever it is. The slope of the melting curve differs from substance to substance, depending on the behavior during freezing. For most materials, the melting curve slopes positively,

indicating that they contract on freezing. That is, the solid phase is denser than the liquid phase. For the majority of items, it is like this.

However, some substances like water expand on freezing. And for these, the melting curve slope is negative. So, friends, you can keep this point in mind. When is the melting curve slope negative? When is it positive?

And when you go back and read the casting process, you would have seen the diagram wherein we would have said solidification with respect to time. So, there you will see all these things; the melting curve slope is always positive, indicating that contraction on freezing happens. So, that means when you pour it, the volume will be high, and when it solidifies, it will shrink; the majority of the sweet shrinks. Right, the sweet when your mother pours it will be just—she will pour it to the vessel end size. But when it solidifies, you can see there will be a gap that forms between the end of your sweet and this.

For example, if she has a tray and then she fills it up like this, and once it solidifies, you will see the sweet will be like this. So, it is nothing but that there is a contraction on freezing that happens.

P-T Diagram of Pure Substances



- **This distinction is crucial in understanding anomalous behaviors such as ice floating on water.**
- Overall, the P-T diagram is a critical tool in thermodynamics and material science, allowing engineers and scientists to predict phase transitions, determine boiling or melting points under varying pressures, and design processes like freeze-drying, refrigeration and high-pressure chemical synthesis.
- The triple point of water is at 4.58 mm Hg and 273.16 K, whereas that of CO₂ is at 3885 mm Hg (about 5 atm) and 216.55 K.
- **So when solid CO₂ ('dry ice') is exposed to 1 atm pressure it gets transformed into vapour directly, absorbing the latent heat of sublimation from the surroundings, which gets cooled or 'refrigerated'.**

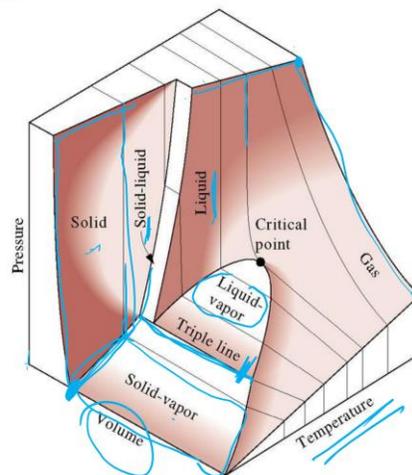
This distinction is crucial in understanding anomalous behavior, such as ice floating on water. When does ice float in water, or why does ice float in water? It is because it is crucial in understanding the anomalous behavior such as floating of ice.

Overall, the PT diagram is a critical tool in thermodynamics and material science. What is a PT diagram? Let us go back and see. This is a PT diagram. I mentioned it in metallurgy and thermodynamics.

In material science, we try to see what happens when you extract an ore and then process it. So in material science, it plays a very important role. Overall, the PT diagram is a critical tool in thermodynamics and material science, allowing engineers and scientists to predict phase transitions, determine boiling or melting points under varying pressure, and design processes like freeze-drying, refrigeration, and high-pressure chemical synthesis. The triple point of water is at 4.5 mm Hg and 273.16 Kelvin. This is the temperature, and this is the pressure, whereas for carbon dioxide, it is 3885 mm Hg at about 5 atmospheric pressure, and the temperature is this. When solid CO₂ (dry ice) is exposed to atmospheric pressure, it transforms directly into vapor.

That's why when you see solid ice or dry ice, which is nothing but solid CO₂, it sublimates when exposed to the atmosphere. In many dramas, weddings, or even movies, you will see smoke scenes created by exposing solid CO₂ to atmospheric pressure. It transforms into a dry vapor. So it creates the fume. Absorbing the latent heat of sublimation from the surroundings, which gets cooled or refrigerated.

P-v-T Surface



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



So, now you will understand why ice floats and why CO₂ transforms into a gas. So, when we try to plot all the three P, V and T diagram, this is a three-dimensional plot. So, you will try to see the three-dimensional behavior of a pure substance. You can see the pressure. So, here when the pressure increases, when the volume is here, you will try to see the substance is continuing to be a solid.

And then when you move in this direction, it gets solid gets into a vapor. So, you can see here till here you can plot it in the temperature. So, the material continues to be a solid, right? And when the temperature goes high, it gets into a solid liquid phase and then into a liquid phase, right? How long will it continue to stay in a liquid phase?

It stays to continue in a liquid phase till this, till this temperature it discontinues. Now, as and when the temperature goes high the liquid gets converted into volume. So, you can see here up to here it is there and then it goes up to the gaseous phase right. So, this is a temperature. So what happens when it gets converted from a solid, solid liquid to a gas?

The volume expands. So that is why you see the volume keeps expanding. So as and when the temperature is going high, the pressure is going high, what happens to the volume and what is the phase in which the material exists is solid vapor. When we go slightly higher, it transitions to liquid vapor. Here, there is a transition.

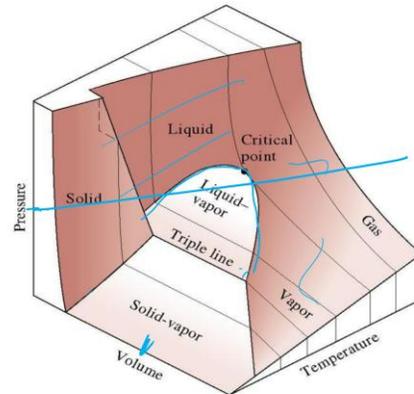
So, that is a triple line here. So, what is a triple line? Triple line is here, here, this is there and then you have here, ok. So, this is a triple M. From this PVT diagram, we try to see the complete phases of material and how it changes with respect to pressure, volume, and temperature. This is very important.

It is easily plotted, but in reality, understanding this in more minute detail is difficult. That is why we always try to take a 2D plot and present it.

P-v-T Surface

The P-v-T surface is a comprehensive 3D thermodynamic representation that depicts the relationship among pressure (P), specific volume (v), and temperature (T) for a pure substance.

- This surface consolidates data from various 2D diagrams like P-v, T-v, and P-T into a unified model, providing a complete visualization of all possible phase states and transitions of a substance.
- It also highlights critical behavior, phase limits, and the thermodynamic paths followed in various engineering applications, such as power generation, refrigeration, and materials processing.



P-v-T surface of a substance that expands on freezing (like water).

The PVT surface is a comprehensive 3D thermodynamic representation that depicts the relationship between pressure, specific volume, and temperature. The surface consolidates data from various 2D plot diagrams like PV, TV, and PT into a unified model, providing a complete visualization of all possible phase states and transitions seen in this graph. It also highlights the critical behavior, phase limits, and the thermodynamic path followed in various engineering applications such as power plants, refrigeration, and material processing. You can try to understand this from this diagram.

P-v-T Surface

- The surface is typically dome-shaped in the center, representing the saturation region where the substance exists as a liquid-vapor mixture.
- This dome is bounded by the **saturated liquid line** on the left and the **saturated vapor line** on the right.
- **The critical point is located at the top of the dome, marking the end of the liquid-vapor phase boundary.**
- Beyond this point, the distinction between liquid and vapor phases disappears and the substance behaves as a supercritical fluid.
- To the left of the saturated liquid line lies the compressed liquid region, where the substance is purely in the liquid phase at a higher pressure than saturation for a given temperature.

The surface is typically dome-shaped in the center, representing the saturation region where the substance exists as a liquid-vapor mixture. So, you can go back to your previous 2D plots and see. This dome is bounded by the saturated liquid line on the left and the saturated vapor line on the right. The critical point is plotted on the top of the dome, marking the end of the liquid-vapor phase boundaries.

Beyond this point, the distinction between liquid and vapor does not exist, so it becomes a supercritical fluid. To the left of the saturated liquid line lies the compressed liquid region, where the substance is purely in the liquid phase at a higher temperature than saturation for a given pressure.

P-v-T Surface



- To the right of the saturated vapor line lies the superheated vapor region, where the substance exists solely as vapor at a higher temperature than the saturation temperature for a given pressure.
- As you move along the surface:
- **At constant pressure**, increasing temperature leads from compressed liquid to saturated liquid, then to a saturated mixture, and finally to superheated vapor—this is visible as a horizontal path cutting through the dome.
- **At constant temperature**, reducing pressure causes similar transitions—this appears as a vertical path through the dome.
- **At constant specific volume**, the path intersects with all three regions and illustrates how a substance can shift phases based on pressure and temperature.



To the right of the saturated vapor line lies the superheated vapor region, where the substance exists as vapor at a higher temperature than the saturation temperature for a given pressure. So, as you move along the surface—where is that?—as you move along this. So now, we are trying to talk about this as you move along the surface. This is a surface, right? The colored one is a surface.

When you move along the surface, you can see what happens at a constant pressure, what happens at a constant temperature, and what happens at a constant specific volume. At a constant pressure, increasing temperature leads from compressed liquid to saturated

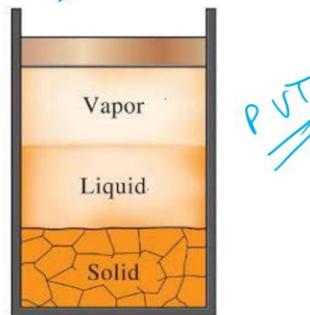
liquid. Then to a saturated mixture and finally to a superheated vapor at a constant pressure. This is visible as the horizontal path cutting through the dome. It cuts through the dome.

You get a superheated vapor. Then, at a constant temperature, reducing the pressure causes a similar transition. This appears as a vertical path through the dome. At a constant specific volume, so it is basically you are trying to play with this constant specific volume line, right? At a constant specific volume, the path intersects with all three regions and illustrates how a substance can shift phase based on pressure and temperature.

P-v-T Surface



- The P-v-T surface is particularly useful because it graphically combines the behaviors shown in individual P-v and T-v diagrams into one 3D representation, enabling a more intuitive understanding of complex thermodynamic processes like boiling, condensation, superheating, compression, and expansion.



https://encrypted-tbn0.gstatic.com/images?q=tbn:ANd9GcTz5_z50lllokpQE2GJ8futDvJ6qwdcBv9UJkILFgzDFYaVplEzOrOaHeclKbKvBmCwXI&usqp=CAU

19

So, when we try to further our understanding, the PVT surface is particularly useful because it graphically combines the behavior as shown individually between PV and TV diagrams in a three-dimensional plot. It enables a more intuitive understanding of complex thermodynamic processes like boiling, condensation, superheating, compression, and expansion. Now you can see, so now everything is very clear. What happens when you put it at a constant pressure? So, at a constant pressure, the pressure is constant.

So, take a line where the pressure is constant. What happens? What happens to the volume? What happens to the temperature? So, this is very useful.

So, solid turns into liquid, and liquid turns into vapor. So, we have the PVT diagram. So, you can define the boiling process, condensation process, superheating process, compression process, and expansion process.

And thank you so much.