Basics of Mechanical Engineering-3

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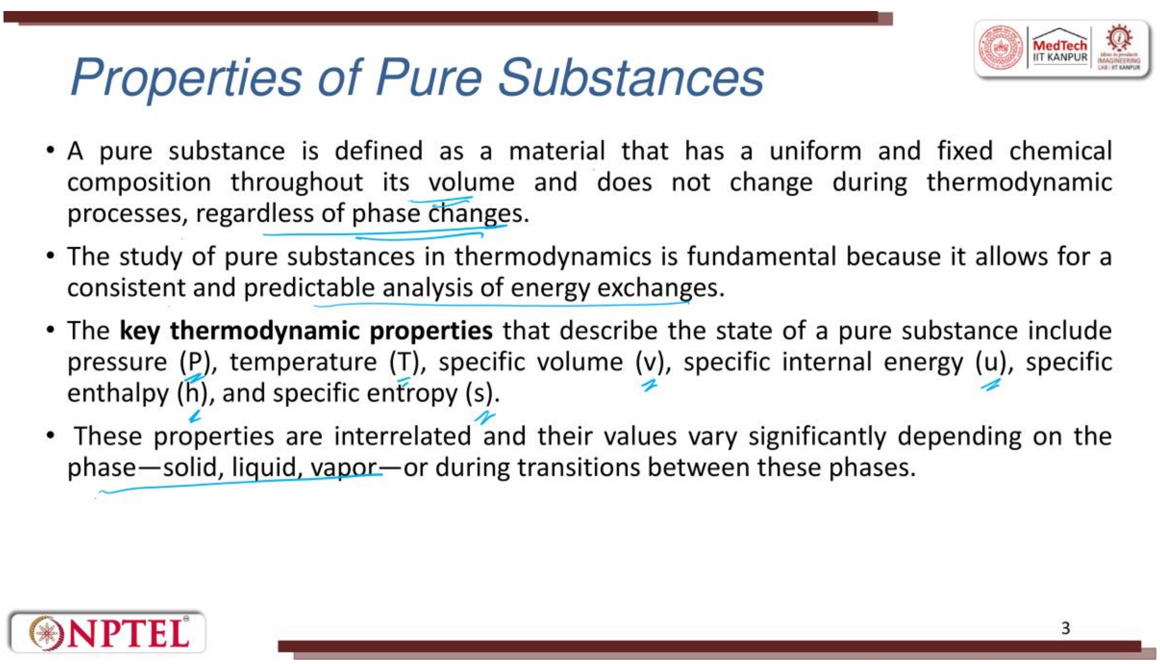
Week 04

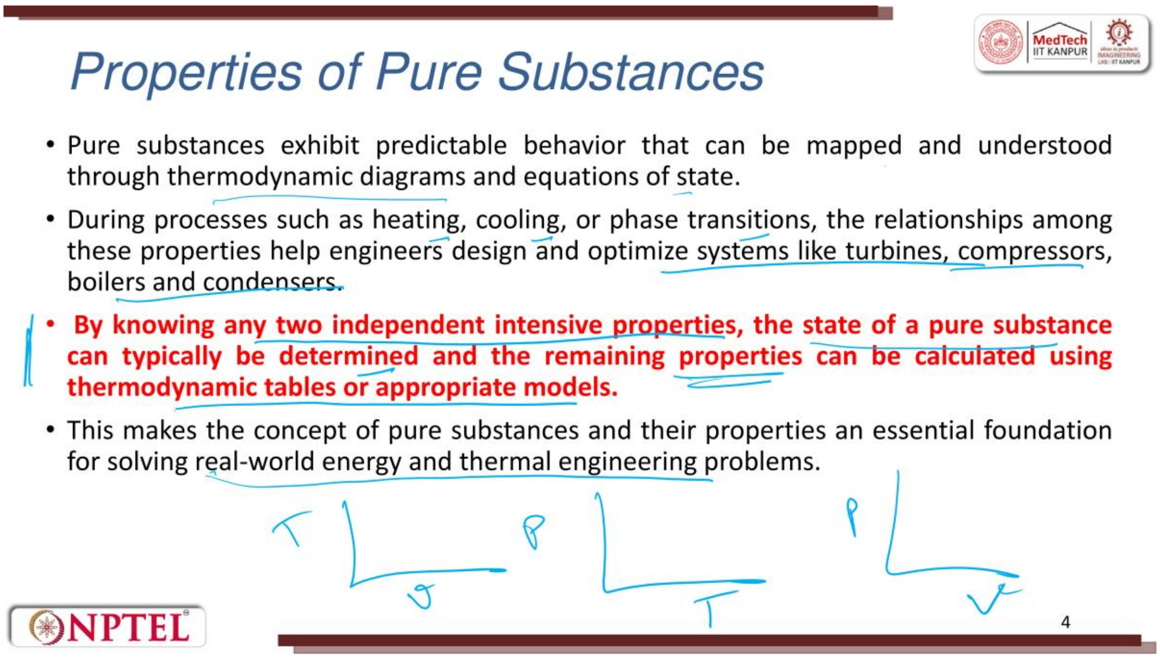
Lecture 17: Properties of Pure Substances

Welcome to the next lecture on Properties of Pure Substances. So, what are the different properties of a pure substance?



A pure substance is defined as a material that has a uniform or fixed chemical composition throughout its volume and does not change during a thermodynamic process, regardless of phase change. This type of pure substance in thermodynamics is fundamental because it allows for a consistent and predictable analysis of energy exchange. So, the key thermodynamic properties are going to be pressure, temperature, specific volume, specific internal energy (U), enthalpy, and entropy.

So, pressure, temperature, specific volume, specific internal energy, specific enthalpy, and specific entropy. These properties are related, and their values significantly depend on the form in which they exist. They can exist in one form or coexist in two forms.



The pure substance exhibits predictable behavior that can be mapped and understood through thermodynamic diagrams and equations of state. So, during heating, cooling, and phase transition, the relationship among these properties helps engineers design and optimize systems for turbines, compression, boilers, and condensation.

So with this, now you will be able to easily appreciate, I know, this diagram for a pure substance. So now, I have the processes like boiling, cooling, condensation, expansion, compression; whatever it is, I know. When I want to compress, I increase the pressure. So I try to maintain temperature, I try to maintain pressure, and I only try to reduce the volume. So whatever it is, or I try to reduce the volume and allow the temperature to go wherever it is.

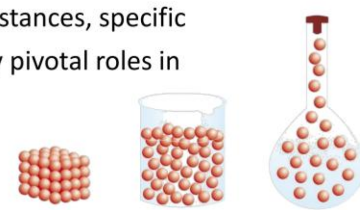
So, that is also possible. Suppose you want two things to be isolated; then, you have to plan your engineering system so nicely. So, that is what it is. So, the engineering processes are known, and pure material responses are known. Now, I try to map so that I can get the best use of it, such that my energy efficiencies are high.

So, here you also saw liquid, vapor, and supercritical fluids—all these things you saw, right? When you study these supercritical fluids, what happens to the basic thermodynamic property? That is the next question. Then, it is a good idea to find out for a working fluid: what is the temperature, or what is the property? What are the values of the property? It is very important to do. So, we try to use this triple-point diagram; we try to use the surface, and then we try to extract the data. The state of the pure substance includes pressure, temperature, specific volume, specific internal energy, specific enthalpy, and specific entropy. By knowing any two independent intensive properties of the state of a pure substance, you can typically determine the remaining properties, which can be calculated using the thermodynamic table and appropriate models.

So, this is very important. By knowing any two independent intensive properties—P-V, P-T, T-V—if you do it. So, then what happens? You will know two properties; then, the state of a pure substance can typically be determined, and the remaining properties can be calculated using the thermodynamic table or an appropriate model. This makes the concept of pure substances and their properties an essential foundation for real-world applications and thermal energy problems.

Volume, Enthalpy and Internal Energy

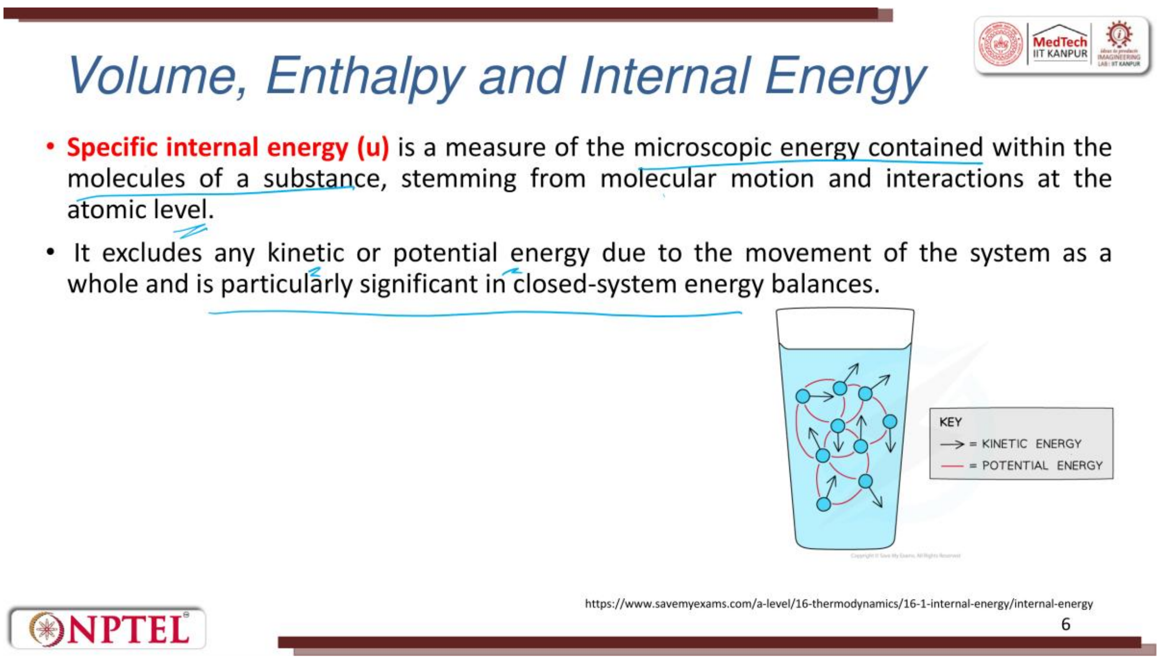
- Among the various thermodynamic properties of pure substances, specific volume, specific internal energy, and specific enthalpy play pivotal roles in describing the physical and energetic state of a system.
- **Specific volume (v),** defined as the volume occupied per unit mass of a substance (typically in m^3/kg), is an indicator of the spatial configuration of the molecules and helps determine fluid density.
- It is especially crucial in analyzing expansion and compression processes, where volume changes are central to performance.



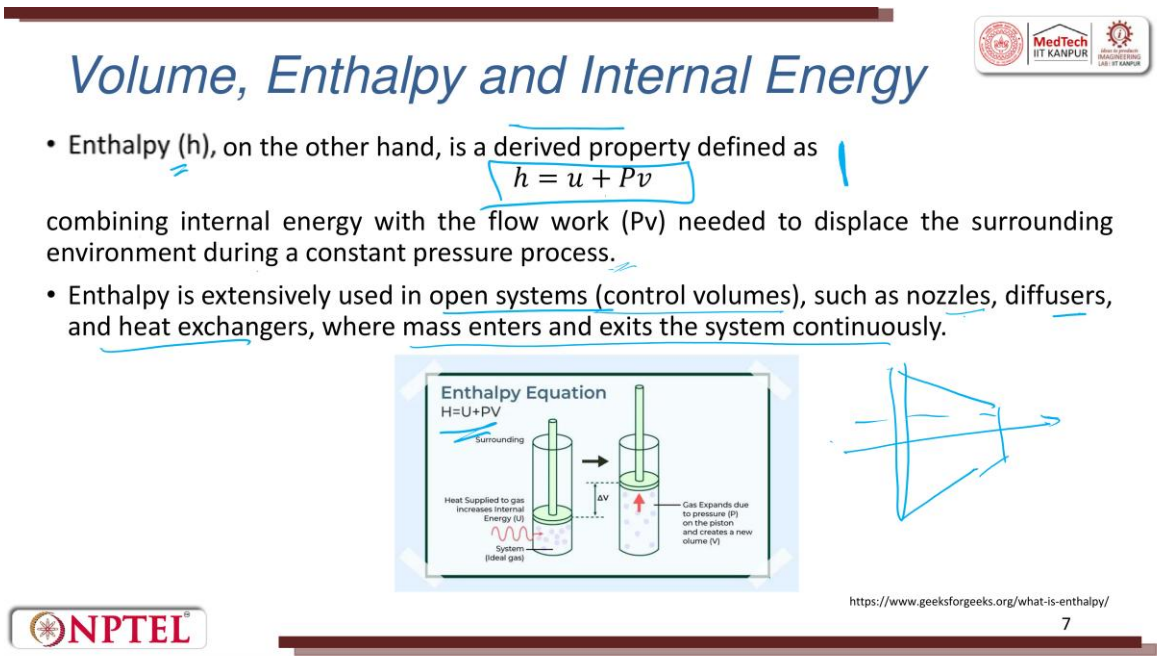
https://www.thoughtco.com/specific-volume-definition-and-examples-4175807

Volume, enthalpy, and internal energy—among the various thermodynamic properties of a pure substance, specific volume, specific internal energy, and specific enthalpy play a very important role.

What is specific volume? Specific volume is defined as the volume occupied per unit mass of a substance, that is, meter cube per kg. So, it is defined as the volume occupied per unit mass of a substance, as an indicator of the spatial configuration of the molecules, and helps determine the fluid density. It is especially crucial in analyzing expansion and compression processes, where volume changes are central to performance. So, specific volume is the volume occupied per unit mass of a substance.



Specific internal energy is a measure of microscopic energy contained within the molecules of a substance, stemming from molecular motion and interaction at the atomic level. It excludes any kinetic or potential energy due to the movement of a substance as a whole and is particularly significant in closed-system energy balance. So, you can see here kinetic energy is the black line, which is drawing arrows representing kinetic energy. The red ones, which are connecting the molecules, represent potential energy. So, specific internal energy is a measure of the microscopic energy contained within the molecules of the substance. Stemming from molecular motion and interaction at the atomic level.

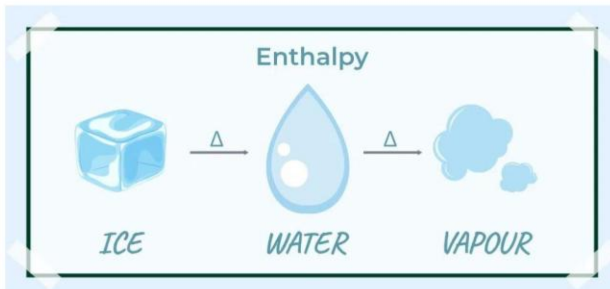


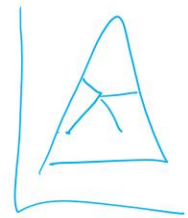
Enthalpy is defined as h = u + Pv. Where it is nothing but the combined internal energy with the flow work PV. Needed to displace the surrounding environment during a constant-pressure process, it is a derived property. This is very important—it is a derived property defined as enthalpy, which is nothing but h = u + Pv, where u is the internal energy and Pv is the flow work.

Enthalpy is extensively used in open-system control volumes. Such as nozzles, diffusers, and heat exchangers where mass enters and exits the system continuously. For example, a nozzle is one such case. Mass enters and exits continuously. Enthalpy is extensively used in open systems such as nozzles, diffusers, and heat exchangers where mass enters and exits the system continuously. So, this is the pictorial diagram of enthalpy.

Volume, Enthalpy and Internal Energy

- These three properties are typically tabulated for substances like water and refrigerants at various pressures and temperatures, enabling engineers to perform accurate energy calculations across a wide range of applications, from power generation to refrigeration and air conditioning systems.

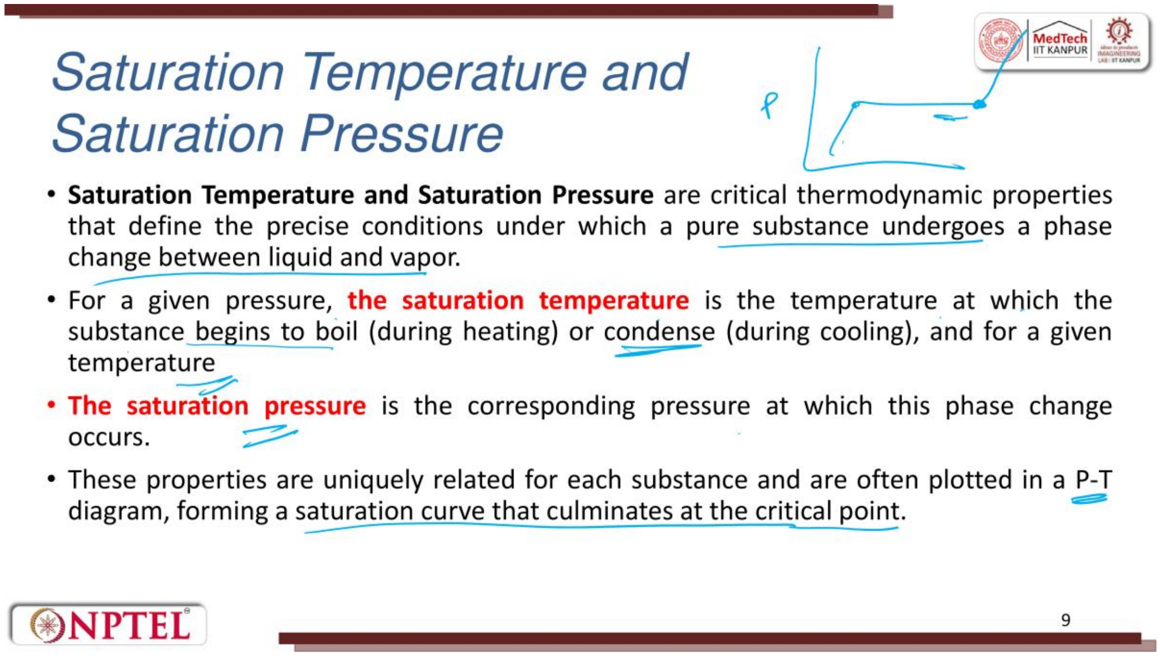




https://www.geeksforgeeks.org/what-is-enthalpy/

So, volume, enthalpy, and internal energy are three properties that are typically tabulated for substances like water and refrigerants at various pressures and temperatures, enabling engineers to perform accurate energy calculations across a wide range of applications, including power plant engineering, refrigeration, and air conditioning systems. So, you have to know at what pressure and temperature this conversion occurs, which can be extracted from a table. So, from a pictorial model, today you also have programs and software codes written. So, you can input the temperature and observe the pressure changes, or you can have a pictorial representation with a pointer that drags to various points, allowing you to see the response of these phases.

So, there are many advanced tools available because once you understand this, you can plan your engineering system.



The saturation temperature and saturated pressure are critical thermodynamic properties that define the precise condition under which a pure substance undergoes a phase change from liquid to vapor. There is a transition for a given pressure. The saturation temperature is the temperature at which the substance begins to boil or condense for a given pressure.

At this point, it can get converted from solid to liquid or liquid back to solid, right. So, during heating and cooling, the beginning of boiling or condensation can occur. So, if you go by the TS diagram, this is where the condensation starts; boiling starts, boiling ends. The saturation pressure is the corresponding pressure at which the phase change occurs from liquid to gas or solid to liquid. So, saturation pressure.

So, these two points are very important. Saturation temperature and saturation pressure. These properties are uniquely related for each substance and often plotted in a PT diagram, forming a saturation curve that culminates at the critical point.

Saturation Temperature and Pressure

- Below the critical point, the substance can exist in distinct liquid and vapor phases and the phase change process occurs at constant temperature and pressure.
- For example, at standard atmospheric pressure (1 atm), water has a saturation temperature of 100°C, meaning it boils at this temperature.
- If the pressure is increased, as in a pressure cooker, the saturation temperature also rises, allowing food to cook faster. **[P α T]**
- Conversely, under vacuum conditions, water can boil at much lower temperatures.
- **These saturation properties are fundamental to design and analysis of systems like steam generators, condensers and refrigeration units.**

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Below the critical point, the substance can exist in distinct liquid and vapor phases. And the phase change process occurs at a constant temperature or pressure. For example, at standard atmospheric pressure (1 atmosphere), water has a saturation temperature of 100 degrees Celsius. After that or above that, it starts boiling. If the pressure is increased, as in a pressure cooker, the saturation temperature also rises, allowing the food to cook faster. P α T. The volume is constant. Conversely, under vacuum conditions, the water can boil.

You put water inside a container and reduce the pressure. The water can boil at a much lower temperature. Now, friends, what is the lead statement you get? So, if you want to change the phase, you can increase the temperature or reduce the pressure. When you reduce the pressure at a lower temperature, the water starts boiling.

So now, you have to plan your process and make it energy-efficient. If you want only a phase change, how do you get it done? That is what it is. These saturation properties are fundamental to the design and analysis of systems like steam generators, condensers, and refrigeration units. Friends, I am repeatedly telling you that there are only three parameters: pressure, volume, and temperature.

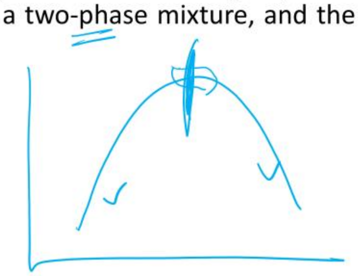
There are three phases: solid, liquid, and gas. So now, is there a distinct point where it goes from solid to liquid or liquid to gas? Is there a distinct point? Yes, there is a distinct point. If that has to happen, what is the pressure, volume, and temperature behavior?

If you want to have a smooth sail transition, then what do you do? How do you do it? For each of these transitions, there is a process: expansion, condensation, compression, right? You have boiling, you have so many processes. So, that has to be linked and understood. Can I get it done for any given material?

It is difficult. So, what we do is we try to do it for a pure material. In a pure material, what they would have done is establish tables, and in those tables, they try to say very clearly: at this pressure, this temperature, what will be the vapor pressure or what will be the vapor content. They will try to give it in a plot, like what we saw in a triple plot or a 3D model. From there, they will try to saturate. So, this is what is important.

Quality (Dryness Fraction)

- In thermodynamics, Quality, also known as the Dryness Fraction, is a crucial parameter used to describe the state of a saturated mixture of a pure substance—specifically during a liquid-vapor phase change.
- **Quality or Dryness Fraction is defined as the ratio of the mass of vapor to the total mass of the mixture and is denoted by the symbol x.**
- This property is significant because, in the saturated region, the substance does not exist entirely as a liquid or vapor but as a two-phase mixture, and the quality quantifies how much of it has turned into vapor.



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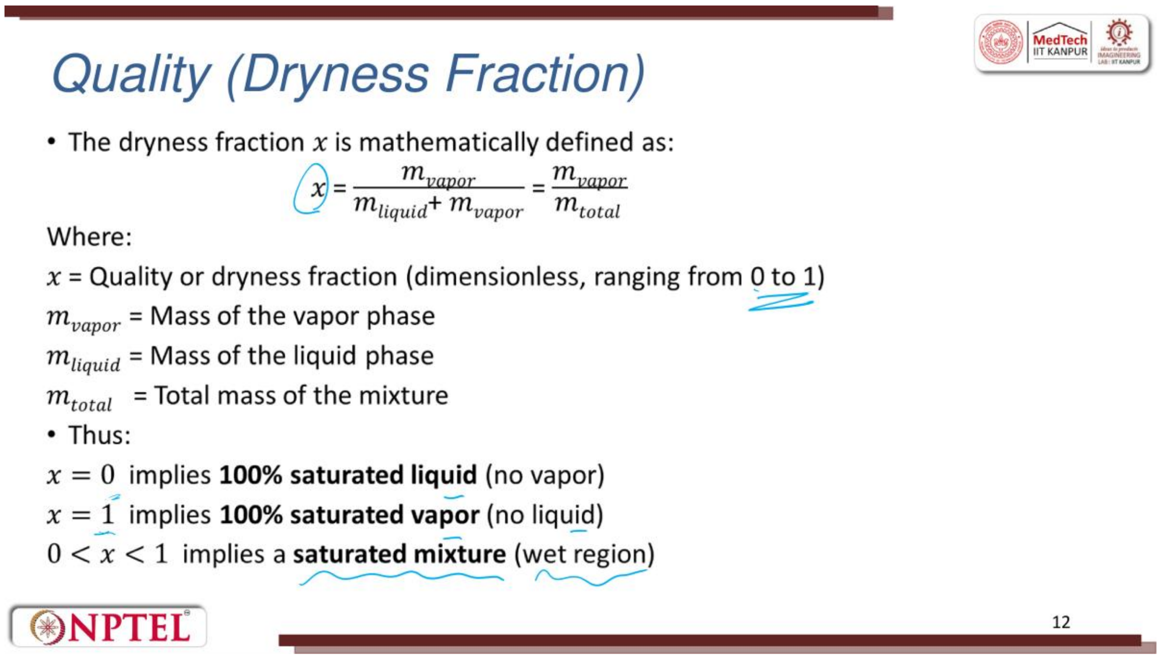
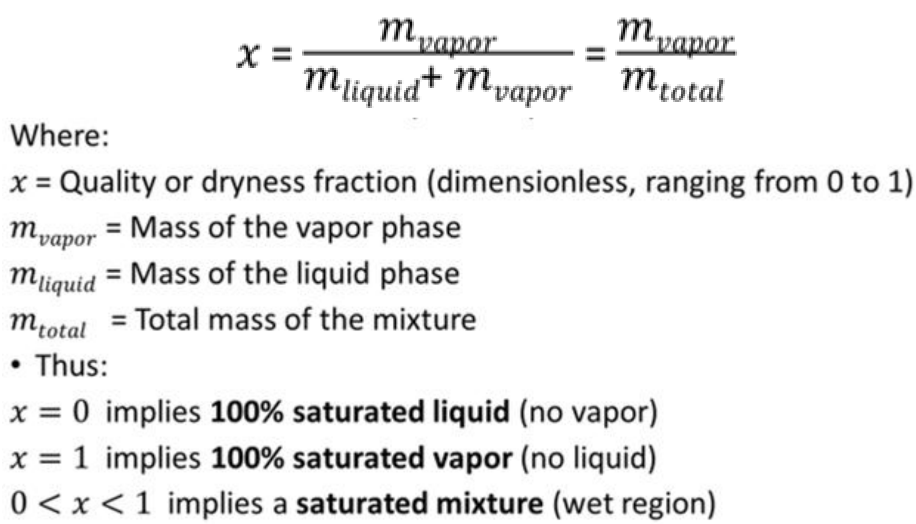
Quality, or dryness fraction, is another important parameter, which is a quality. In thermodynamics, quality, also known as dryness fraction, is a crucial parameter used to describe the state of a saturated mixture of a pure substance. Specifically, during liquid-vapor phase change. When does a liquid-vapor phase change occur? This is saturated liquid, this is saturated vapor, this point, right.



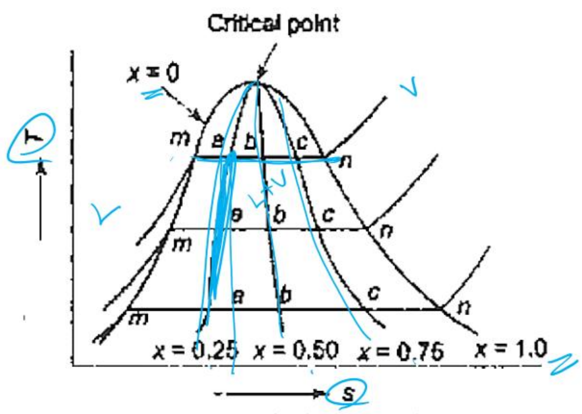
So the quality or the dryness fraction is defined as



This property is significant, why? Because, in the saturated region the substance does not exist entirely as liquid or vapor, but it exists in two phase mixture. And the quality quantifies how much of it has turned into vapor at this point. Critical point it changes, right.

Close to this region, you can keep. And in real time, you will never have a clear distinct point; it is very difficult. You will have a small range. So this is very important. Quality or dryness fraction is defined as a ratio of the mass of vapor to the mass of the mixture.

Quality (Dryness Fraction)



Constant quality lines on T-s dig.

https://www.engineersedge.com/thermodynamics/images/temp_e8.gif

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So here it is a T-S diagram. So you will try to see this hump we have. This is liquid. This is liquid plus vapor. This is vapor. So now you will try to see what happens when x = 0.25, X = 0.5, and X = 0.75.

So when that meets a constant temperature line, what is the response, and what is the entropy you get? So this is the dryness fraction, which is defined.

Quality (Dryness Fraction)

- Points a, b, and c at various pressures indicate the situations when the masses of vapour reached 25%, 50%, and 75% of the total mass.
- i.e. At point a, the mass of liquid is 75% and the mass of vapour is 25% of the total mass.
- At point b, the mixture consists of 50% Liquid and 50% vapour by mass.
- At points c, the mixture consists of75% vapour and 25% liquid by mass.
- The lines passing through points a, b and c are the constant quality lines of 0.25, 0.50, and 0.75 respectively.

- **Constant quality lines start from the critical point.**

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Points a, b, and c at various pressures indicate the situation where the mass of the vapor reaches 25%, 50%, and 75%. When you go down, you can see here 25%, 50%, and 75%—A, B, and C.

At point A, the mass of the liquid is 75%; this one, this line, 75% and the mass of the vapor is 25% of the total mass. At point B, it is 50% liquid and 50% vapor mass. At point C, 75% is vapor and 25% is liquid mass. The line passes through points A, B, and C at constant quality lines of 0.25, 0.5, and 0.75, respectively. The constant quality line starts from the critical point. The critical point only we saw where there is a transition.

Quality (Dryness Fraction)

- In the saturated mixture region, properties such as specific volume, internal energy, enthalpy, and entropy vary with quality and can be calculated using the following general formula:

$$y = y_f + x\,(y_{fg})$$

$y_{fg} = y_g - y_f$

Where:

y = Desired property of the mixture (e.g., v,u,h,s)

y_f = Property of the saturated liquid

y_g = Property of the saturated vapor

y_{fg}= y_g− y_f = Difference between saturated vapor and saturated liquid property

So in a saturated mixture region, properties such as specific volume, internal energy, enthalpy, entropy vary with the quality, dryness fraction, right. And can be calculated as $y = y_f + x\ (y_{fg})$

Where:

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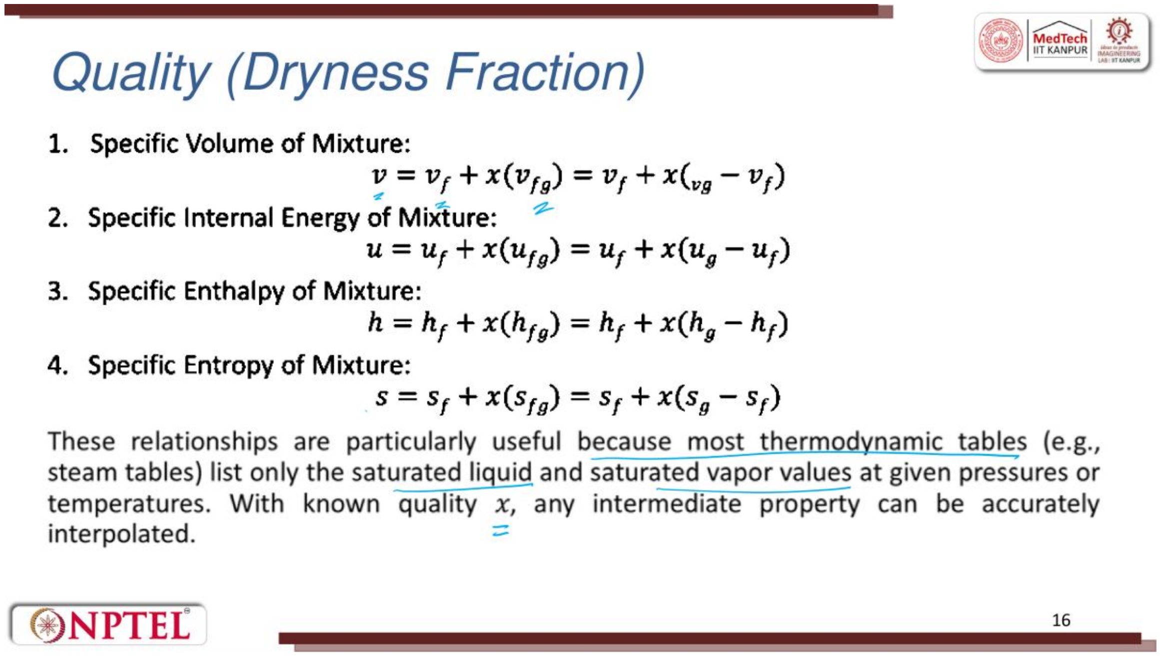

1. Specific Volume of Mixture:

$$v = v_f + x(v_{fg}) = v_f + x(_{vg} - v_f)$$

2. Specific Internal Energy of Mixture:

$$u = u_f + x(u_{fg}) = u_f + x(u_g - u_f)$$

3. Specific Enthalpy of Mixture:

$$h = h_f + x(h_{fg}) = h_f + x(h_g - h_f)$$

4. Specific Entropy of Mixture:

$$s = s_f + x(s_{fg}) = s_f + x(s_g - s_f)$$

These relationships are particularly useful because most thermodynamic tables, steam tables, list only the saturated liquid and saturated vapor values at a given pressure and temperature. So, with a known quality x, any intermediate points can be calculated. That is what we are seeing.

Quality (Dryness Fraction)

- The concept of quality is foundational in analyzing thermodynamic systems such as **steam turbines**, **condensers**, **boilers**, and **refrigeration units**, where phase change plays a critical role.
- For instance, in a steam turbine, the inlet steam should ideally be dry or superheated to avoid blade erosion caused by liquid droplets.
- Engineers often calculate the dryness fraction at various points to determine **thermal efficiency**, evaluate **entropy generation**, and ensure that devices operate within safe and efficient limits.
- Additionally, in **energy balance calculations** for Rankine or refrigeration cycles, knowing the quality helps estimate **heat transfer (Q)** and **work done (W)** with greater precision.
- It is also crucial for evaluating the **latent heat** involved in vaporization or condensation, which corresponds to the enthalpy change h_{fg}.

So the concept of quality is foundational in analyzing thermodynamic systems such as steam turbines, condensers, boilers, or refrigeration units. For instance, in a steam turbine, the inlet steam should ideally be dry or superheated to avoid blade erosion caused by liquid droplets.

Because it is completely vapor, it is going to be easy, as the vapor hitting the turbine blade will start rotating. If there is a molecule of water along with the vapor at very high pressures, then what happens? This becomes like a small bullet trying to hit the blade. The blades have a profile. So, it is very difficult to manufacture blades. So, they always try to have dry or superheated steam to get inside.

Engineers often calculate the dryness fraction at various points to determine the thermal efficiency and the entropy generation. Additionally, in energy balance calculations, we will also see the Rankine cycle and the refrigeration cycle. Knowing the quality helps us to find out the heat transfer and the work done. So, for energy balance, heat transfer, and work done, everywhere in this PV diagram, TS diagram, the dryness comes into existence, and dryness, you know, can be 25 percent, 50 percent, or 75 percent, which you can try to define. So, finally, we will try to see what supercritical fluid behavior is.

Supercritical Fluid Behavior

- In thermodynamics, the critical point of a pure substance represents a unique condition at which the distinction between the liquid and vapor phases ceases to exist.
- This point is characterized by a specific critical temperature (T_c), critical pressure (P_c), and critical volume (v_c), beyond which the substance enters a supercritical state.
- **At this state, the fluid exhibits properties of both gases and liquids and is referred to as a supercritical fluid (SCF).**
- These fluids do not undergo phase change in the traditional sense; instead, their density and other properties vary continuously with pressure and temperature, allowing them to behave as highly compressible liquids or dense gases depending on conditions.

In thermodynamics, the critical point of a pure substance represents a unique condition at which the distinction between the liquid and vapor phases ceases to exist. This point is characterized by a specific critical temperature, Tc. And the pressure at this point is called Pc. And the volume is called Vc.

Supercritical Fluid Behavior

- A supercritical fluid exists at conditions above the critical point (i.e., $T > Tc$ and $P > Pc$).
- SCFs are unique in that they:

➢ Have liquid-like densities, allowing for high solvating power

➢ Exhibit gas-like viscosities, enabling rapid diffusion

➢ Have tunable properties—small changes in temperature or pressure lead to significant changes in density and other physical properties

These features make SCFs extremely valuable in engineering applications such as supercritical extraction, clean energy systems, supercritical water oxidation (SCWO), and supercritical Rankine cycles for efficient power generation.

Beyond this point, the substance enters a supercritical state. In this state, the fluid exhibits properties of both gas and liquid, and it is referred to as a supercritical fluid. Here, the properties can exist in both gas and liquid forms. These fluids do not undergo phase changes in the traditional sense. Instead, their density and other properties vary continuously with pressure and temperature, allowing them to behave like a highly compressed liquid or a dense gas, depending on the conditions. So, this is a very important supercritical fluid.

So, supercritical fluid exhibits both the properties of a gas and a liquid. So what is that? Allowing them to behave like a highly compressed fluid. When you use a highly compressed fluid, the energy transition is very high. So the work done will be very high, or the dense gas, depending on the condition.

A supercritical fluid exists at a condition above the critical temperature, T is greater than Tc, and P is greater than Pc. The SCFs are unique in that they have liquid-like density, allowing for high solvating power, exhibit gas-like viscosity, enabling rapid diffusion inside, have tunable properties, and small changes in temperature or phase lead to significant changes in density or other physical properties. They have liquid-like density, allowing for high solvating power. It exhibits gas-like rapid diffusion.

Tunable properties: a small change in temperature or pressure leads to significant changes in density and other properties. Density is mass by volume. Now you should understand when it is moved, how does it happen? These features make SCFs extremely valuable in engineering applications such as supercritical extraction, clean energy systems, supercritical water oxidation, and supercritical Rankine cycles for efficient power generation.

Supercritical Fluid Behavior

- The critical point is defined as the highest temperature and pressure at which a substance can coexist in equilibrium as liquid and vapor.
- Mathematically:
- At $T = Tc$ and $P = Pc$, the saturated liquid and saturated vapor states become identical, so:

$$v_f = vg$$
$$h_f = hg$$
$$s_f = sg$$

Beyond this point, no latent heat of vaporization exists, because there is no distinct phase change.

So, the critical point is defined as the highest temperature and pressure at which the substance can coexist in equilibrium in liquid and vapor phases. So, mathematically, at $T = Tc$ and $P = Pc$, the saturated liquid and saturated vapor states become identical. So, it can be represented in this way. Fluid is equal to gas. Beyond this point, no latent heat of vaporization exists because there is no distinct phase change happening here. So, they are now called cutting-edge technology.

Supercritical Fluid Behavior

- **Supercritical fluids are used in cutting-edge technologies:**

I. **Supercritical CO_2 extraction:** for decaffeinating coffee, extracting essential oils, and pharmaceutical purification.

II. **Supercritical water reactors:** in next-gen nuclear power

III. **Rankine cycles:** improve thermal efficiency in power plants by operating above the critical point of the working fluid (e.g., water, CO_2).

IV. **Enhanced oil recovery (EOR):** using supercritical CO_2 injected into oil wells.

Their unique ability to combine solvency, diffusivity, and compressibility makes them ideal for clean and efficient energy and separation processes.

Supercritical CO_2 extraction is widely discussed for decaffeinating coffee, extracting essential oils, and pharmaceutical purification. In all these applications, supercritical CO_2 extraction is used. Supercritical water reactors are the next-generation nuclear power plants. The Rankine cycle improves efficiency in power plants by operating with a critical fluid working fluid, which can be water or CO_2. Enhanced oil recovery (EOR) is another application where supercritical CO_2 is injected into oil wells to extract more oil. This unique ability to combine solvency, diffusivity, and compressibility makes them ideal fluids for clean and efficient energy and separation processes.

Friends, in this lecture, we discussed what pure substances are and the different phases of pure substances. What do you understand by P, V, T diagrams? Then, a combination of these, followed by a three-dimensional plot. Then, why is the study of properties of pure substances very important in thermodynamics? Then, basic properties like volume, enthalpy, internal energy, and entropy were covered.

Then, what are saturated pressure and saturated temperature? What is the quality described—the quality of air or the dryness fraction of air—was discussed. And finally, we saw supercritical fluids—why they are very important today and where they are going to be used. So, these are some of the topics we discussed in this lecture. This lecture is going to be the foundation for the cycles we will study in the future. So, before I close, I wanted to give you some examples so that you can try to conduct those experiments or fundamental studies for your own understanding.

One is the supercritical fluid they are talking about. So now, it is very clear that if you operate in supercritical fluid, it is going to give us a higher yield. But what are the limitations? I just wanted you to browse through. If it is so easy, why are we not able to do it?

That is point number one. The second thing is, we have been talking about turbines. This turbine is nothing but a disc. On the disc, there will be many blades. What are these blade profiles?

Two. Three, typically try to look at the cross-section of the fan that rotates above you. Take a blade and try to observe several sections; what is its profile? That's the third thing. Fourth, when there is very high relative humidity in the atmosphere, what do you feel when you run the fan at high speeds?

And on a dry sunny day, when you run the fan at very high speeds, what is the response or what do you feel? Then, when you switch on the AC and parallelly switch on the fan, when do you enjoy the coolness in the room? What is the time period? Next time, don't switch off the fan; run the AC for maybe half an hour, and then switch on the fan. What do you feel?

The third thing is, run the AC for one hour, then switch on the fan and switch off the AC. When does the coolness reduce? These are some real-time experiments you can do by yourself. Then start understanding how engineering plays an important role in maintaining pressure, volume, temperature, and humidity. Relative humidity is nothing but water present in the air.

When you go to a very high temperature, steam is present in water and in the air. So, you can understand the implications of it. So, if you do these experiments, you will start enjoying this course.

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These are some of the standard references we have been using for this lecture.

Thank you.