

**Thermodynamics**  
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**Lecture 45**  
**Two Phase System - Part 2**

We looked at a steam-water system in the previous lecture.

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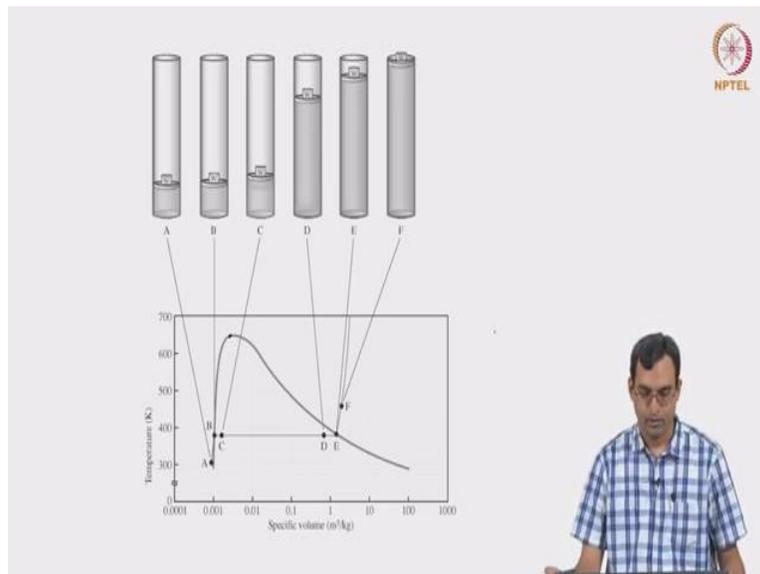
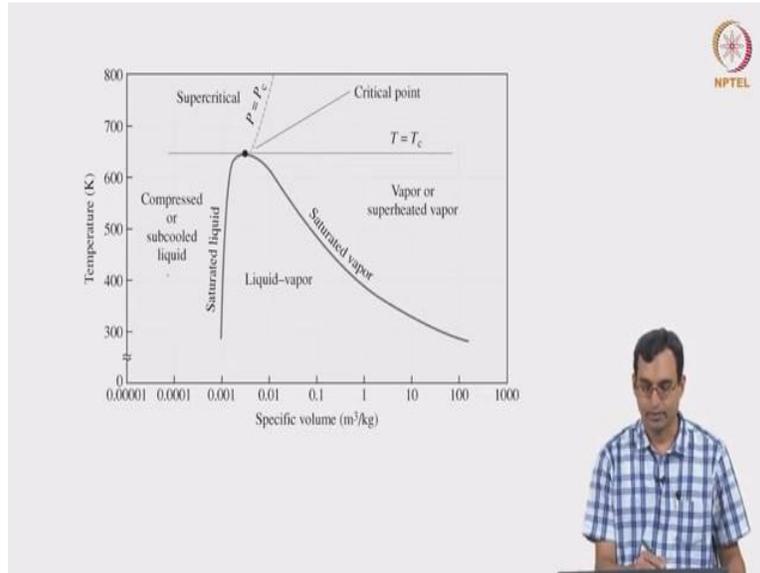


Figure 1.

During the phase change process (state B to state E), the temperature and the pressure stay constant (see Fig. 1). The specific volume change is very small from state A to state B. This change is large from state B to state E, whereas, it is moderate from state E to state F. The liquid on the left of saturated liquid line is called compressed liquid because at a given temperature, it is compressed so much that it cannot become vapor.

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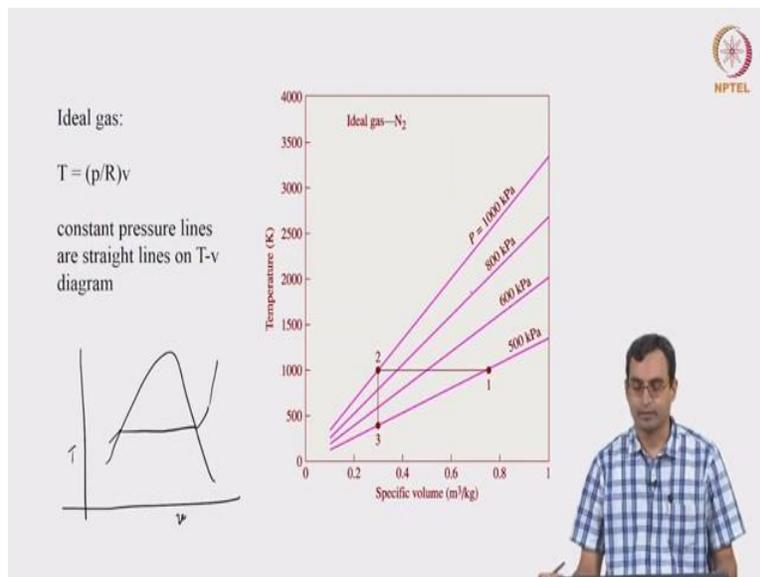


Figure 2.

We looked at the graph shown in Fig. 2 when we discussed ideal gases. It shows isobars for an ideal gas. The equation of those lines is  $T = \frac{p}{R}v$ . In Fig. 2, an isobar on a liquid-vapor dome is also drawn. It is not a straight line in this region. In the two-phase region, it is straight and parallel to the  $v$  axis. Outside the dome and near to it, it is curved. It

becomes straight line ( $T = \frac{p}{R} v$ ) as shown in the pink graph far away towards right from the liquid-vapor dome.

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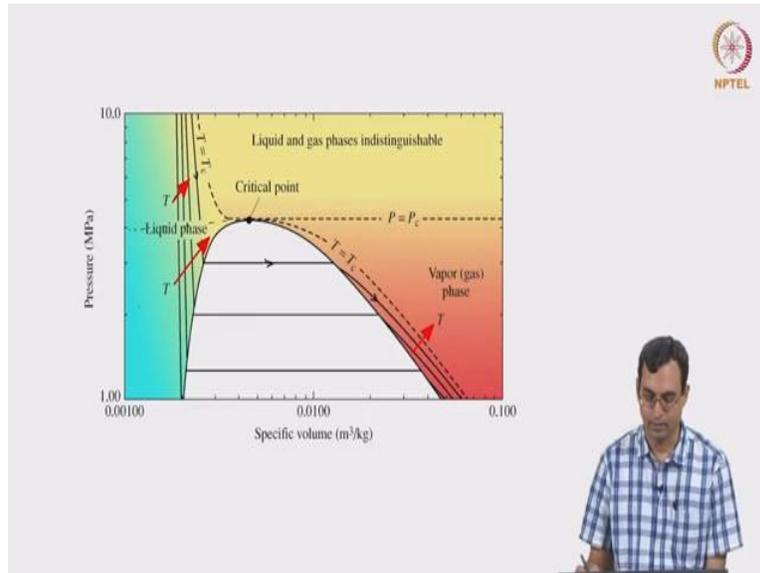


Figure 3.

Figure 3 shows a p-v diagram for a mixture of liquid and vapor (we will look at solids a little later). Here, we have a liquid-vapor dome the topmost point of which is the critical point as shown in Fig. 3. Different isotherms are shown. The temperature increases in the direction of the red arrow. At low temperature, the specific volume is low. As the temperature increases, the pressure and the specific volume at which the boiling starts also increase. Within the liquid-vapor dome (if the boiling happens at constant pressure as considered in the previous lecture), the temperature also remains constant. The isotherm and the isobar overlap in the liquid-vapor dome. They are parallel to the v-axis.

If you want to boil water at constant temperature (along an isotherm), you need to change pressures which fall on that particular isotherm as shown in Fig. 3.

The isotherm which goes through the critical point is a critical isotherm. The critical isobar is a line parallel to the v-axis on a p-v diagram (Fig. 3).

As in the T-v diagram, we have a saturated liquid line and a saturated vapor line on the p-v diagram too which separate liquid region (single phase region), a mixture of liquid and vapor (two-phase region), and gas/vapor region (single phase region).

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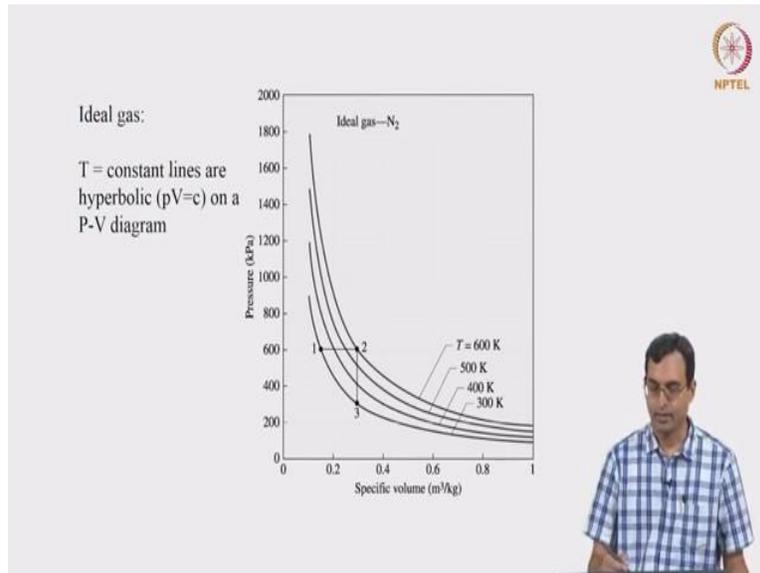


Figure 4.

Figure 4 shows isotherms for an ideal gas which can be represented by the equation  $pv = constant$  (which represents rectangular hyperbola on a p-v diagram). We discussed this when we studied the concept of an ideal gas.

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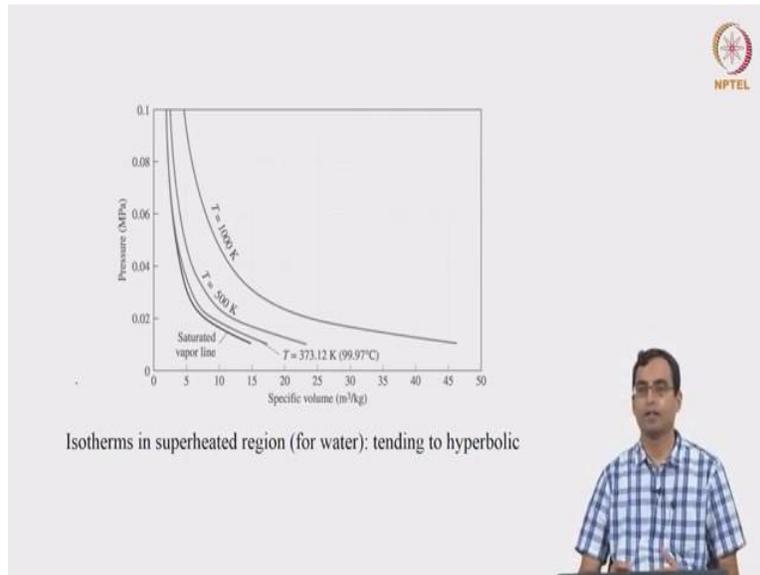
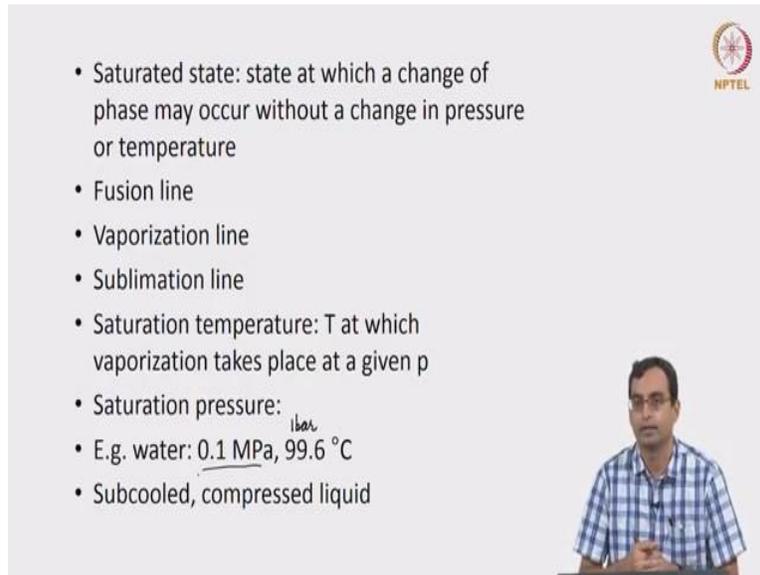


Figure 5.

Figure 5 shows isotherms which are close to a saturated vapor line on a p-v diagram. The isotherms close to the saturated vapor line are not hyperbolic. However, as you go away from the saturated vapor line (essentially the liquid-vapor dome) towards right on a p-v diagram, isotherms look like hyperbola (Fig. 5). In this region, the steam/vapor can be treated as ideal gas. Hence, in the region close to the liquid-vapor dome, we cannot use ideal gas relation to find gas/steam/vapor properties. We can get those properties from tables.

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- Saturated state: state at which a change of phase may occur without a change in pressure or temperature
- Fusion line
- Vaporization line
- Sublimation line
- Saturation temperature: T at which vaporization takes place at a given p
- Saturation pressure:
- E.g. water: 0.1 MPa, <sup>1 bar</sup> 99.6 °C
- Subcooled, compressed liquid

Figure 6.

A saturated state in general is a state at which there is a change of phase which may occur without a change in pressure or temperature; if the pressure is fixed, the temperature is fixed, or if the temperature is fixed, the pressure is fixed. The change of state can be either from solid to liquid or vice versa, liquid to vapor or vice versa, solid to vapor or vice versa. The saturation temperature is a temperature at which vaporization takes place at a given pressure. Similarly, the saturation pressure is a pressure at which vaporization takes place at a given temperature. For example, at 1 bar pressure, the boiling point of water is 99.6 °C. Hence, 1 bar is the saturation pressure at 99.6 °C and 99.6 °C is the saturation temperature at 1 bar pressure.

If the temperature for a given pressure is below the boiling point, the fluid is in subcooled region/compressed liquid region. For a given pressure if the temperature is above the boiling point, the fluid is in superheated region. Similarly, for a given temperature, if the pressure is higher than the pressure at which boiling happens (saturation pressure), then the fluid is in the compressed liquid/subcooled liquid zone. If the pressure is lower than the saturation pressure at a given temperature, the fluid is in superheated state. If the fluid is at saturation pressure at given temperature, then the fluid is in the two-phase region.

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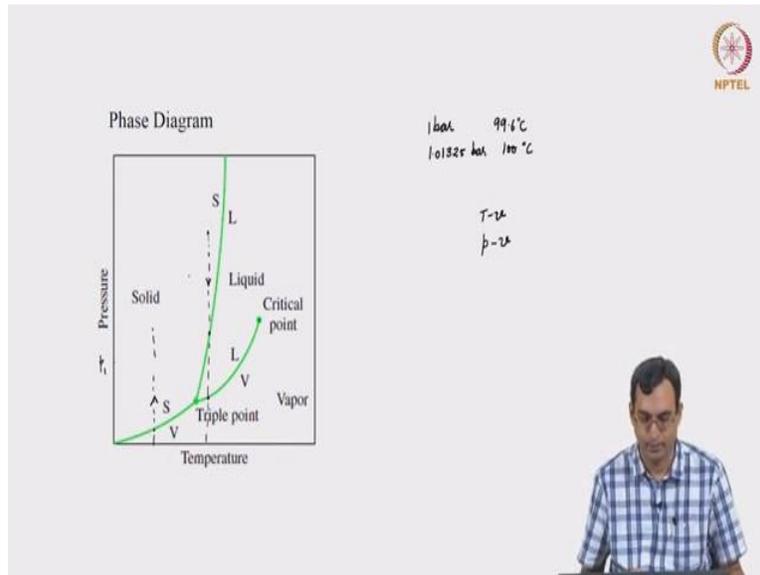


Figure 7.

Let's look at a p-T diagram. We know that during phase change, the pressure and the temperature remains constant. This pressure and the corresponding saturation temperature form a point on p-t diagram. Similarly, different pressures and the corresponding saturation temperature can be represented by different points on a p-T diagram. If we join all these points, we get curves as shown in Fig. 7, which are for a substance which contract on freezing. On a p-T diagram, you don't get a liquid-vapor dome (two phase region). The curves in Fig. 7 show a fusion line, a sublimation line and a vaporization line. A substance changes phase from solid (S) to liquid (L) across the fusion line. A substance changes phase from liquid (L) to vapor (V) across the vaporization line. A substance changes phase from solid (S) to vapor (V) across the sublimation line. These lines separate regions of three phases of a substance. These lines meet at the triple point where a mixture of solid, liquid and gaseous phases of a substance exists in equilibrium. Till now, we were looking at only the conversion from liquid to vapor. For example, in Fig. 7, the complete conversion of a given amount of liquid substance to vapor at saturated conditions happen at a point on the vaporization line (L-V line). A critical point is also shown in Fig .7.

Consider a substance at pressure below critical pressure and above triple point pressure and heat it at constant pressure. Initially, the substance is in solid state. As we keep heating it, its temperature rises. As we continue to heat, the temperature hits the melting point (S-L curve or the fusion line). The complete conversion from solid to liquid happens at constant temperature (a point on the fusion line represents this entire process). Once the entire solid converts into liquid and we continue to heat, the temperature of the liquid rises till it reaches the vaporization line (L-V line). Again, the complete conversion from liquid to vapor happens at a constant temperature. As the heating continues, the temperature of the vapor increases. If we consider the substance at pressure higher than the critical pressure and heat it, we see only a conversion from solid to supercritical fluid. At very low pressures (less than triple point pressure), we see a conversion from solid to vapor (across S-V line or sublimation line), which is known as sublimation.

Similarly, consider a substance at very low temperature (less than the triple point temperature) and increase the pressure at that temperature. At very low temperature and low pressure, the substance is in vapor state. As the pressure increases, the molecules are forced to come closer and closer. At a pressure corresponding to S-V line, the vapor starts getting converted into solid. This conversion, again, happens at constant pressure and temperature (it is a point on S-V line). As the pressure increases, the substance stays in the solid region.

A substance at a temperature above triple point temperature, below critical point temperature and low pressure is in a vapor state. As the pressure increases at the same temperature, the vapor starts becoming liquid at a point on the S-L line. During this conversion, the pressure and the temperature remain constant. As the pressure increases, the liquid starts converting into solid at a point on S-L line. Again, the pressure and the temperature remain constant during this conversion. After that as the pressure increases, the substance stays in the solid phase.

All the above discussion is for a substance which contracts on freezing.

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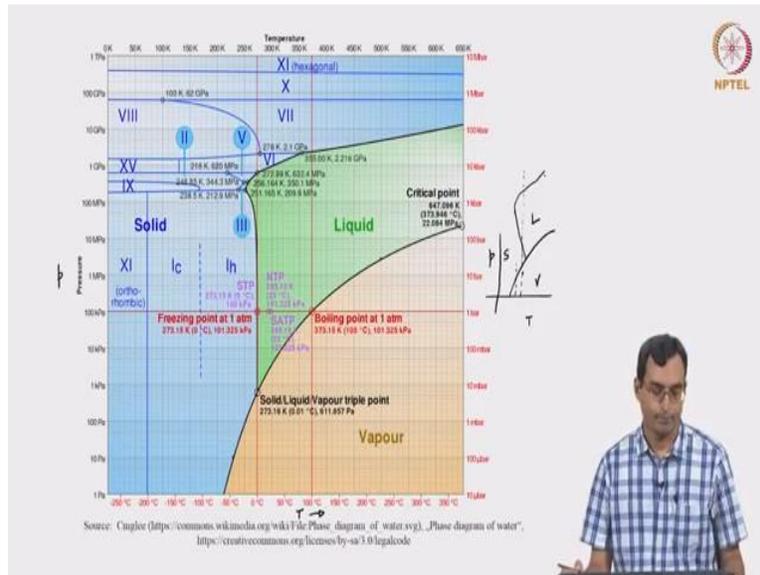


Figure 8.

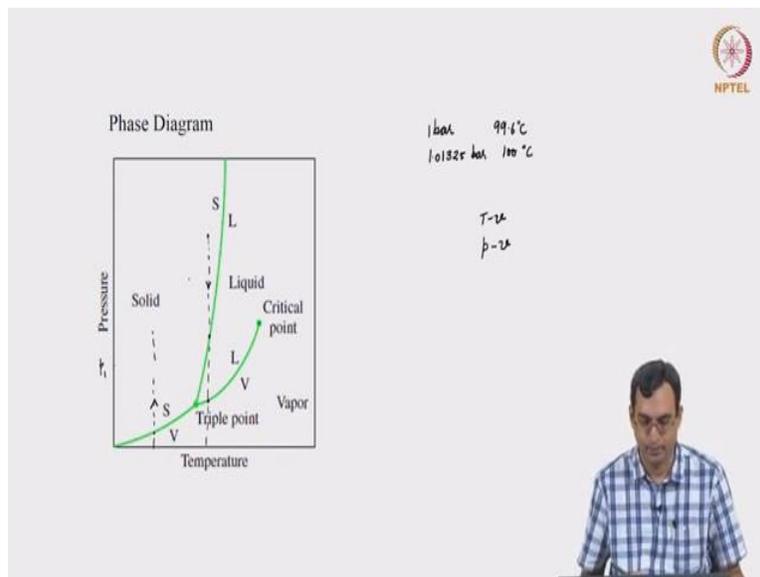


Figure 8 shows a p-T diagram for water. Water expands on freezing (anomalous behavior of water). Freezing point (0 °C) and the boiling point (100 °C) at 1 atm are shown in Fig. 8. All the discussion above in the case of a substance which contracts on freezing is valid for water also. For example, at a pressure of 1 atm and at low temperature, we have ice. As we heat it at a constant pressure, it becomes liquid and ultimately vapor. We can have ice at 100 °C at 10 GPa. As the pressure reduces at 100 °C, this ice becomes liquid and ultimately vapor at 100 °C. There is a special region on the p-T diagram of the water. At

temperature in this region and at very high pressure, we have ice. As the pressure reduces at constant temperature, the ice becomes liquid, then solid and then vapor. This region is drawn in the magnified view in Fig. 8. This happens because of the anomalous behavior of water. For water, the temperature and pressure at the critical point are 374 °C and 220.6 bar.

The fusion line, the vaporization line and the sublimation line represent states at which two phases of a substance are in equilibrium. The properties of a substance in each phase do not change at equilibrium. For example, if we have a mixture of water and its vapor in equilibrium at certain temperature and pressure, the properties of liquid water and vapor such as pressure, temperature, mass, specific volume, etc. do not change with time. For all substances, there is one particular state where we can have a substance in liquid, vapor and solid form in equilibrium with each other and that state is called a triple point. For water, the triple point corresponds to temperature of 0.01 °C and pressure of 611 Pa. At these conditions, we can find ice, liquid water and steam in equilibrium.

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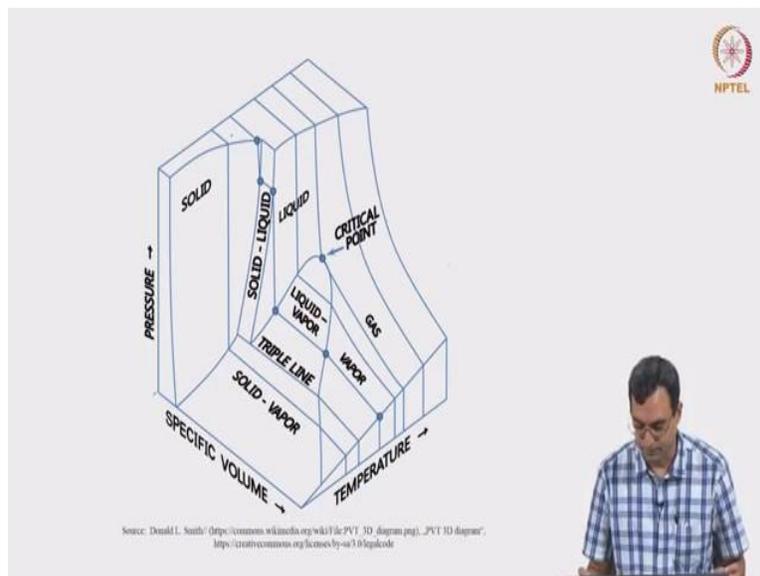


Figure 9.

We have been looking at p-v, p-T and T-v diagrams. There are three variables, p, v and T. It means that we can show a state of a substance on a surface in three dimensional p-v-T

space. Such a p-v-T surface is shown in Fig .9 for a substance which contracts on freezing. Figure 10 shows the p-v-T surface for a substance which expands on freezing such as water along with the p-v-T surface for a substance which contracts on freezing.

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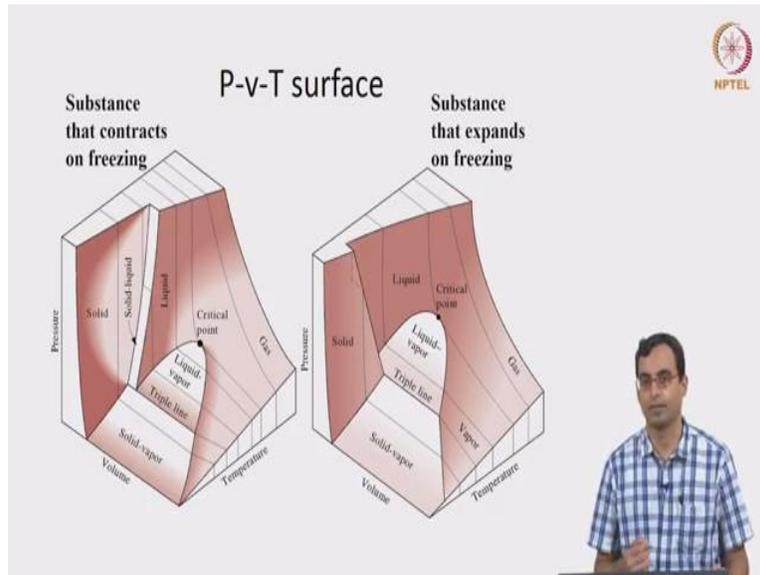


Figure 10.

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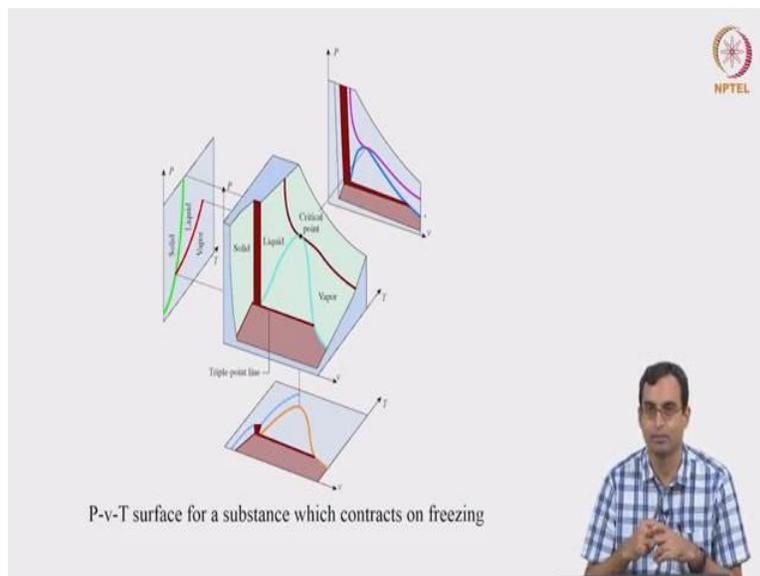


Figure 11.

Figure 11 shows projections of a  $p$ - $v$ - $T$  surface on  $p$ - $v$ ,  $p$ - $T$  and  $T$ - $v$  planes which are our regular  $p$ - $v$ ,  $p$ - $T$  and  $T$ - $v$  diagrams. Such a  $p$ - $v$ - $T$  surface can be printed using a 3D printer.