Chapter two

PROPERTIES OF PURE SUBSTANCES

objective

- Introduce the concept of a pure substance.
- Discuss the physics of phase-change processes.
- Illustrate the *P*-*v*, *T*-*v*, and *P*-*T* property diagrams and *P*-*v*-*T* surfaces of pure substances.
- Demonstrate the procedures for determining thermodynamic properties of pure substances from tables of property data.
- Describe the hypothetical substance "ideal gas" and the ideal-gas equation of state.
- Apply the ideal-gas equation of state in the solution of typical problems.
- Introduce the compressibility factor, which accounts for the deviation of real gases from ideal-gas behavior.
- Present some of the best-known equations of state.

PURE SUBSTANCE

- A substance that has a fixed chemical composition throughout is called a **pure substance.**
- For example water, nitrogen, helium, and carbon dioxide, are pure substances.
- A pure substance does not have to be of a single chemical element or compound.
- A mixture of various chemical elements or compounds also qualifies as a pure substance as long as the mixture is homogeneous.
- Air, for example, is a mixture of several gases, but it is often considered to be a pure substance because it has a uniform chemical composition.
- However, a mixture of oil and water is not a pure substance.
- A mixture of two or more phases of a pure substance is still a pure substance as long as the chemical composition of all phases is the same.
- A mixture of ice and liquid water, for example, is a pure substance because both phases have the same chemical composition.

PHASES OF A PURE SUBSTANCE

- We all know from experience that substances exist in different phases.
- At room temperature and pressure, copper is a solid, mercury is a liquid, and nitrogen is a gas.
- Even though there are three principal phases **solid, liquid, and gas** a substance may have several phases within a principal phase, each with a different molecular structure.
- for example: Carbon may exist as **graphite or diamond** in the solid phase.
- Helium has two liquid phases
- iron has three solid phases.

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- Intermolecular bonds are strongest in **solids** and weakest in **gases**. One reason is that molecules in **solids** are closely packed together, whereas in **gases** they are separated by relatively large distances.
- While molecular spacing in the **liquid** phase is not much different from that of the solid phase, except the molecules are no longer at fixed positions relative to each other and they can rotate and translate freely. In a liquid, the intermolecular forces are weaker relative to solids, but still relatively strong compared with gases.
- Because of the small distances between molecules in a solid, the attractive forces of molecules on each other are large and keep the molecules at fixed positions.

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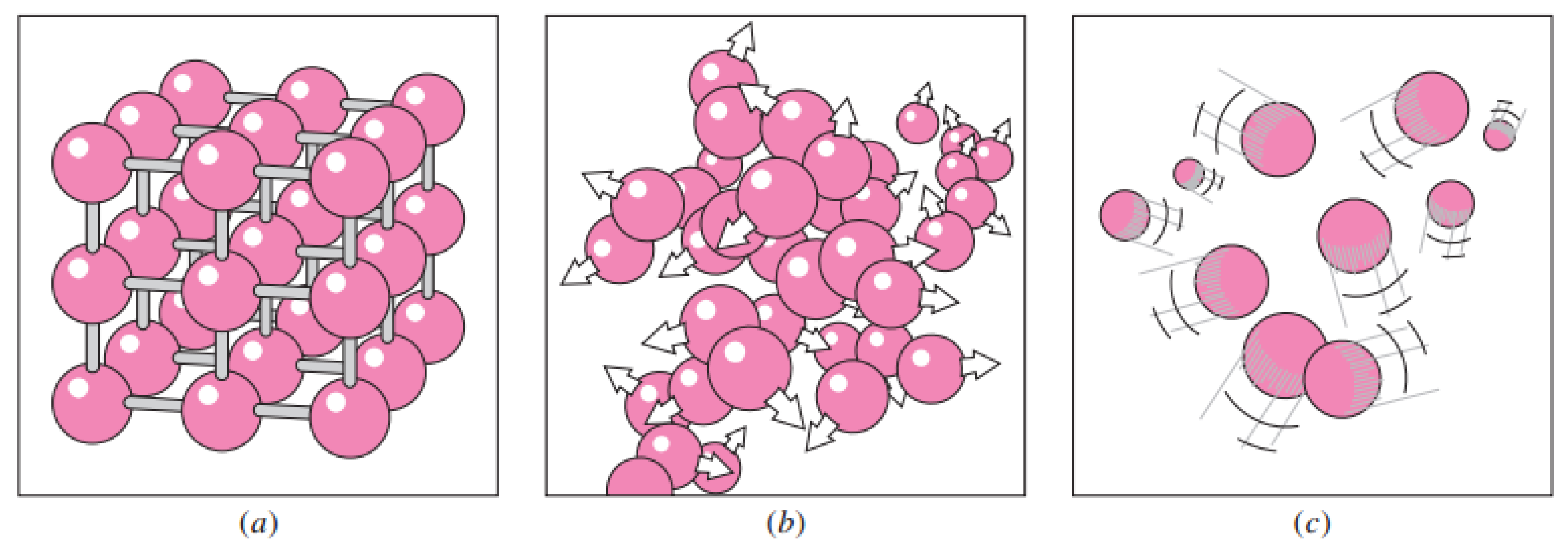
(a)
(b)
(c)

Fig 3.1:The arrangement of atoms in different phases

(a) molecules are at relatively fixed positions in a solid,

(b) groups of molecules move about each other in the liquid phase, and

(c) molecules move about at random in the gas phase.

PHASE CHANGE PROCESSES OF PURE SUBSTANCES

- Let's study the phase change processes takes place by taking water as example at constant pressure.(all pure substance exhibit the same general behavior)
- Consider a piston–cylinder device containing liquid water at 20°C and 1 atm pressure (state 1, Fig. below). Under these conditions, water exists in the liquid phase, and it is called a **compressed liquid, or a subcooled liquid, meaning** that it is not about to vaporize.

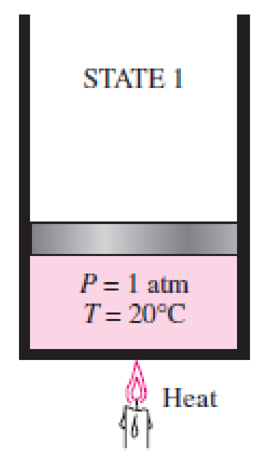

Fig. At 1 atm and 20°C, water exists in the liquid phase (*compressed liquid*).

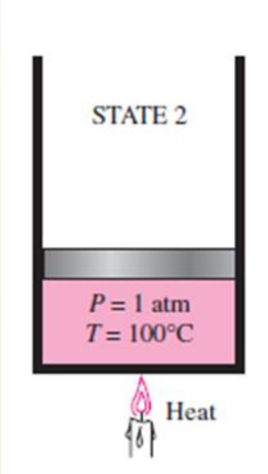

Fig. At 1 atm pressure and 100°C, water exists as a liquid that is ready to vaporize (*saturated liquid*).

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- Heat is now transferred to the water until its temperature rises to, say, 40°C. As the temperature rises, the liquid water expands slightly, and so its specific volume increases.
- To accommodate this expansion, the piston moves up slightly. The pressure in the cylinder remains constant at 1 atm during this process since it depends on the outside barometric pressure and the weight of the piston, both of which are constant. Water is still a compressed liquid at this state since it has not started to vaporize.
- As more heat is transferred, the temperature keeps rising until it reaches 100°C (state 2, Fig. below). At this point water is still a liquid, but any heat addition will cause some of the liquid to vaporize. That is, a phase-change process from liquid to vapor is about to take place.

A liquid that is about to vaporize is called a **saturated liquid. Therefore, state 2 is a saturated liquid** state.

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- Once boiling starts, the temperature stops rising until the liquid is completely vaporized.
- That is, the temperature will remain constant during the entire phase-change process if the pressure is held constant.
- During a boiling process, the only change we will observe is a large increase in the volume and a steady decline in the liquid level as a result of more liquid turning to vapor.
- Midway about the vaporization line (state 3, Fig. below), the cylinder contains equal amounts of liquid and vapor.

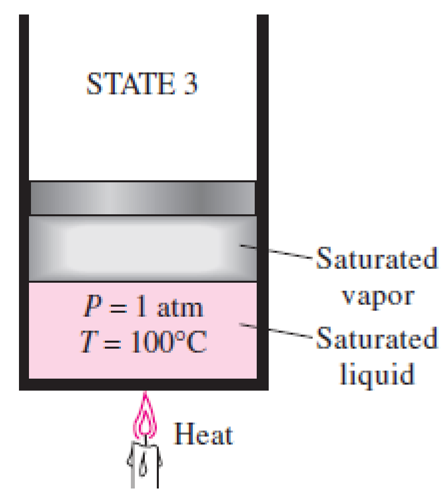

Fig. As more heat is transferred, part of the saturated liquid vaporizes (*saturated liquid–vapor mixture).*

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- As we continue transferring heat, the vaporization process continues until the last drop of liquid is vaporized (state 4, Fig. below).
- At this point, the entire cylinder is filled with vapor that is on the borderline of the liquid phase.
- Any heat loss from this vapor will cause some of the vapor to condense (phase change from vapor to liquid).
- A vapor that is about to condense is called a **saturated vapor. Therefore, state 4 is a saturated** vapor state.

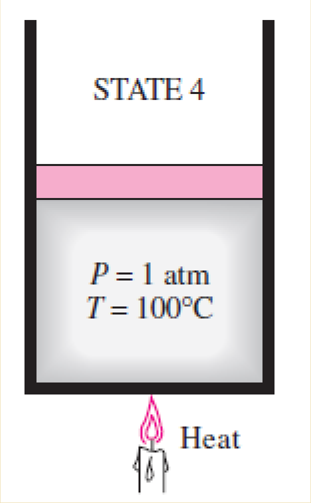

Fig. At 1 atm pressure, the temperature remains constant at 100°C until the last drop of liquid is vaporized (*saturated vapor*).

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- A substance at states between 2 and 4 is referred to as a **saturated liquid–vapor mixture since the liquid and vapor phases coexist in** equilibrium at these states.
- Once the phase-change process is completed, we are back to a single phase region again (this time vapor), and further transfer of heat results in an increase in both the temperature and the specific volume At state 5, the temperature of the vapor is, let us say, 300°C; and if we transfer some heat from the vapor, the temperature may drop some what but no condensation will take place as long as the temperature remains above 100°C(for P=1 atm).
- A vapor that is not about to condense is called a **superheated vapor.**

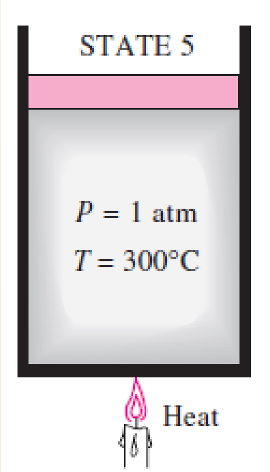

Fig. As more heat is transferred, the temperature of the vapor starts to rise (*superheated vapor*).

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- This constant-pressure phase-change process is illustrated on a T-v diagram in Fig. below.

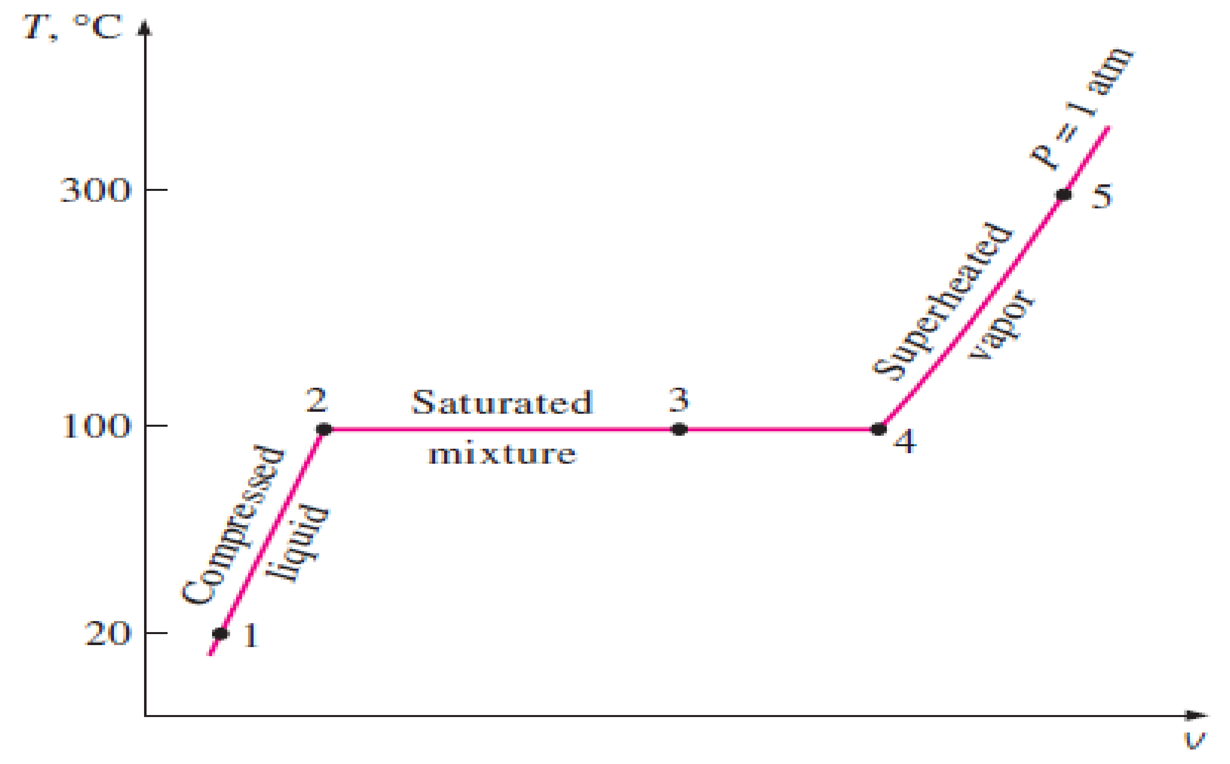

Fig. 3.2T-v diagram for the heating process of water at constant pressure.

Saturation Temperature and Saturation Pressure

- It probably came as no surprise to you that water started to boil at 100°C.
- Strictly speaking, the statement “water boils at 100°C” is incorrect.
- The correct statement is “water boils at 100°C at 1 atm pressure.”
- The only reason water started boiling at 100°C was because we held the pressure constant at 1 atm (101.325 kPa).
- If the pressure inside the cylinder were raised to 500kPa by adding weights on top of the piston, water would start boiling at 151.8°C.
- That is, the temperature at which water starts boiling depends on the pressure; therefore, if the pressure is fixed, so is the boiling temperature.

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- At a given pressure, the temperature at which a pure substance changes phase is called the saturation temperature.
- Likewise, at a given temperature, the pressure at which a pure substance changes phase is called the saturation pressure.

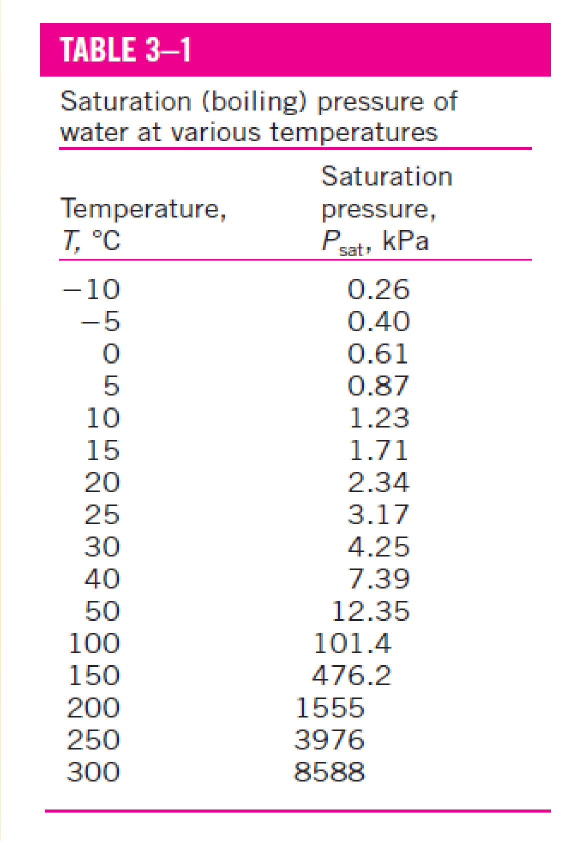

TABLE 3–1

Saturation (boiling) pressure of water at various temperatures

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
100	101.4
150	476.2
200	1555
250	3976
300	8588

Cont..

- It takes a large amount of energy to melt a solid or vaporize a liquid. The amount of energy absorbed or released during a phase-change process is called the **latent heat.**
- More specifically, the amount of energy absorbed during melting is called the **latent heat of fusion** and is equivalent to the amount of energy released during freezing.
- Similarly, the amount of energy absorbed during vaporization is called the **latent heat of vaporization and** is equivalent to the energy released during condensation.
- The magnitudes of the latent heats depend on the temperature or pressure at which the phase change occurs.
- At 1 atm pressure, the latent heat of fusion of water is 333.7kJ/kg and the latent heat of vaporization is 2256.5 kJ/kg.

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- During a phase-change process, pressure and temperature are obviously dependent properties, and there is a definite relation between them, that is, Tsat = f (Psat).
- A plot of Tsat versus Psat, such as the one given for water in Fig. below, is called a **liquid–vapor saturation curve.** A curve of this kind is characteristic of all pure substances.

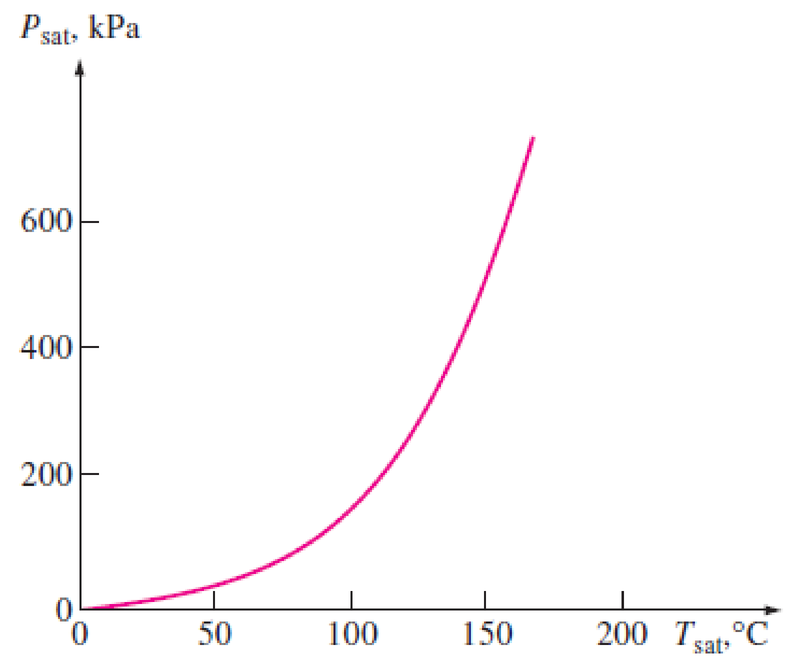

Fig. 3.3 The liquid–vapor saturation curve of a pure substance (numerical values are for water).

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- It is clear from above Fig. that *Tsat* increases with *Psat*. Thus, a substance at higher pressures boils at higher temperatures.
- In the kitchen, higher boiling temperatures mean shorter cooking times and energy savings.
- A beef stew, for example, may take 1 to 2 h to cook in a regular pan that operates at 1 atm pressure, but only 20 min in a pressure cooker operating at 3 atm absolute pressure (corresponding boiling temperature: 134°C).
- The atmospheric pressure, and thus the boiling temperature of water, decreases with elevation.
- Therefore, it takes longer to cook at higher altitudes than it does at sea level (unless a pressure cooker is used).
- For example, the standard atmospheric pressure at an elevation of 2000 m is 79.50kPa, which corresponds to a boiling temperature of 93.3°C as opposed to100°C at sea level (zero elevation).
- The variation of the boiling temperature of water with altitude at standard atmospheric conditions is given in Table below.

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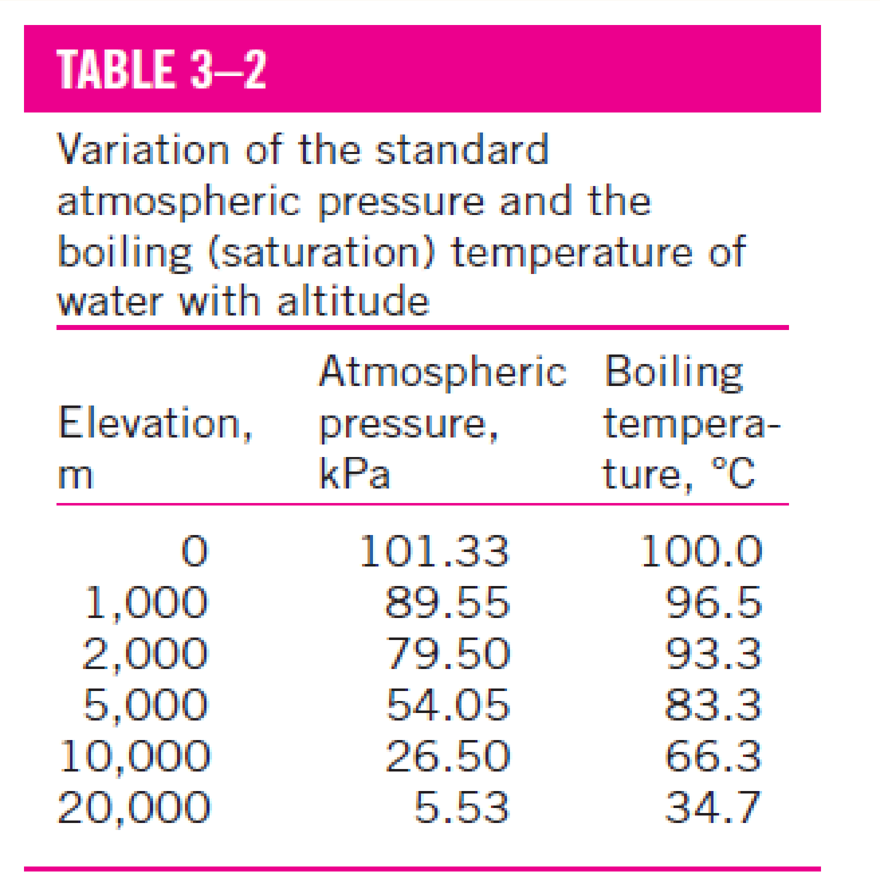

TABLE 3–2

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

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

- For each 1000 m increase in elevation, the boiling temperature drops by a little over 3°C. Note that the atmospheric pressure at a location, and thus the boiling temperature, changes slightly with the weather conditions. But the corresponding change in the boiling temperature is no more than about 1°C.

PROPERTY DIAGRAMS FOR PHASE-CHANGE PROCESSES

The *T-v Diagram*

- Let us add weights on top of the piston until the pressure inside the cylinder reaches 1 MPa.
- At this pressure, water has a somewhat smaller specific volume than it does at 1 atm pressure.
- As heat is transferred to the water at this new pressure, the process follows a path that looks very much like the process path at 1 atm pressure as shown in Fig. , but there are some noticeable differences.
- First, water starts boiling at a much higher temperature (179.9°C) at this pressure.
- Second, the specific volume of the saturated liquid is larger and the specific volume of the saturated vapor is smaller than the corresponding values at 1 atm pressure.
- That is, the horizontal line that connects the saturated liquid and saturated vapor states is much shorter.

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- As the pressure is increased further, this saturation line continues to shrink, as shown in Fig 3.4 below, and it becomes a point when the pressure reaches 22.06 MPa for the case of water.
- This point is called the **critical point, and it is defined as *the point at which the saturated liquid and saturated*** *vapor states are identical.*

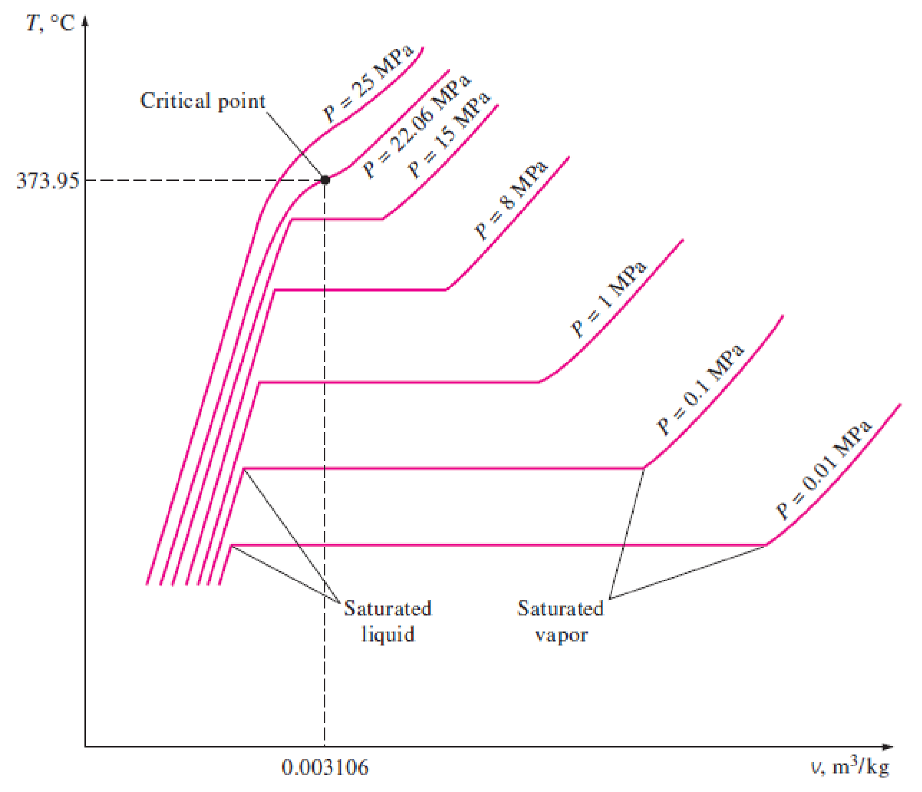

fig.3.4 *T-v* diagram of constant-pressure phase-change processes of a pure substance at various pressures (numerical values are for water)

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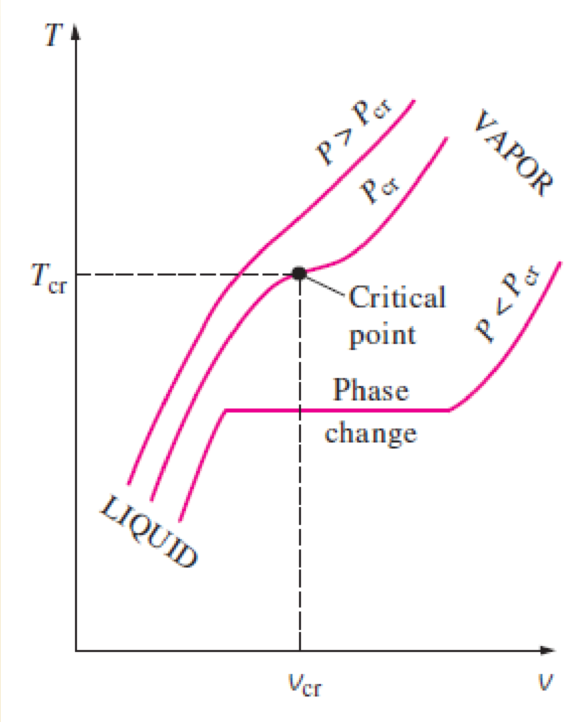
- The critical-point properties of water are:
- At pressures above the critical pressure, there is not a distinct phase change process.

$$P_{cr} = 22.06 MPa, T_{cr} = 373.95 o_C, and\ V_{cr} = 0.003106\ m^3/kg$$



- At supercritical pressures (*P* >*Pcr*),there is no distinct phase-change (boiling) process

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- Instead, the specific volume of the substance continually increases, and at all times there is only one phase present.
- The saturated liquid states in Fig. 3.4 can be connected by a line called the **saturated liquid line, and saturated vapor states in the same figure can** be connected by another line, called the **saturated vapor line.**
- These two lines meet at the critical point, forming a dome as shown in Fig. 3.5.
- All the compressed liquid states are located in the region to the left of the saturated liquid line, called the **compressed liquid region.**
- All the superheated vapor states are located to the right of the saturated vapor line, called the **superheated vapor region.**
- In these two regions, the substance exists in a single phase, a liquid or a vapor.

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- All the states that involve both phases in equilibrium are located under the dome, called the **saturated liquid vapor mixture region, or the wet region.**

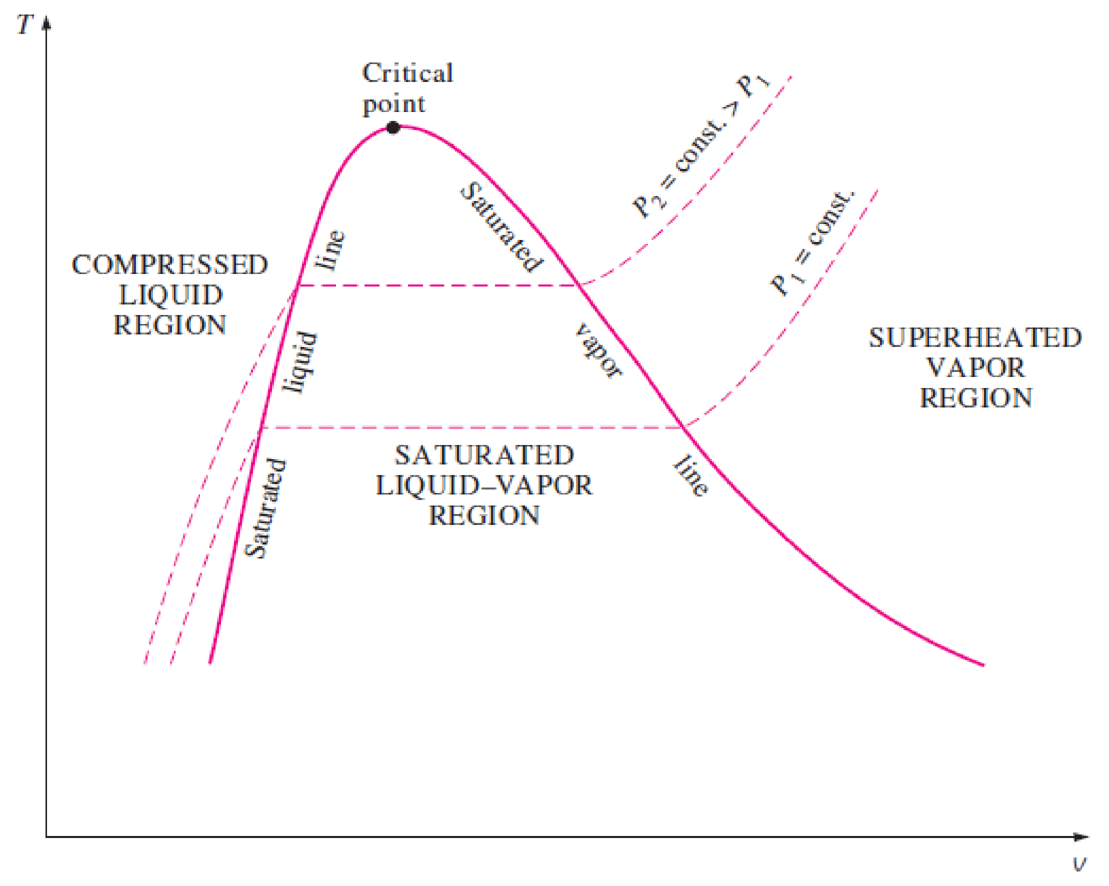

Fig. 3.5 *T-v* diagram of a pure substance.

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The P-v Diagram

- The general shape of the *P*-*v diagram of a pure substance is very much like* the *T-v diagram, but the T=constant lines on this diagram have a downward* trend, as shown in Fig. 3.6.

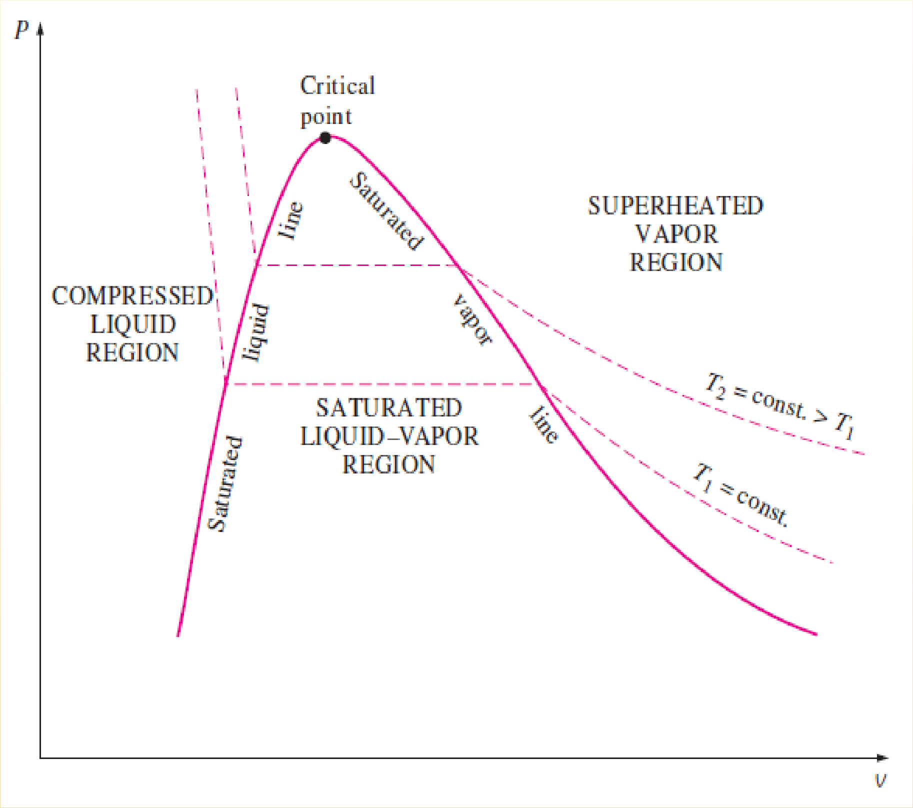

Fig:3.6 P-v diagram of a pure substance

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- Consider again a piston–cylinder device that contains liquid water at 1 MPa and 150°C.
- Water at this state exists as a compressed liquid.
- Now the weights on top of the piston are removed one by one so that the pressure inside the cylinder decreases gradually (Fig. 3.7).
- The water is allowed to exchange heat with the surroundings so its temperature remains constant.
- As the pressure decreases, the volume of the water increases slightly.
- When the pressure reaches the saturation-pressure value at the specified temperature (0.4762 MPa), the water starts to boil.
- When the process is repeated for other temperatures, similar paths are obtained for the phase-change processes. Connecting the saturated liquid and the saturated vapor states by a curve, we obtain the *P-v diagram of a* pure substance, as shown in the figure below.

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- During this vaporization process, both the temperature and the pressure remain constant, but the specific volume increases.
- Once the last drop of liquid is vaporized, further reduction in pressure results in a further increase in specific volume.

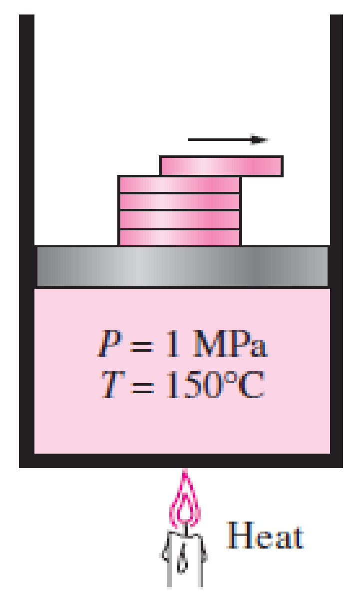

Fig.3.7 The pressure in a piston–cylinder device can be reduced by reducing the weight of the piston.

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- Extending the Diagrams to Include the Solid Phase
- The two equilibrium diagrams developed so far represent the equilibrium states involving the liquid and the vapor phases only.
- However, these diagrams can easily be extended to include the solid phase as well as the solid–liquid and the solid–vapor saturation regions.
- The basic principles discussed in conjunction with the liquid–vapor phase-change process apply equally to the solid–liquid and solid–vapor phase-change processes.
- Most substances contract during a solidification (i.e., freezing) process.
- Others, like water, expand as they freeze.
- The *P-v diagrams for both groups of substances* are given in Figs. 3–21 and 3–22.

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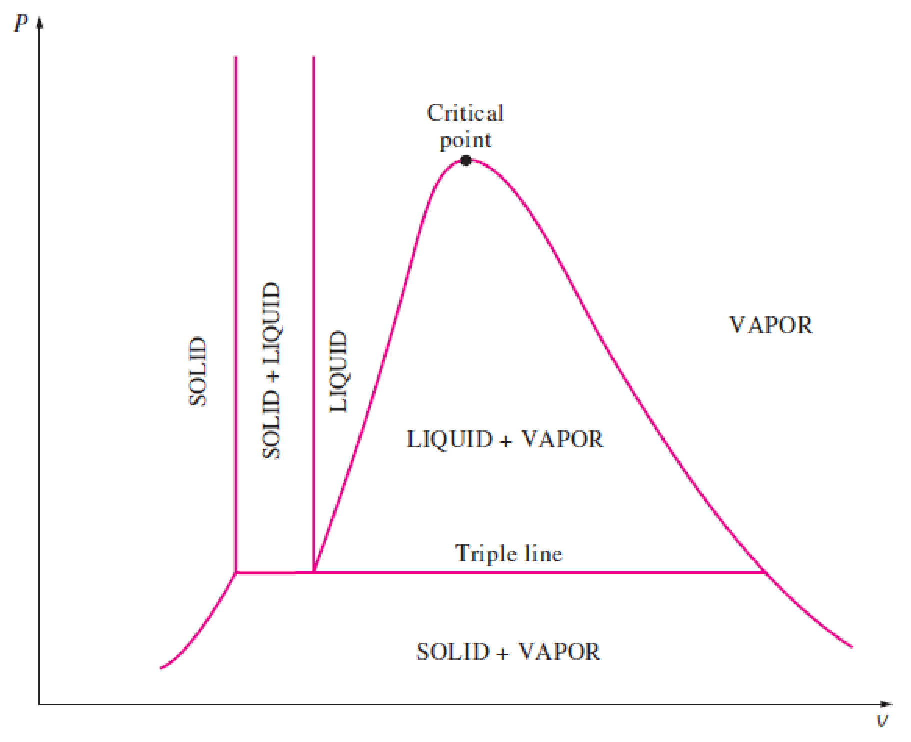
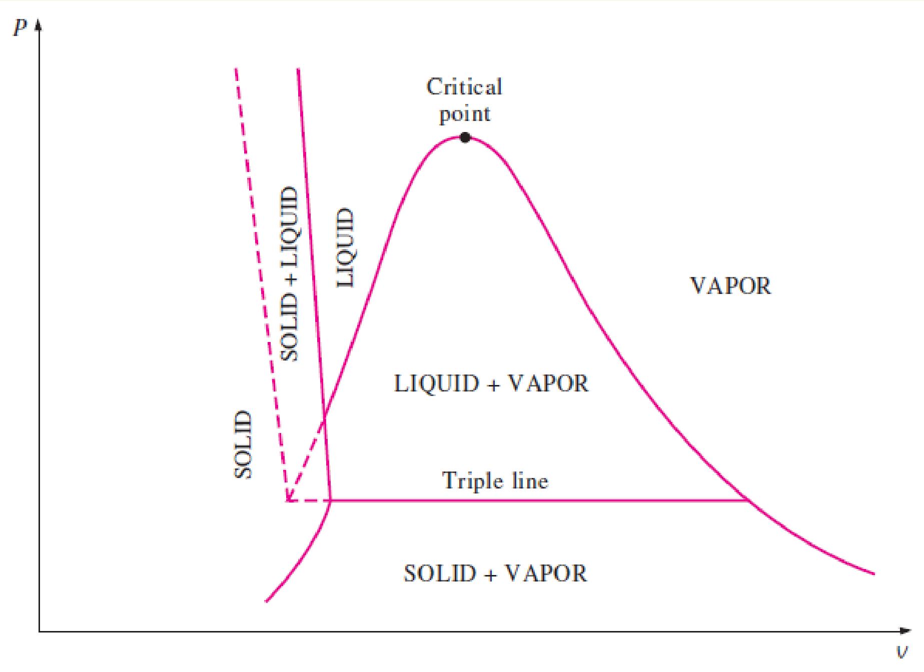
- *P-v diagram of a substance that* contracts on freezing



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



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- The fact that water expands upon freezing has vital consequences in nature.
- If water contracted on freezing as most other substances do, the ice formed would be heavier than the liquid water, and it would settle to the bottom of rivers, lakes, and oceans instead of floating at the top.
- The sun's rays would never reach these ice layers, and the bottoms of many rivers, lakes, and oceans would be covered with ice at times, seriously disrupting marine life.
- We are all familiar with two phases being in equilibrium, but under some conditions all three phases of a pure substance coexist in equilibrium (Fig. 3–23).
- On *P-v or T-v diagrams, these triple-phase states form a line* called the **triple line.**
- The states on the triple line of a substance have the same pressure and temperature but different specific volumes.

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- The triple line appears as a point on the *P-T diagrams and, therefore, is often called* the **triple point.**
- There are two ways a substance can pass from the solid to vapor phase:

  1.either it melts first into a liquid and subsequently evaporates, or

  2.it evaporates directly without melting first.
- Passing from the solid phase directly into the vapor phase is called **sublimation.**
- For substances that have a triple-point pressure above the atmospheric pressure such as solid CO_2 (dry ice), sublimation is the only way to change from the solid to vapor phase at atmospheric conditions.

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The P-T Diagram

- Figure 3–25 shows the *P-T diagram of a pure substance.*
- This diagram is often called the **phase diagram since all three phases are separated from** each other by three lines.
- The sublimation line separates the solid and vapor regions, the vaporization line separates the liquid and vapor regions, and the melting (or fusion) line separates the solid and liquid regions.
- These three lines meet at the triple point, where all three phases coexist in equilibrium.

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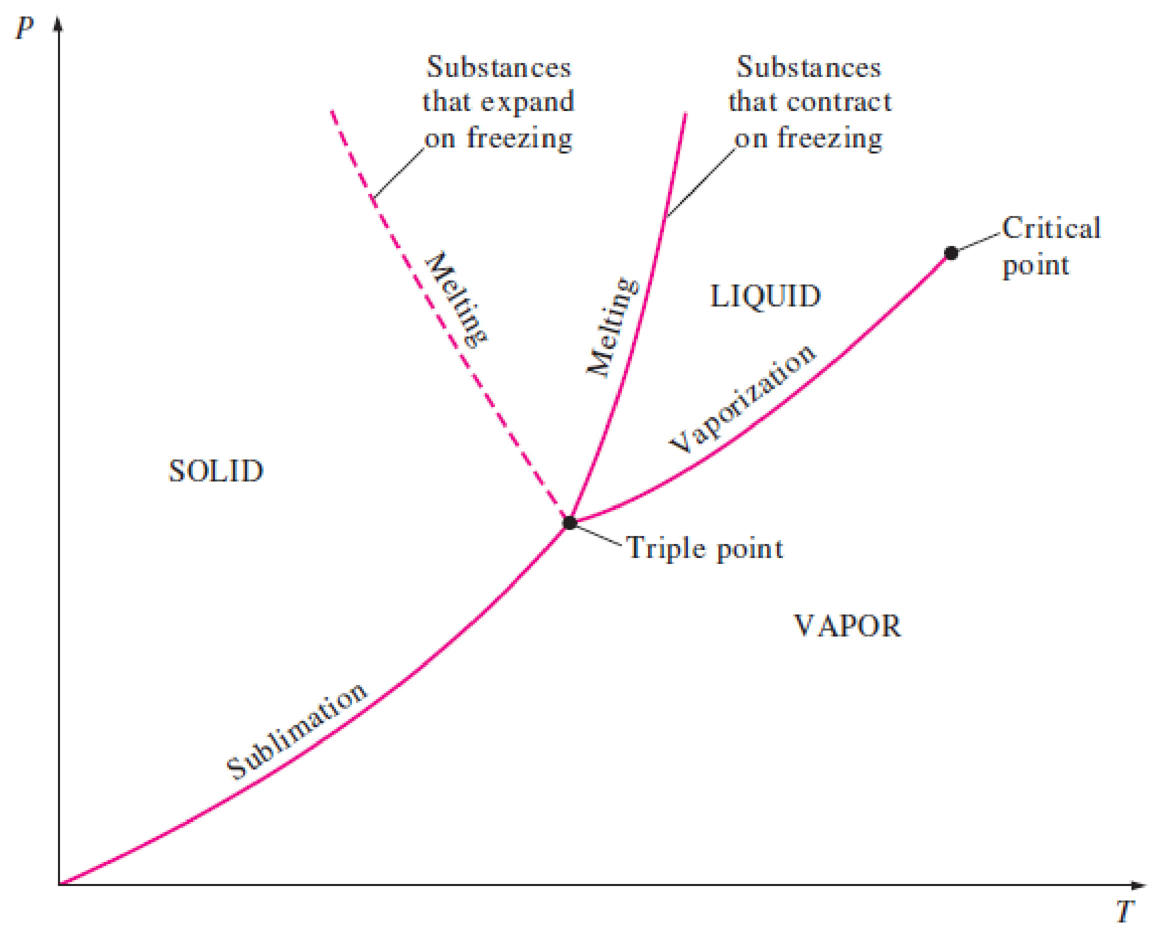

Fig 3.8 P-T diagram of a pure substance.

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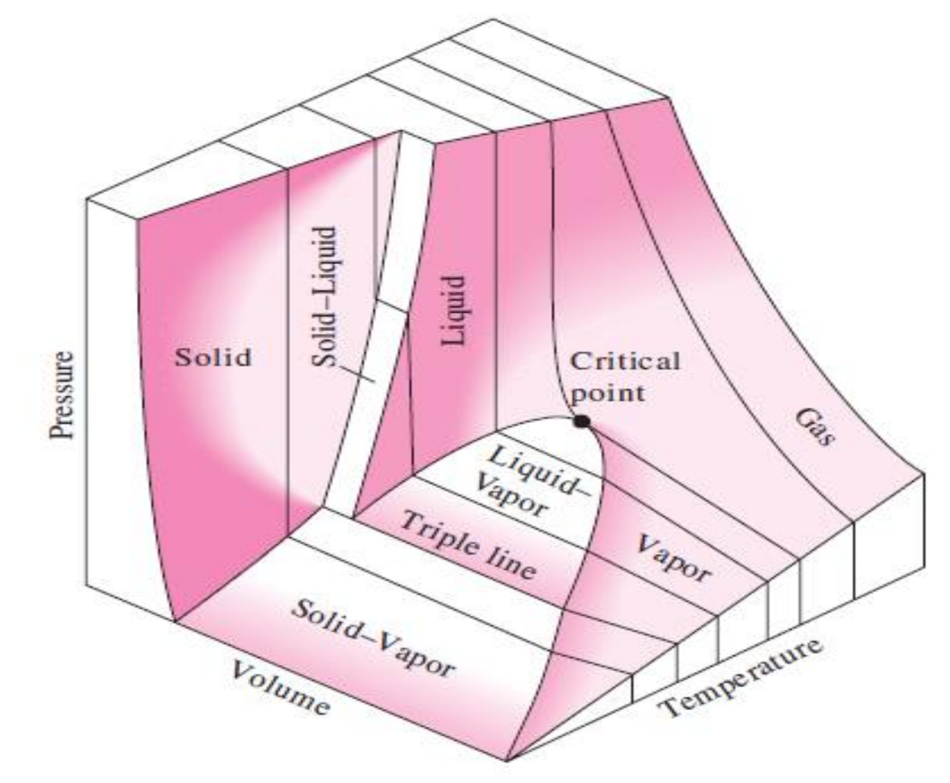
- *The P-v-T Surface*
- The state of a simple compressible substance is fixed by any two independent, intensive properties.
- Once the two appropriate properties are fixed, all the other properties become dependent properties.



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PROPERTY TABLES

- For most substances, the relationships among thermodynamic properties are too complex to be expressed by simple equations.
- Therefore, properties are frequently presented in the form of tables.
- Before we get into the discussion of property tables, we define a new property called *enthalpy*.
- *Enthalpy: A Combination Property*
- A person looking at the tables will notice two new properties: enthalpy *h and entropy s*.
- Entropy is a property associated with the second law of thermodynamics, and we will not use it until it is properly defined in Chap. 6.
- However, it is appropriate to introduce enthalpy at this point.

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- In the analysis of certain types of processes, particularly in power generation and refrigeration , we frequently encounter the combination of properties $u + Pv$.
- For the sake of simplicity and convenience, this combination is defined as a new property, **enthalpy, and given the symbol *h*:-**

$$h = u + Pv \qquad (\mathrm{kJ/kg})$$

Saturated Liquid and Saturated Vapor States

- The properties of saturated liquid and saturated vapor for water are listed in Tables A–4 and A–5.
- Both tables give the same information. The only difference is that in Table A–4 properties are listed under temperature and in Table A–5 under pressure.

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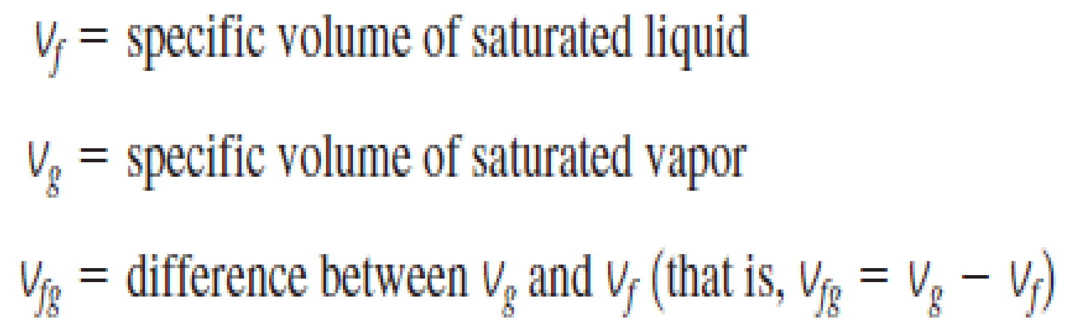
- Therefore, it is more convenient to use Table A–4 when *temperature is given and Table A–5 when pressure is given. The use* of Table A–4 is illustrated in Fig. 3–30.

- The subscript *“f “is used to denote properties of a saturated liquid, and the* subscript *“g” to denote the properties of saturated vapor.*

- Another subscript commonly used is *“fg”, which denotes the difference between* the saturated vapor and saturated liquid values of the same property.

- For example,



v_f = specific volume of saturated liquid

v_g = specific volume of saturated vapor

v_{fg} = difference between v_g and v_f (that is, $v_{fg} = v_g - v_f$)

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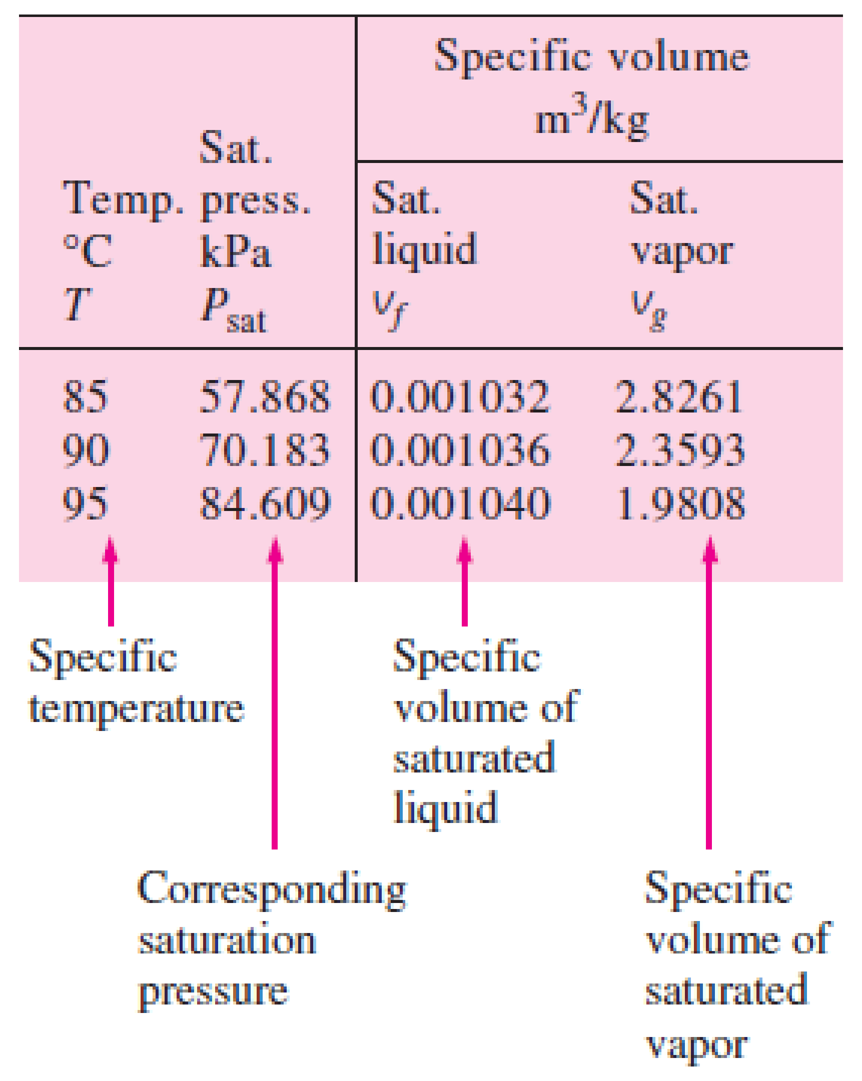

Temp. °C T	Sat. press. kPa P_{sat}	Specific volume m^3/kg Sat. liquid v_f	 Sat. vapor v_g
85	57.868	0.001032	2.8261
90	70.183	0.001036	2.3593
95	84.609	0.001040	1.9808

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- The quantity h_{fg} *is called the* ***enthalpy of vaporization (or latent heat*** of vaporization).
- It represents the amount of energy needed to vaporize a unit mass of saturated liquid at a given temperature or pressure.
- It decreases as the temperature or pressure increases and becomes zero at the critical point.

❖ Example:-

1. A rigid tank contains 50 kg of saturated liquid water at 90°C. Determine the pressure in the tank and the volume of the tank.
2. A mass of 200 g of saturated liquid water is completely vaporized at a constant pressure of 100kPa. Determine (*a) the volume change and (b) the* amount of energy transferred to the water.

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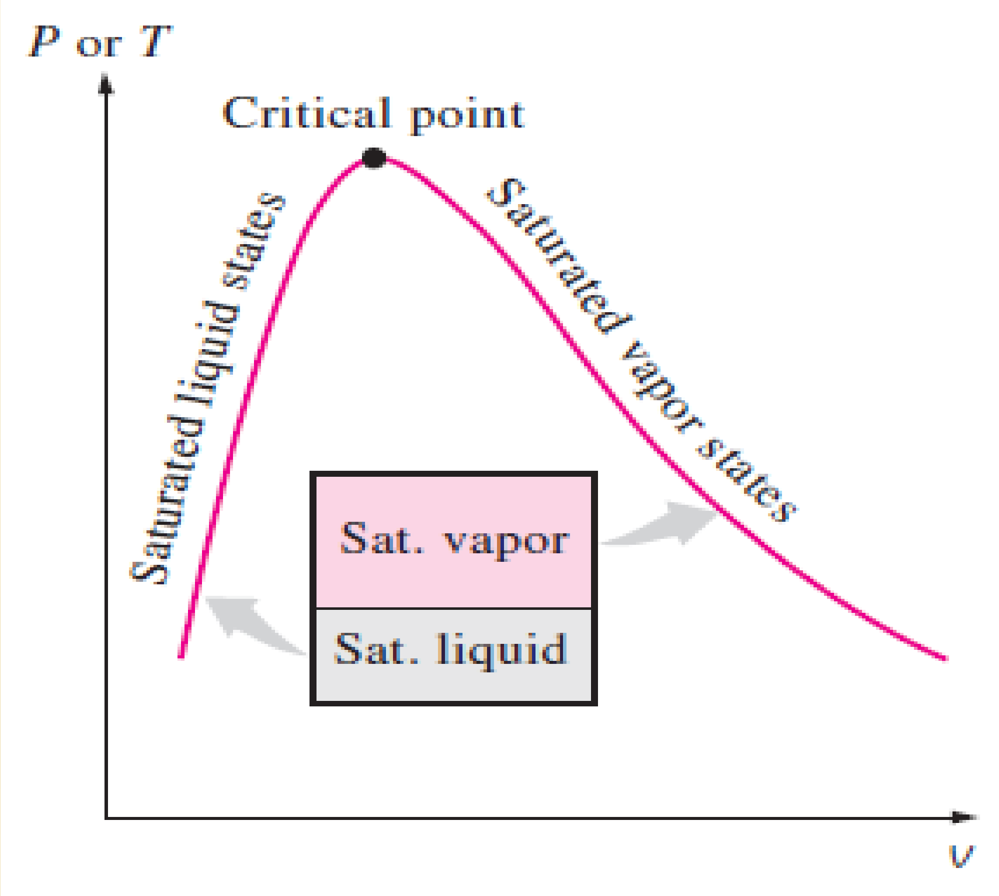
Saturated Liquid–Vapor Mixture

- During a vaporization process, a substance exists as part liquid and part vapor.
- That is, it is a mixture of saturated liquid and saturated vapor (Fig. 3–34).



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- To analyze this mixture properly, we need to know the proportions of the liquid and vapor phases in the mixture.
- This is done by defining a new property called the **quality** ***x as the ratio of the mass of vapor to the*** total mass of the mixture:-

$$x = \frac{m_{\text{vapor}}}{m_{\text{total}}}$$

- Where: $m_{\text{total}} = m_{\text{liquid}} + m_{\text{vapor}} = m_f + m_g$
- Quality has significance for *saturated mixtures only.*
- It has no meaning in the compressed liquid or superheated vapor regions.
- Its value is between 0 and 1.
- The quality of a system that consists of *saturated liquid is 0 (or 0* percent), and the quality of a system consisting of *saturated vapor is 1 (or* 100 percent).

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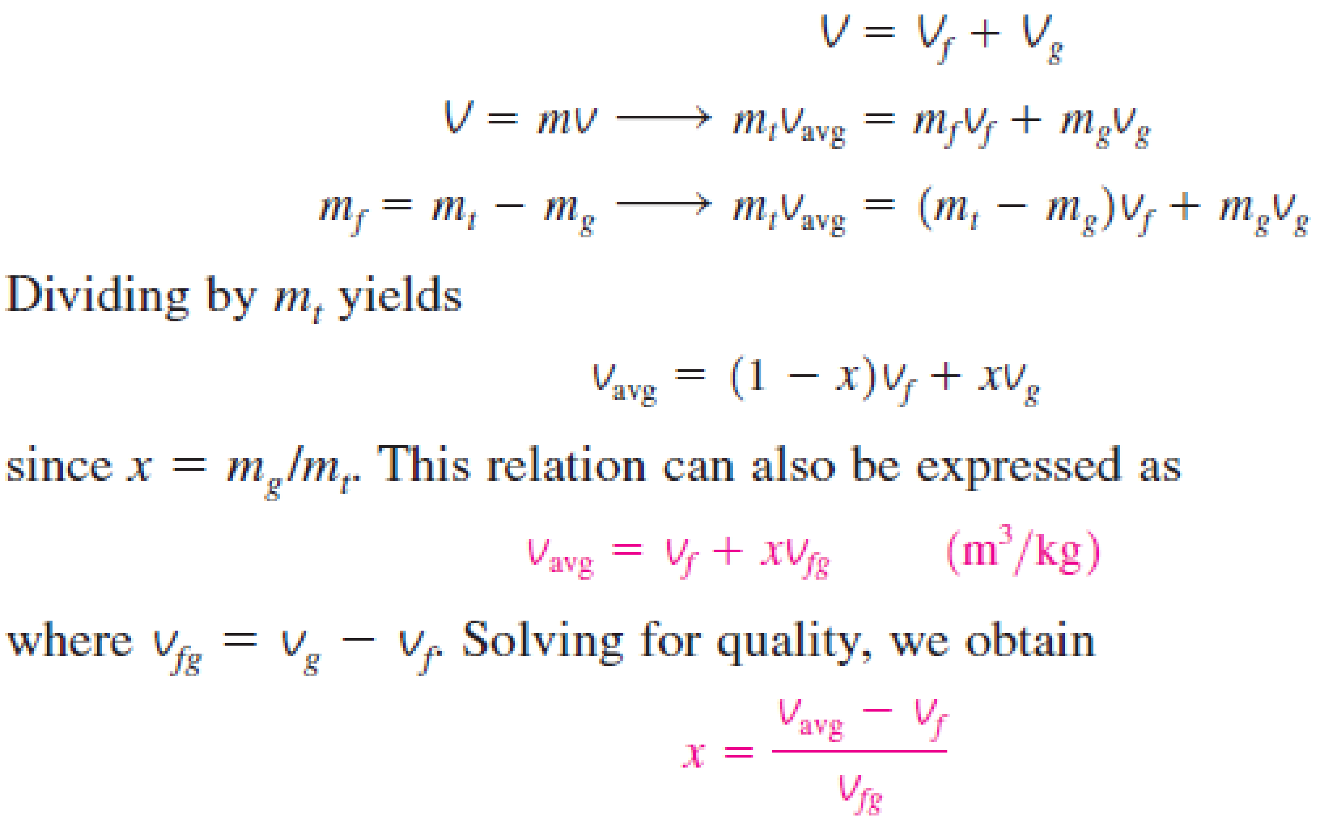
- In saturated mixtures, quality can serve as one of the two independent intensive properties needed to describe a state.
- Note that *the properties of the saturated liquid are the same whether it exists alone or in a mixture with saturated vapor.*
- During the vaporization process, only the amount of saturated liquid changes, not its properties. The same can be said about a saturated vapor.
- A saturated mixture can be treated as a combination of two subsystems:-the saturated liquid and the saturated vapor.

Cont…

- Consider a tank that contains a saturated liquid–vapor mixture.
- The volume occupied by saturated liquid is V_f *and the volume occupied by saturated* vapor is V_g
- *The total volume V is the sum of the two*



$$V = V_f + V_g$$

$$V = mv \longrightarrow m_t v_{\text{avg}} = m_f v_f + m_g v_g$$

$$m_f = m_t - m_g \longrightarrow m_t v_{\text{avg}} = (m_t - m_g)v_f + m_g v_g$$

Dividing by m_t yields

$$v_{\text{avg}} = (1 - x)v_f + x v_g$$

since $x = m_g/m_t$. This relation can also be expressed as

$$v_{\text{avg}} = v_f + x v_{fg} \qquad (\text{m}^3/\text{kg})$$

where $v_{fg} = v_g - v_f$. Solving for quality, we obtain

$$x = \frac{v_{\text{avg}} - v_f}{v_{fg}}$$

Cont…

- The analysis given above can be repeated for internal energy and enthalpy with the following results:-

$$u_{\text{avg}} = u_f + xu_{fg} \qquad (\text{kJ/kg})$$

$$h_{\text{avg}} = h_f + xh_{fg} \qquad (\text{kJ/kg})$$

- All the results are of the same format, and they can be summarized in a single equation as:-

$$y_{\text{avg}} = y_f + xy_{fg}$$

- where *y is v, u, or h.*
- The subscript "avg" (for "average") is usually dropped for simplicity.
- The values of the average properties of the mixtures are always *between the values of the saturated liquid and the saturated vapor* properties . That is, $y_f \leq y_{\text{avg}} \leq y_g$
- Finally, all the saturated-mixture states are located under the saturation curve, and to analyze saturated mixtures, all we need are saturated liquid and saturated vapor data (Tables A–4 and A–5 in the case of water).

Cont…

- Example:-

1. A rigid tank contains 10 kg of water at 90°C. If 8 kg of the water is in the liquid form and the rest is in the vapor form, determine (*a) the pressure in* the tank and (*b) the volume of the tank.*
2. An 80-L vessel contains 4 kg of refrigerant-134a at a pressure of 160 kPa. Determine (*a) the temperature*, *(b) the quality*, *(c) the enthalpy of the refrigerant*, and (*d) the volume occupied by the vapor phase*

Cont…

. *Superheated Vapor*

- In the region to the right of the saturated vapor line and at temperatures above the critical point temperature, a substance exists as superheated vapor.
- In the region to the right of the saturated vapor line and at temperatures above the critical point temperature, a substance exists as superheated vapor.
- *Example:*

1. Determine the temperature of water at a state of $P=0.5$ *MPa and* $h=2890$ kJ/kg.

Cont…

Compressed Liquid

- In the absence of compressed liquid data, a general approximation is *to treat compressed liquid as saturated liquid at the given temperature (Fig. 3–42).*
- This is because the compressed liquid properties depend on temperature much more strongly than they do on pressure. Thus,

$$y \cong y_{f\,@\,T}$$

- for compressed liquids, where *y is v, u, or h.*
- *Example:*

1. Determine the internal energy of compressed liquid water at 80°C and 5 MPa, using (*a*) *data from the compressed liquid table and (b) saturated liquid* data. What is the error involved in the second case?

Cont…

THE IDEAL-GAS EQUATION OF STATE

- Any equation that relates the pressure, temperature, and specific volume of a substance is called an **equation of state.**
- There are several equations of state, some simple and others very complex.
- The simplest and best-known equation of state for substances in the gas phase is the ideal-gas equation of state.
- That is:

$$P = R\left(\frac{T}{v}\right)$$

or

$$Pv = RT$$

- where the constant of proportionality *R is called the* ***gas constant.***

The above equation is called the **ideal-gas equation of state, or simply the ideal-gas relation,** and a gas that obeys this relation is called an **ideal gas.**

Cont…

- In this equation, *P is the absolute pressure, T is the absolute temperature, and v is the* specific volume.

- The gas constant *R is different for each gas (Fig. 3–45) and is determined* from:-

$$R = \frac{R_u}{M} \qquad (\mathrm{kJ/kg \cdot K \ or \ kPa \cdot m^3/kg \cdot K})$$

- where R_u *is the* ***universal gas constant and M is the molar mass (also*** called *molecular weight) of the gas.*

- The constant R_u *is the same for all substances,* and its value is

$$R_u = \begin{cases} 8.31447 \ \mathrm{kJ/kmol \cdot K} \\ 8.31447 \ \mathrm{kPa \cdot m^3/kmol \cdot K} \\ 0.0831447 \ \mathrm{bar \cdot m^3/kmol \cdot K} \\ 1.98588 \ \mathrm{Btu/lbmol \cdot R} \\ 10.7316 \ \mathrm{psia \cdot ft^3/lbmol \cdot R} \\ 1545.37 \ \mathrm{ft \cdot lbf/lbmol \cdot R} \end{cases}$$

Cont…

- The mass of a system is equal to the product of its molar mass *M and the* mole number *N*:-

$$m = MN \qquad \text{(kg)}$$

- The ideal-gas equation of state can be written in several different forms:-

$$V = mv \longrightarrow PV = mRT$$

$$mR = (MN)R = NR_u \longrightarrow PV = NR_uT$$

$$V = N\overline{v} \longrightarrow P\overline{v} = R_uT$$

where $\overline{v}$ is the molar specific volume, that is, the volume per unit mole (in $m^3/kmol$ or $ft^3/lbmol$).

- the properties of an ideal gas at two different states are related to each other by:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Cont…

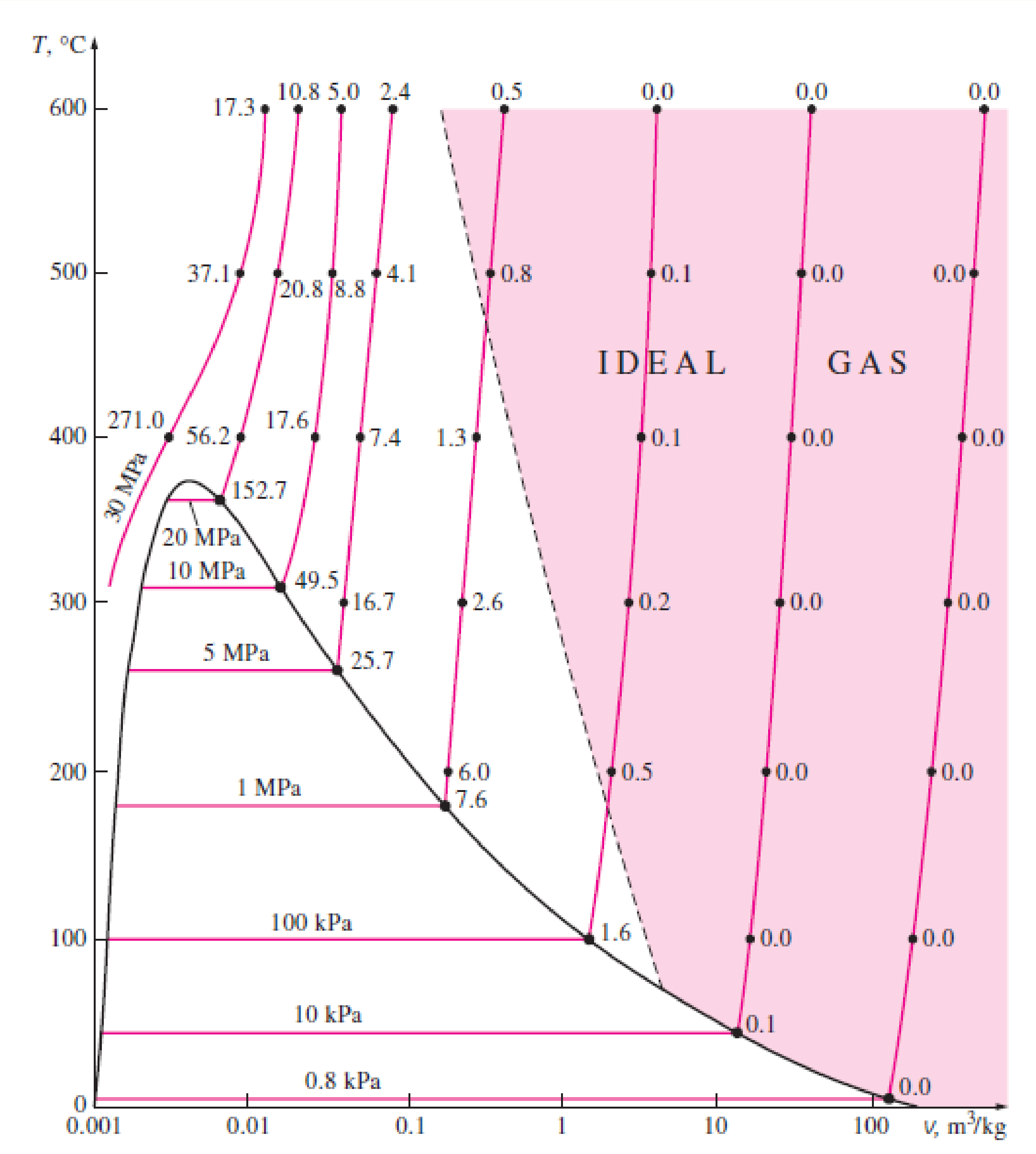
- Example:

1. Determine the mass of the air in a room whose dimensions are 4 m * 5 m * 6 m at 100 kPa and 25°C.

Is Water Vapor an Ideal Gas?

- This question cannot be answered with a simple yes or no.
- The error involved in treating water vapor as an ideal gas is calculated and plotted in the figure below.
- It is clear from this figure that at pressures below 10 kPa, water vapor can be treated as an ideal gas, regardless of its temperature, with negligible error (less than 0.1 percent).

Cont…


T, °C
600
500
400
300
200
100
0
0.001
0.01
0.1
1
10
100
v, m^3/kg
17.3
10.8
5.0
2.4
0.5
0.0
0.0
0.0
37.1
20.8
8.8
4.1
0.8
0.1
0.0
0.0
IDEAL GAS
271.0
56.2
17.6
7.4
1.3
0.1
0.0
0.0
30 MPa
152.7
20 MPa
10 MPa
49.5
16.7
2.6
0.2
0.0
0.0
5 MPa
25.7
6.0
7.6
0.5
0.0
0.0
1 MPa
100 kPa
1.6
0.0
0.0
10 kPa
0.1
0.8 kPa
0.0

Compressibility Factor A Measure of Deviation From Ideal-gas Behavior

- The ideal-gas equation is very simple and thus very convenient to use.
- However, as illustrated in Fig. 3–49, gases deviate from ideal-gas behavior significantly at states near the saturation region and the critical point.
- This deviation from ideal-gas behavior at a given temperature and pressure can accurately be accounted for by the introduction of a correction factor called the **compressibility factor *Z*** ***defined as:***

$$Z = \frac{Pv}{RT}$$

or

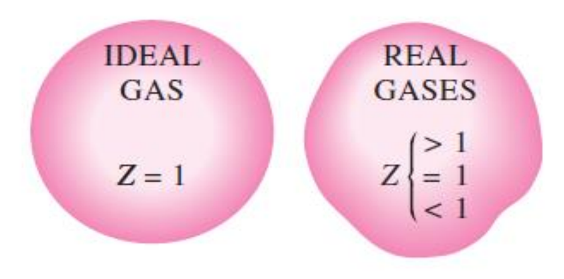
$$Pv = ZRT$$

- It can also be expressed as

$$Z = \frac{v_{\text{actual}}}{v_{\text{ideal}}}$$

Cont…

- Where $v_{\text{ideal}} = RT/P$.
- Obviously, $Z = 1$ *for ideal gases. For real gases* Z *can* be greater than or less than unity. The farther away Z *is from* unity, the more the gas deviates from ideal-gas behavior.



- We have said that gases follow the ideal-gas equation closely at low pressures and high temperatures.
- But what exactly constitutes low pressure or high temperature?
- Is -100°C a low temperature?

Cont…

- It definitely is for most substances but not for air.
- Air (or nitrogen) can be treated as an ideal gas at this temperature and atmospheric pressure with an error under 1 percent.
- This is because nitrogen is well over its critical temperature (-147°C) and away from the saturation region.
- At this temperature and pressure, however, most substances would exist in the solid phase.
- Therefore, the pressure or temperature of a substance is high or low relative to its critical temperature or pressure.
- Gases behave differently at a given temperature and pressure, but they behave very much the same at temperatures and pressures normalized with respect to their critical temperatures and pressures.
- The normalization is done as:-

$$P_R = \frac{P}{P_{\mathrm{cr}}} \quad \text{and} \quad T_R = \frac{T}{T_{\mathrm{cr}}}$$

Cont…

- Here P_R *is called the* ***reduced pressure and*** T_R *the* ***reduced temperature.***

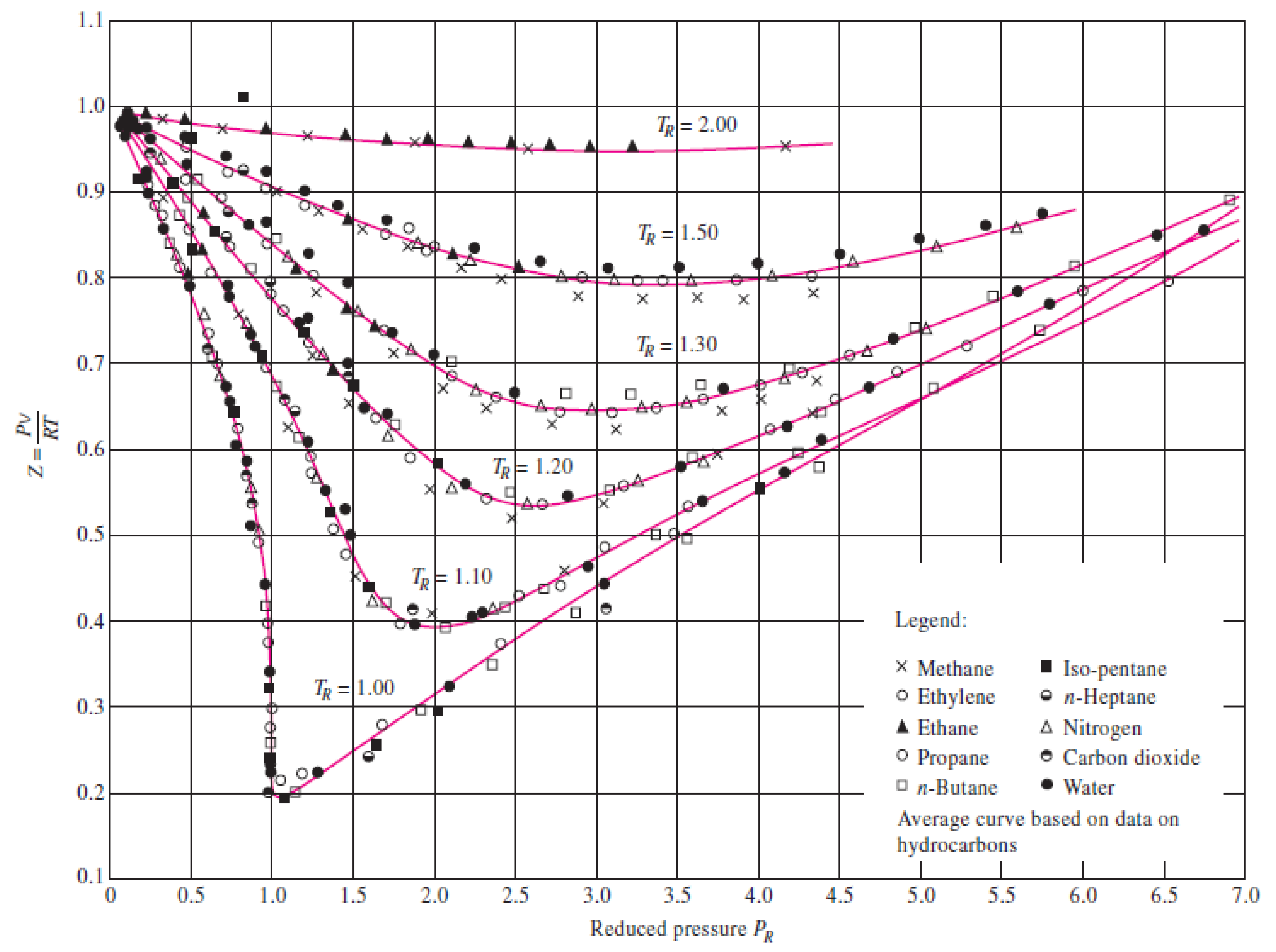
- The *Z factor for all gases is approximately the same at the same reduced* pressure and temperature. This is called the **principle of corresponding states.**

- In Fig. 3–51, the experimentally determined *Z values are plotted* against P_R *and* T_R *for several gases. The gases seem to obey the principle of* corresponding states reasonably well. By curve-fitting all the data, we obtain the **generalized compressibility chart that can be used for all gases.**

- The following observations can be made from the generalized compressibility chart:-

1. At very low pressures ($P_R << 1$), *gases behave as an ideal gas regardless* of temperature.
2. At high temperatures ($T_R >2$), *ideal-gas behavior can be assumed with* good accuracy regardless of pressure (except when $P_R>>1$).
3. The deviation of a gas from ideal-gas behavior is greatest in the vicinity of the critical point.

Cont…


1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
$Z = \frac{Pv}{RT}$
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
Reduced pressure P_R
$T_R = 2.00$
$T_R = 1.50$
$T_R = 1.30$
$T_R = 1.20$
$T_R = 1.10$
$T_R = 1.00$
Legend:
× Methane
○ Ethylene
▲ Ethane
○ Propane
□ n-Butane
■ Iso-pentane
◒ n-Heptane
△ Nitrogen
◓ Carbon dioxide
● Water
Average curve based on data on hydrocarbons

Cont..

- Example:-
- Determine the specific volume of refrigerant-134a at 1 MPa and 50°C, using (*a*) *the ideal-gas equation of state and (b) the generalized compressibility* chart. Compare the values obtained to the actual value of 0.021796 m3/kg and determine the error involved in each case.

Solution:

- When *P and v, or T and v, are given instead of P and T, the generalized* compressibility chart can still be used to determine the third property, but it would involve tedious trial and error.
- Therefore, it is necessary to define one more reduced property called the **pseudo-reduced specific volume V_R *as:***

$$v_R = \frac{v_{\text{actual}}}{RT_{\text{cr}}/P_{\text{cr}}}$$

- Note that V_R *is defined differently from* P_R *and* T_R*. It is related to* T_{cr} *and* P_{cr} instead of v_{cr}.