



PROPERTIES OF PURE SUBSTANCES

CHAPTER 3

DR. HADI ALI MADKHALI

OBJECTIVES

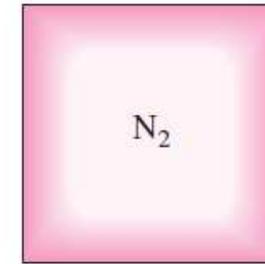
- Introduce the concept of a pure substance.
- Discuss the physics of phase-change processes.
- Illustrate the P - v , T - v , and P - T property diagrams and P - v - T surfaces of pure substances.
- Demonstrate the procedures for determining thermodynamic properties of pure substances from tables of 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. Such as, water, helium, carbon dioxide.

A mixture of various chemical elements or compounds also qualifies as a pure substance as long as the mixture is homogeneous.

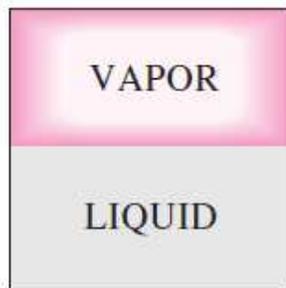
A mixture of two or more phases of a pure substance is still a pure substance as long as the chemical composition of all phases is the same.



Air is a mixture of several gases, but it is often considered to be a pure substance **because it has a uniform chemical composition.**

How about?

A mixture of oil and water!

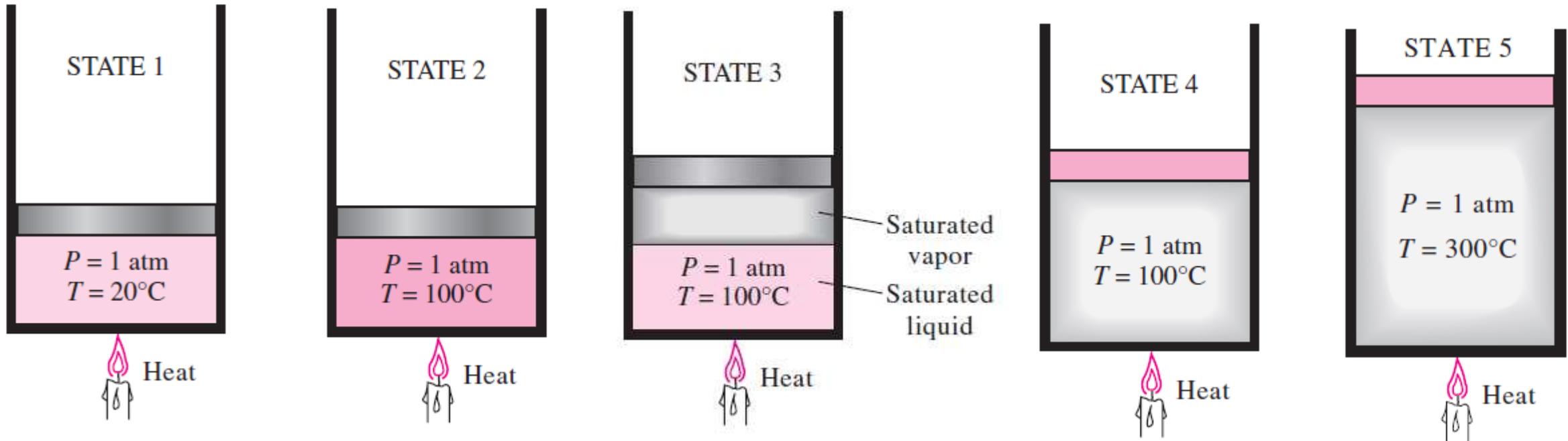


(a) H₂O



(b) AIR

PHASE-CHANGE PROCESSES OF PURE SUBSTANCES



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

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

3) As more heat is transferred, part of the saturated liquid vaporizes (saturated liquid-vapor mixture).

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

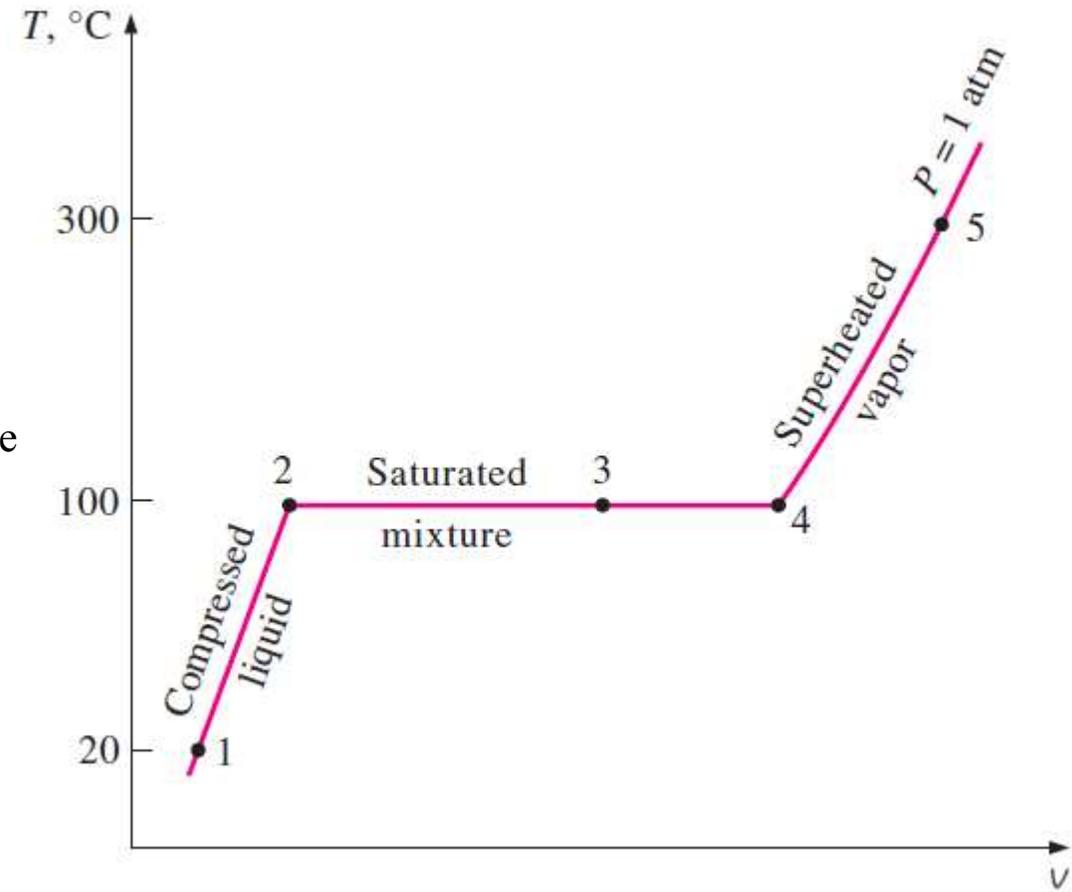
5) As more heat is transferred, the temperature of the vapor starts to rise (superheated vapor).

CONTINUE...

The statement “water boils at 100°C” !
Is it correct or no? Explain

At a given pressure, the temperature at which a pure substance changes phase is called the saturation temperature T_{sat} .

Likewise, at a given temperature, the pressure at which a pure substance changes phase is called the saturation pressure P_{sat} .

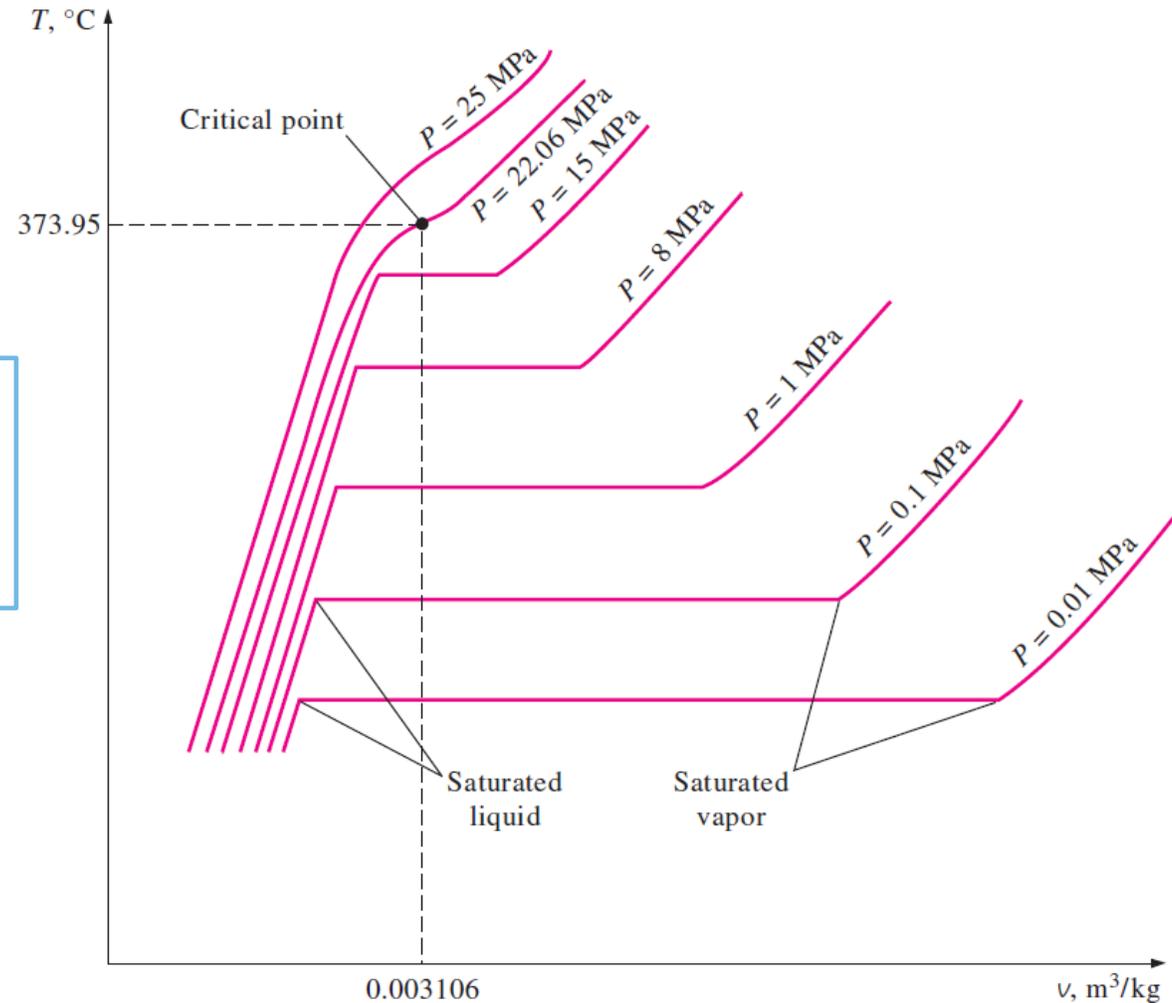


CONTINUE...

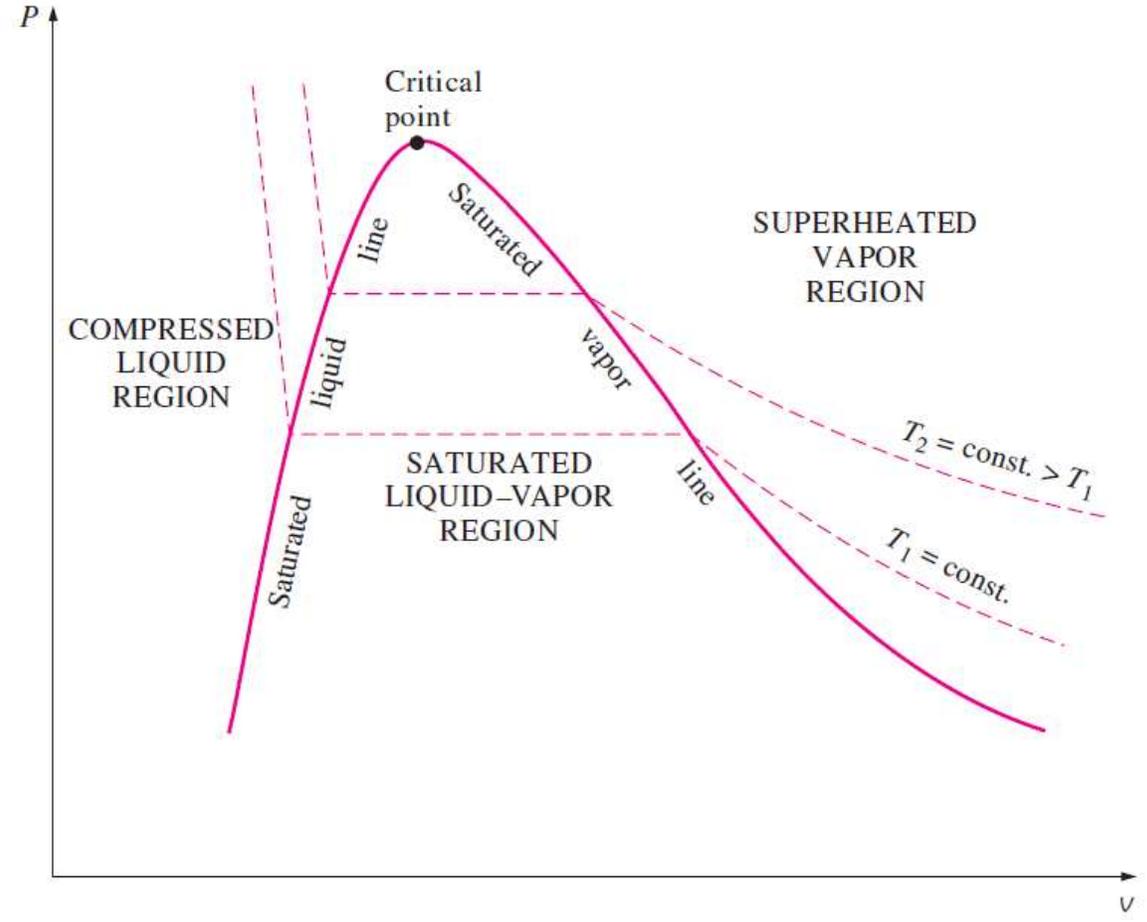
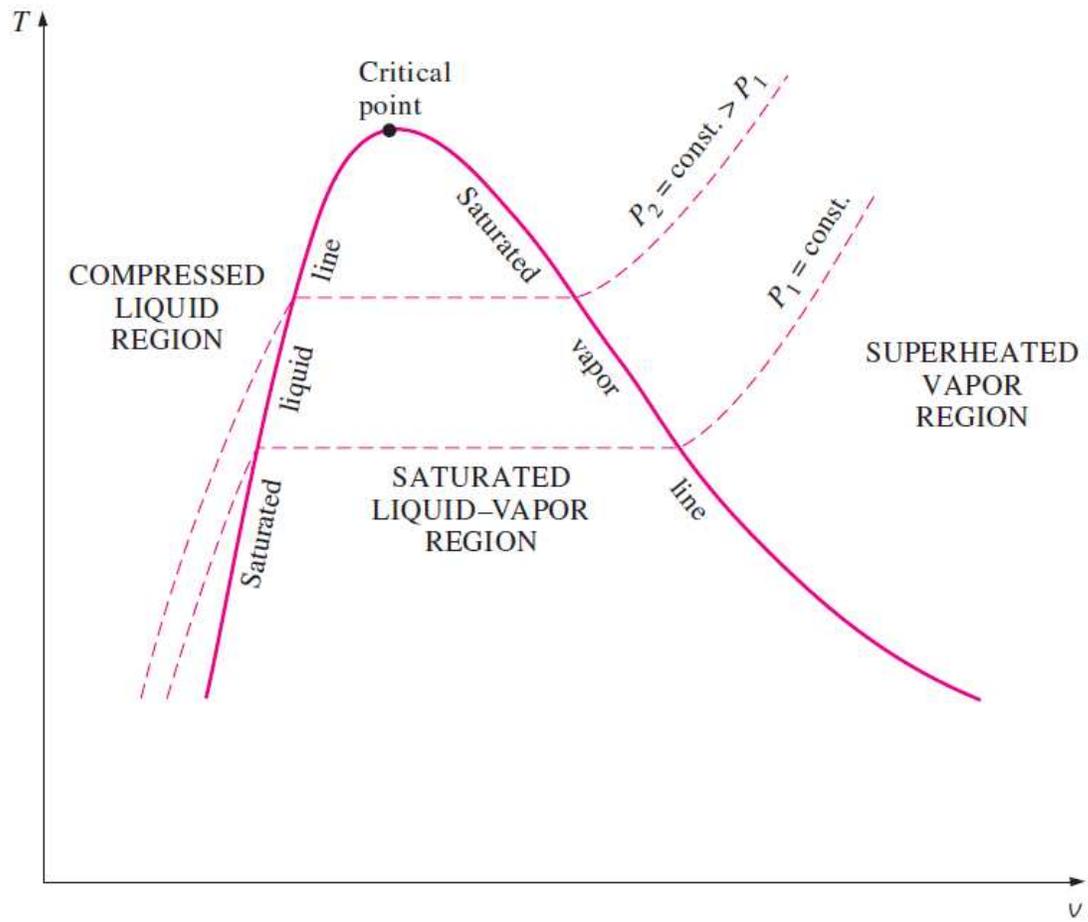
The T - v Diagram at different pressures:

Critical point, and it is defined as *the point at which the saturated liquid and saturated vapor states are identical*.

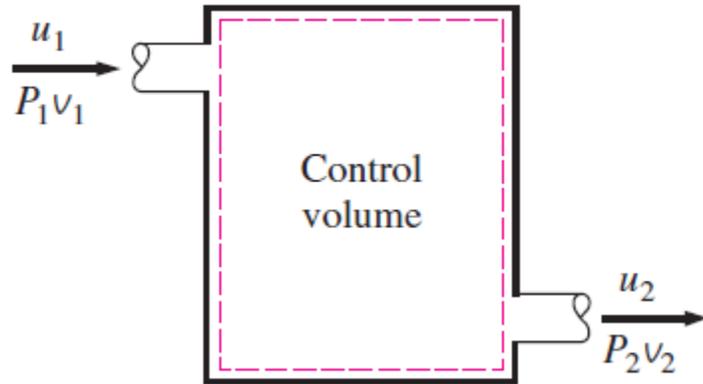
The temperature, pressure, and specific volume of a substance at the critical point are called, respectively, the *critical temperature T_{cr}* , *critical pressure P_{cr}* , and *critical specific volume v_{cr}* .



THE P-V DIAGRAM



ENTHALPY—A COMBINATION PROPERTY



$$h = u + Pv \quad (\text{kJ/kg})$$

$$H = U + PV \quad (\text{kJ})$$

PROPERTY TABLES

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. Therefore, it is more convenient to use Table A–4 when *temperature* is given and Table A–5 when *pressure* is given.

The subscript *f* is used to denote properties of a saturated liquid, and the subscript *g* to denote the properties of saturated vapor. These symbols are commonly used in thermodynamics and originated from German. 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, $v_{fg} = v_g - v_f$)

DR. HADI ALI MADKHALI

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

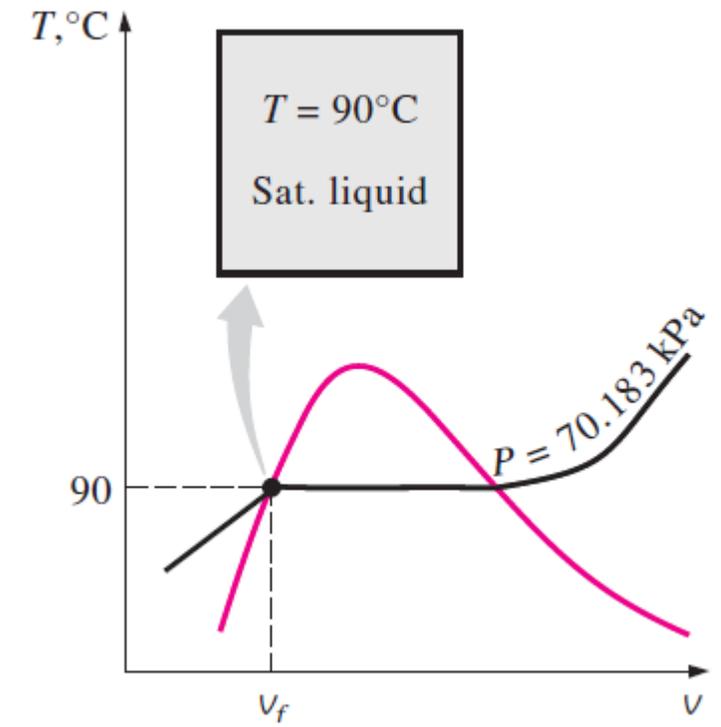
Specific temperature (points to 85, 90, 95)
 Corresponding saturation pressure (points to 57.868, 70.183, 84.609)
 Specific volume of saturated liquid (points to 0.001032, 0.001036, 0.001040)
 Specific volume of saturated vapor (points to 2.8261, 2.3593, 1.9808)

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.

Saturated Liquid and Saturated Vapor States:

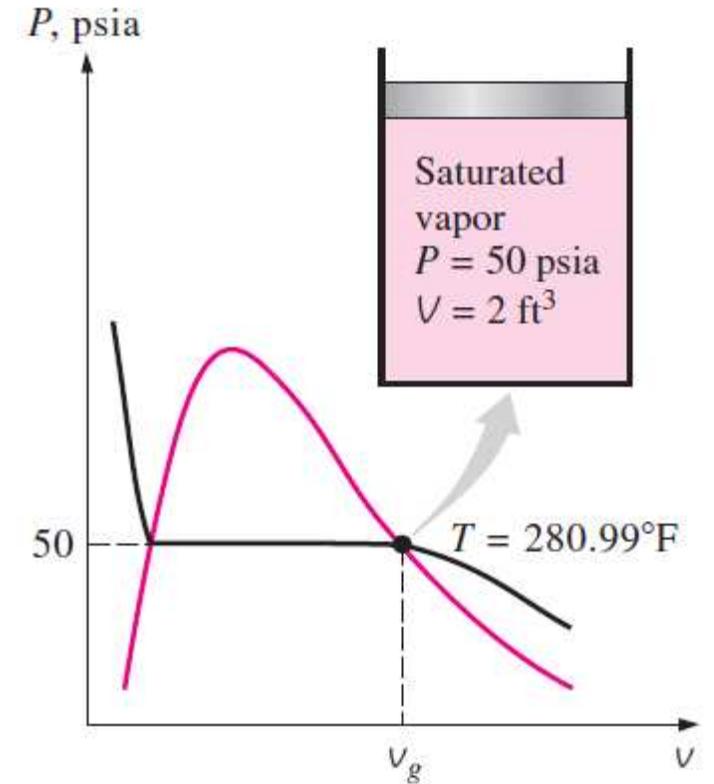
Example:

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.

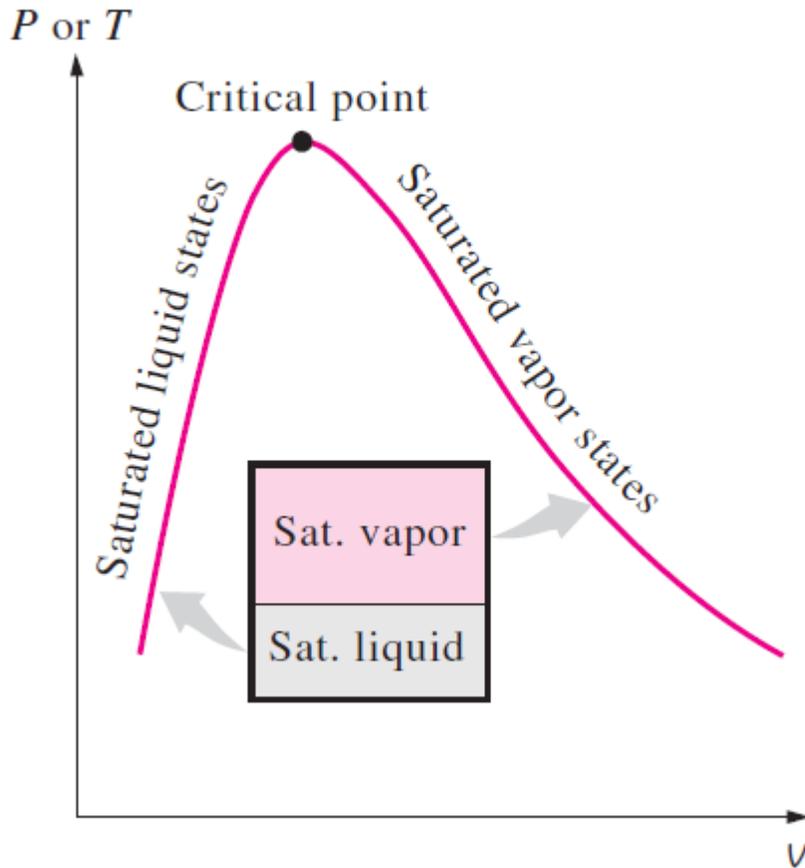


Example:

A piston cylinder device contains 0.06 m^3 of saturated water vapor at 350 kPa pressure. Determine the temperature and the mass of the vapor inside the cylinder.



Saturated Liquid – Vapor Mixture



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

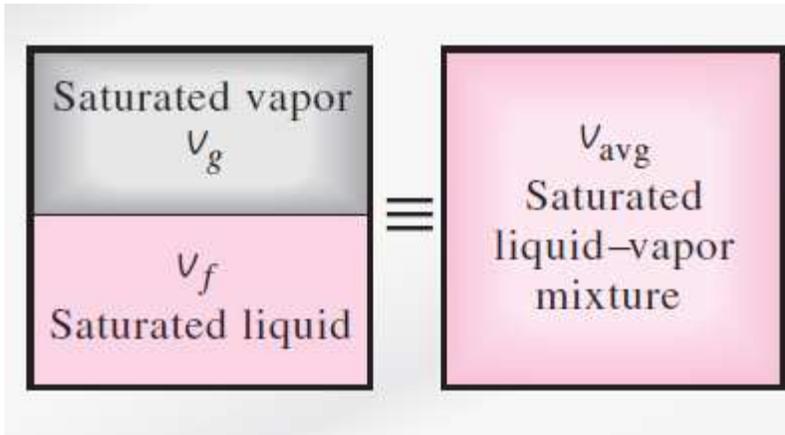
$$m_{\text{total}} = m_{\text{liquid}} + m_{\text{vapor}} = m_f + m_g$$

Quality (x) value is between 0 and 1

The quality of a system that consists of *saturated liquid* is ? (or ? %).

The quality of a system consisting of *saturated vapor* is ? (or ? %).

Continue,.... Saturated Liquid – Vapor Mixture



A saturated mixture can be treated as a combination of two subsystems: **the saturated liquid** and **the saturated vapor**.

However, the amount of mass for each phase is usually not known. Therefore, it is often more convenient to imagine that the two phases are mixed well, forming a homogeneous mixture.

Then the properties of this “mixture” will simply be the average properties of the saturated liquid–vapor mixture under consideration.

$$V = V_f + V_g$$

$$V = mV \longrightarrow m_t V_{\text{avg}} = m_f v_f + m_g v_g$$

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

By $\div m_t$

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

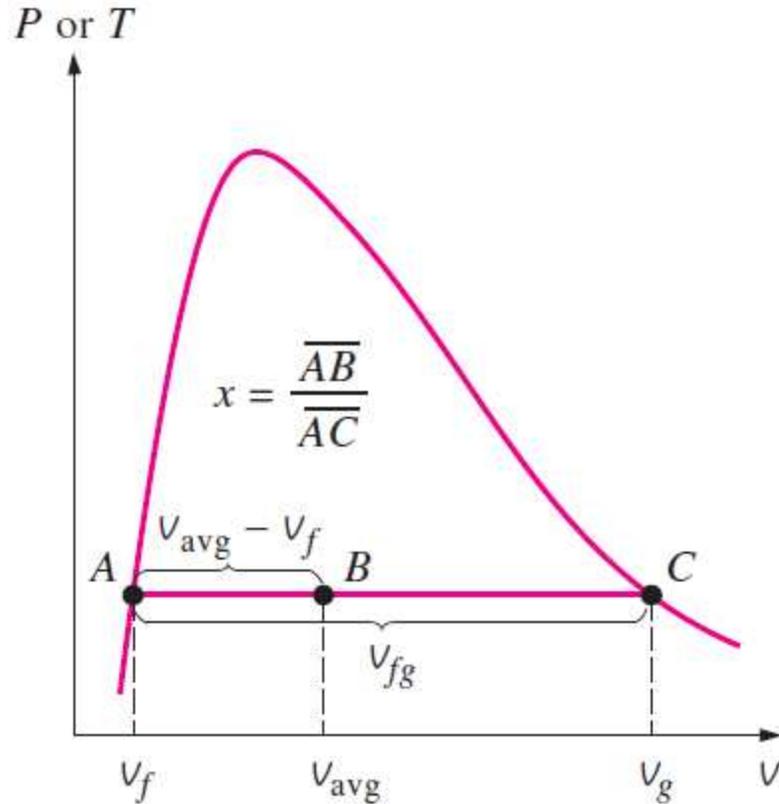
since $x = \frac{m_g}{m_t}$

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

where $v_{fg} = v_g - v_f$, solving for quality, we obtain:

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

Continue,... Saturated Liquid – Vapor Mixture



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

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

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

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

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

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.

$$y_f \leq y_{avg} \leq y_g$$

Example

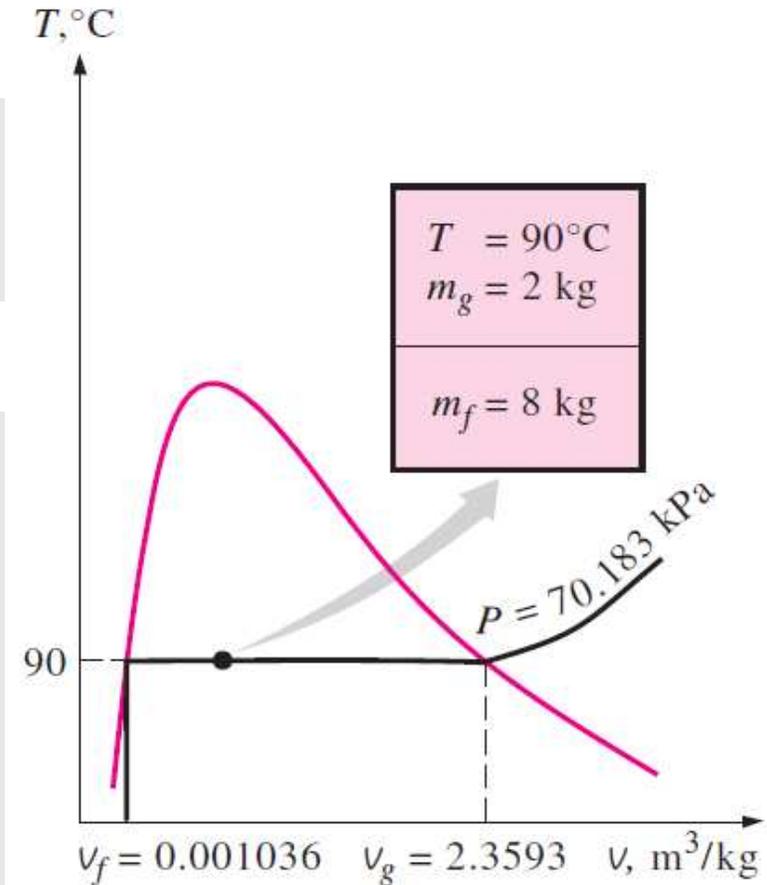
A rigid tank contains 10 kg of water at 90°C. If 8 kg of the water is in the liquid form and the rest is in the vapor form, determine (a) the pressure in the tank and (b) the volume of the tank.

Solution

$$P = P_{\text{sat @ } 90^\circ\text{C}} = \mathbf{70.183 \text{ kPa}} \quad (\text{Table A-4})$$

(b) At 90°C, we have $v_f = 0.001036 \text{ m}^3/\text{kg}$ and $v_g = 2.3593 \text{ m}^3/\text{kg}$ (Table A-4). One way of finding the volume of the tank is to determine the volume occupied by each phase and then add them:

$$\begin{aligned} V &= V_f + V_g = m_f v_f + m_g v_g \\ &= (8 \text{ kg})(0.001036 \text{ m}^3/\text{kg}) + (2 \text{ kg})(2.3593 \text{ m}^3/\text{kg}) \\ &= \mathbf{4.73 \text{ m}^3} \end{aligned}$$



Another way is to first determine the quality x , then the average specific volume v , and finally the total volume:

$$x = \frac{m_g}{m_t} = \frac{2 \text{ kg}}{10 \text{ kg}} = 0.2$$

$$\begin{aligned} v &= v_f + xv_{fg} \\ &= 0.001036 \text{ m}^3/\text{kg} + (0.2)[(2.3593 - 0.001036) \text{ m}^3/\text{kg}] \\ &= 0.473 \text{ m}^3/\text{kg} \end{aligned}$$

and

$$V = m v = (10 \text{ kg})(0.473 \text{ m}^3/\text{kg}) = 4.73 \text{ m}^3$$

Example

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.

Solution

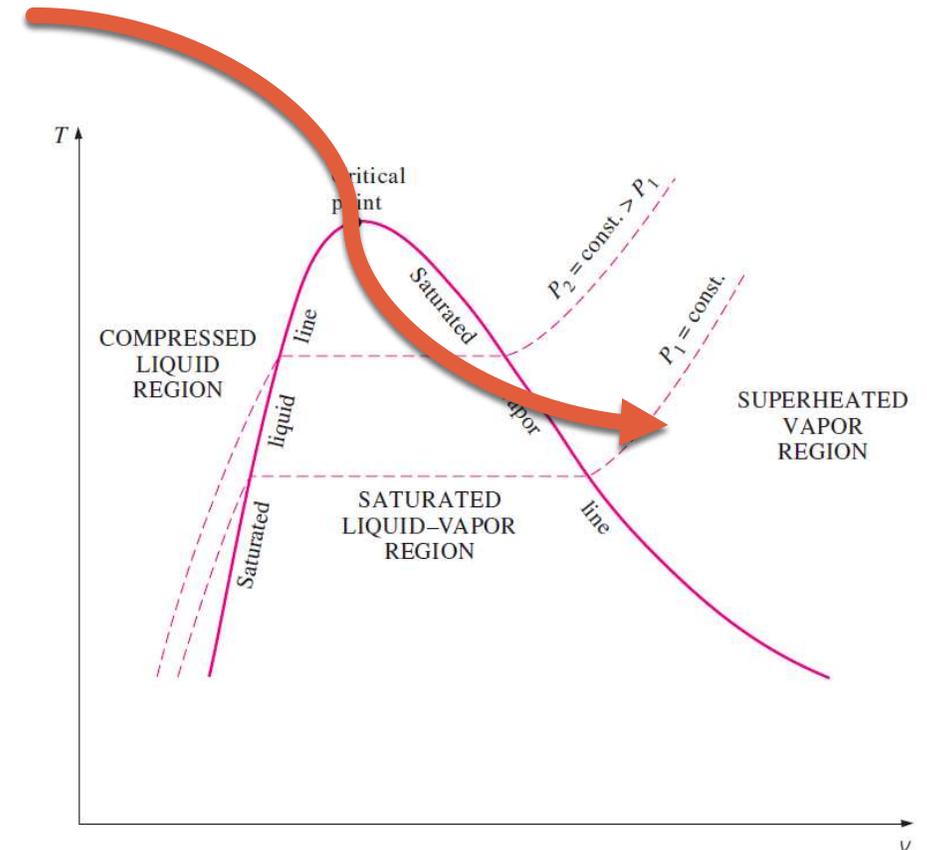
Use Table A–12

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.

Compared to saturated vapor, superheated vapor is characterized by:

- Lower pressures ($P < P_{\text{sat}}$ at a given T)
- Higher temperatures ($T > T_{\text{sat}}$ at a given P)
- Higher specific volumes ($v > v_g$ at a given P or T)
- Higher internal energies ($u > u_g$ at a given P or T)
- Higher enthalpies ($h > h_g$ at a given P or T)



Example

Determine the internal energy of water at 200 kPa and 300°C.

Solution

$$u = 2808.8 \text{ kJ/kg}$$

HOW?

Example

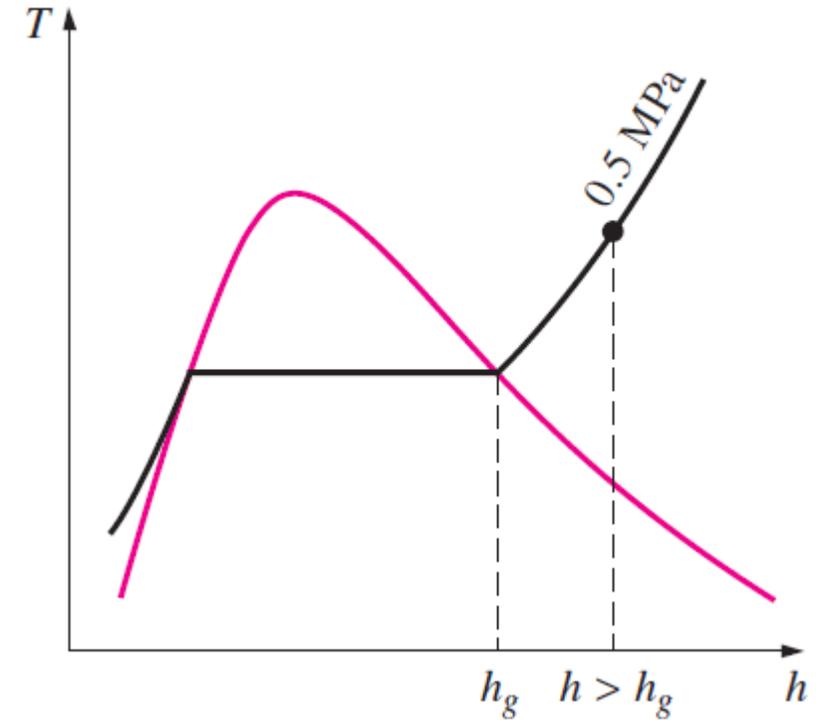
Determine the temperature of water at a state of $P = 0.5 \text{ MPa}$ and $h = 2890 \text{ kJ/kg}$.

At 0.5 MPa , the enthalpy of saturated water vapor is $h_g = 2748.1 \text{ kJ/kg}$. Since $h > h_g$, as shown in the figure, we have superheated vapor. Under 0.5 MPa in Table A-6 we read:

$T, ^\circ\text{C}$	$h, \text{kJ/kg}$
200	2855.8
250	2961.0

By interpolation:

$$T = 216.3 \text{ } ^\circ\text{C}$$



By interpolation:

200	2855.8
T?	2890.0
250	2961.0

$$\frac{200 - T?}{200 - 250} = \frac{2855.8 - 2890.0}{2855.8 - 2961.0}$$

$$T? = 216.3$$

Compressed Liquid

Compressed liquid tables are not as commonly available, and Table A–7 is the only compressed liquid table in this text. The format of Table A–7 is very much like the format of the superheated vapor tables.

In the absence of compressed liquid data, a general approximation is *to treat compressed liquid as saturated liquid at the given temperature*

This is because the compressed liquid properties depend on temperature much more strongly than they do on pressure.

In general, a compressed liquid is characterized by

- Higher pressures ($P > P_{\text{sat}}$ at a given T)
- Lower temperatures ($T < T_{\text{sat}}$ at a given P)
- Lower specific volumes ($v < v_f$ at a given P or T)
- Lower internal energies ($u < u_f$ at a given P or T)
- Lower enthalpies ($h < h_f$ at a given P or T)

But unlike superheated vapor, the compressed liquid properties are not much different from the corresponding saturated liquid values.

Example

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?

Solution

At 80°C, the saturation pressure of water is 47.416 kPa, and since 5 MPa > P_{sat} , we obviously have compressed liquid

(a) From the compressed liquid table (Table A-7)

$$\left. \begin{array}{l} P = 5 \text{ MPa} \\ T = 80^\circ\text{C} \end{array} \right\} u = \mathbf{333.82 \text{ kJ/kg}}$$

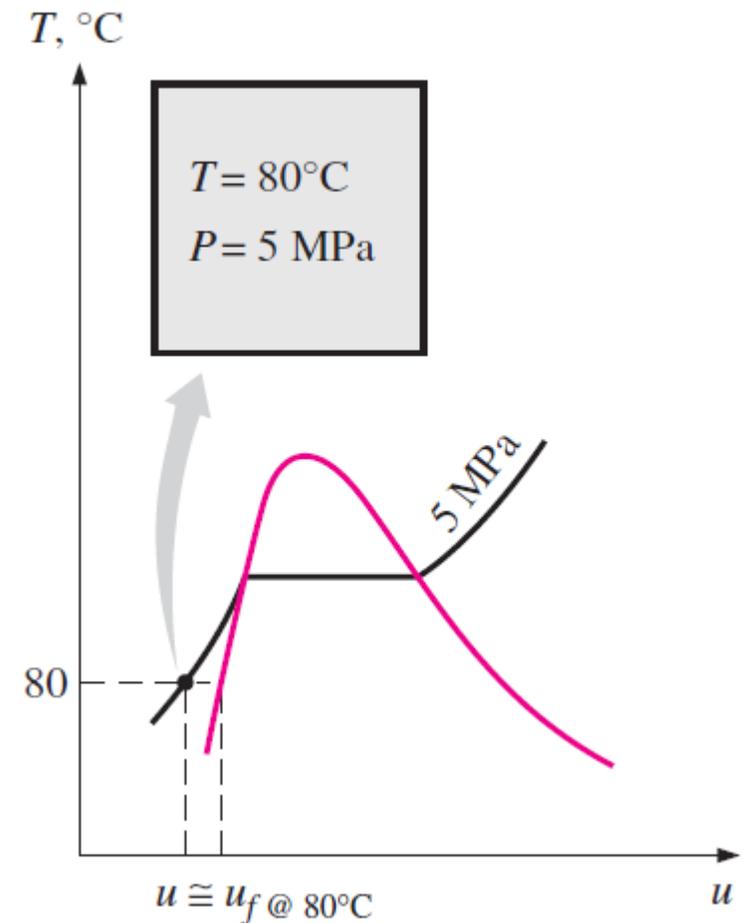
(b) From the saturation table (Table A-4), we read

$$u \cong u_{f@80^\circ\text{C}} = \mathbf{334.97 \text{ kJ/kg}}$$

The error involved is

$$\frac{334.97 - 333.82}{333.82} \times 100 = \mathbf{0.34\%}$$

which is less than 1 percent.



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.** This equation predicts the P - v - T behavior of a gas quite accurately within some properly selected region.

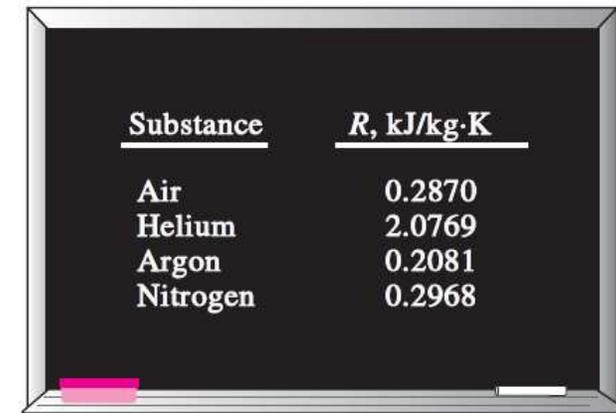
Gas and *vapor* are often used **as synonymous words**.

$$P = R \left(\frac{T}{v} \right) \quad PV = RT \quad \text{ideal-gas equation of state}$$

where the constant of proportionality R is called the **gas constant**. P is the absolute pressure, T is the absolute temperature, and v is the specific volume.

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

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



<u>Substance</u>	<u>R, kJ/kg·K</u>
Air	0.2870
Helium	2.0769
Argon	0.2081
Nitrogen	0.2968

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

The **molar mass** M can simply be defined as *the mass of one mole* (also called a *gram-mole*, abbreviated gmol) *of a substance in grams*, or *the mass of one kmol* (also called a *kilogram-mole*, abbreviated kgmol) *in kilograms*.

When we say the molar mass of nitrogen is 28, it simply means the mass of 1 kmol of nitrogen is 28 kg, or the mass of 1 lbmol of nitrogen is 28 lbm. That is, $M = 28 \text{ kg/kmol} = 28 \text{ lbm/lbmol}$.

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

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

The values of R and M for several substances are given in Table A-1.

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

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

$$V = m\bar{v} \longrightarrow PV = mRT \quad (1^*)$$

$$mR = (MN)R = NR_u \longrightarrow PV = NR_uT \quad (2^*)$$

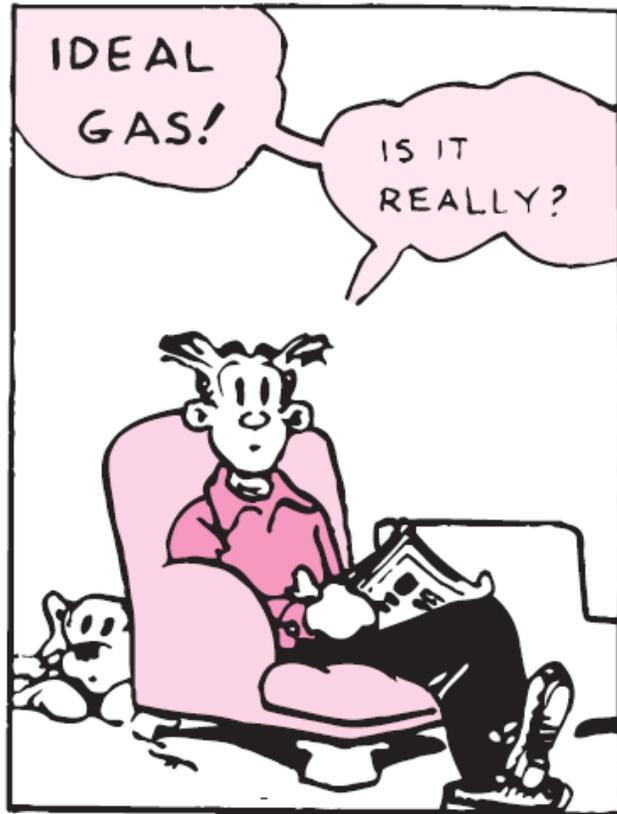
$$V = N\bar{V} \longrightarrow P\bar{V} = R_uT \quad (3^*)$$

Where \bar{V} is the molar specific volume, that is, the volume per unit mole (in m^3/kmol or f^3/lbmol). A bar above a property denotes values on a *unit-mole basis* throughout this text

By writing equation (1*) twice for a fixed mass and simplifying, the properties of an ideal gas at two different states are related to each other by:

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

Per unit mass	Per unit mole
$v, m^3/\text{kg}$	$\bar{v}, m^3/\text{kmol}$
$u, \text{kJ}/\text{kg}$	$\bar{u}, \text{kJ}/\text{kmol}$
$h, \text{kJ}/\text{kg}$	$\bar{h}, \text{kJ}/\text{kmol}$



An ideal gas is an *imaginary* substance that obeys the relation $Pv = RT$

It has been experimentally observed that the ideal-gas relation given closely approximates the P - v - T behavior of real gases at low densities. At low pressures and high temperatures, the density of a gas decreases, and the gas behaves as an ideal gas under these conditions.

In the range of practical interest, many familiar gases such as air, nitrogen, oxygen, hydrogen, helium, argon, neon, krypton, and even heavier gases such as carbon dioxide can be treated as ideal gases with negligible error (often less than 1%).

Dense gases such as water vapor in steam power plants and refrigerant vapor in refrigerators, however, should not be treated as ideal gases. Instead, the property tables should be used for these substances.

Example

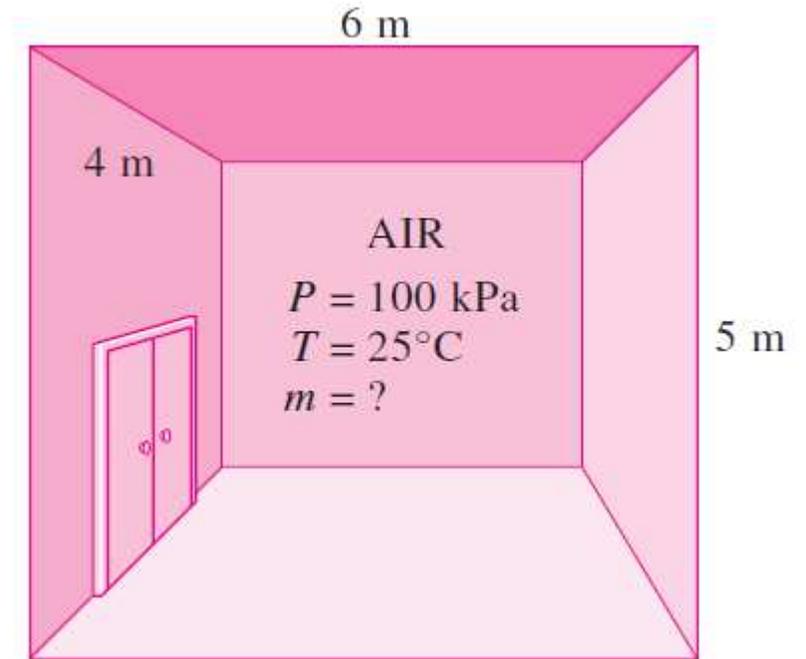
Determine the mass of the air in a room whose dimensions are 4 m X 5 m X 6 m at 100 kPa and 25°C.

Air at specified conditions can be treated as an ideal gas. From Table A-1, the gas constant of air is $R = 0.287 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K}$, and the absolute temperature is $T = 25^\circ\text{C} + 273 = 298 \text{ K}$.

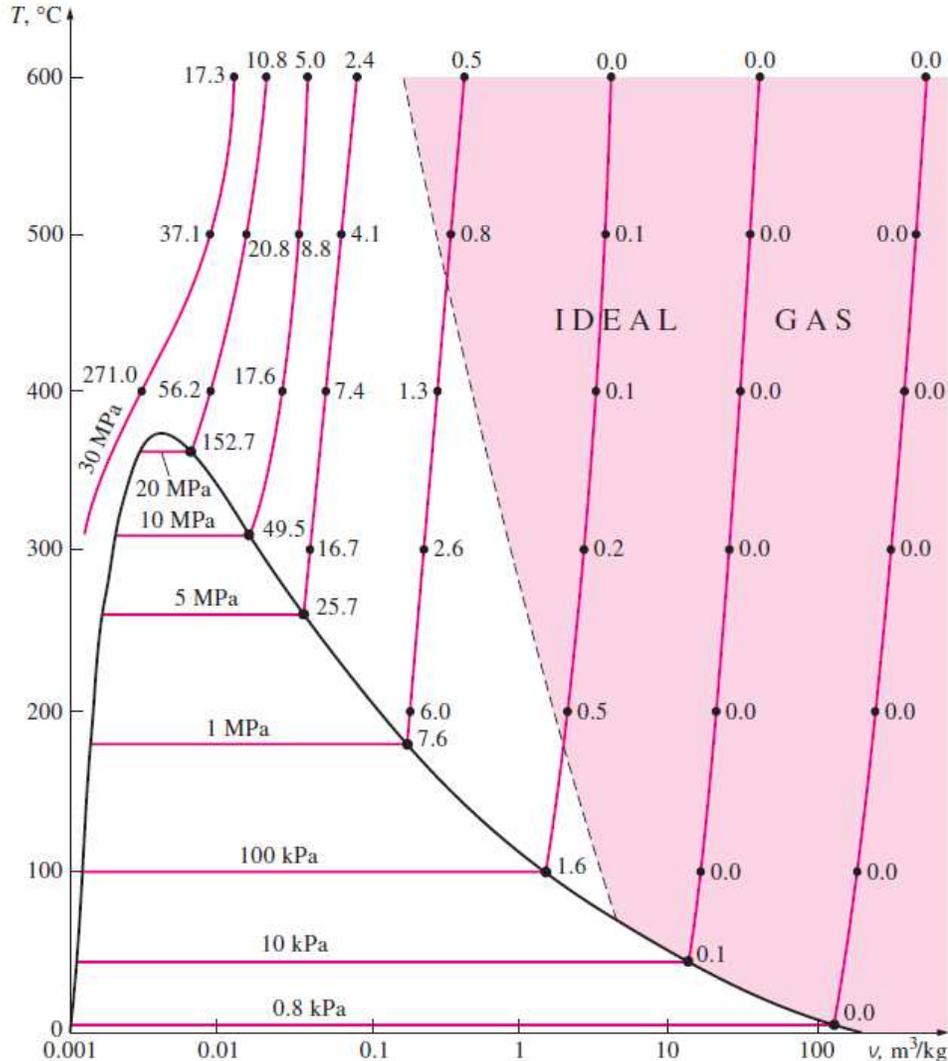
Solution

$$m = 140.3 \text{ kg}$$

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Is Water Vapor an Ideal Gas?



At higher pressures, however, the ideal gas assumption yields unacceptable errors.

Therefore, in air-conditioning applications, the water vapor in the air can be treated as an ideal gas with essentially no error since the pressure of the water vapor is very low. In steam power plant applications, however, the pressures involved are usually very high; therefore, ideal-gas relations should not be used.

COMPRESSIBILITY FACTOR—A MEASURE OF DEVIATION FROM IDEAL-GAS BEHAVIOR

The 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:

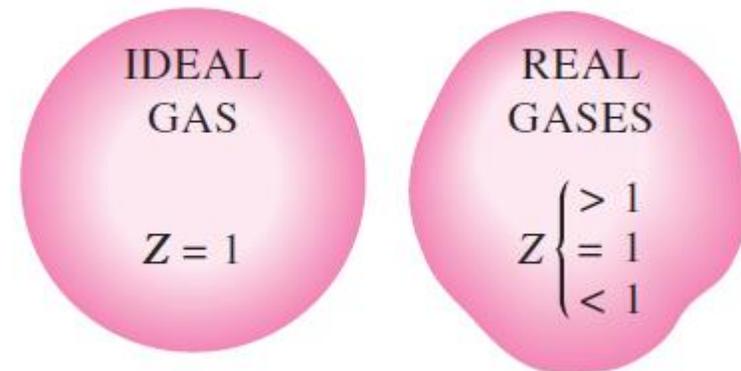
$$Z = \frac{Pv}{RT}$$

$$Pv = ZRT$$

It can also be expressed as:

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

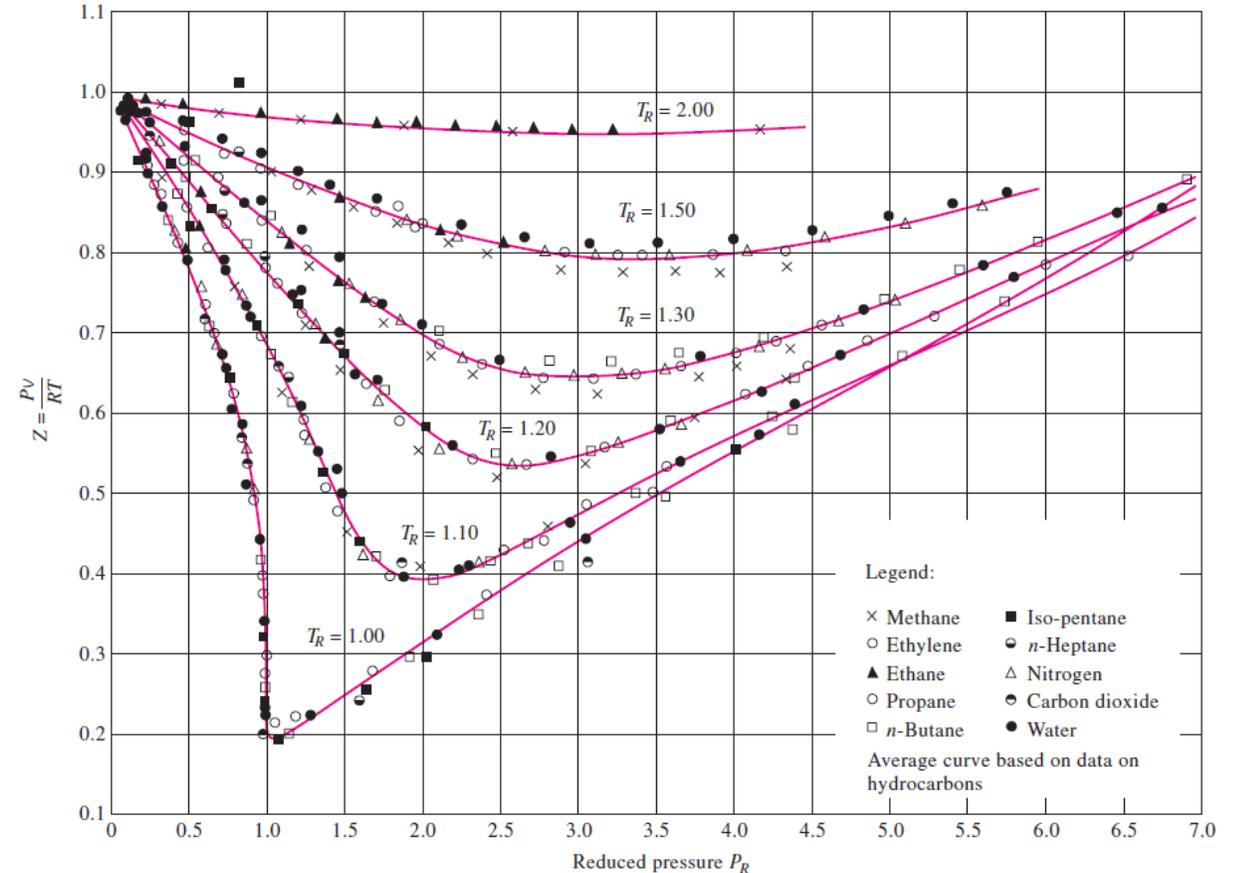
where $v_{\text{ideal}} = RT/P$. Obviously, $Z = 1$ for ideal gases. For real gases Z can be greater than or less than unity. The farther away Z is from unity, the more the gas deviates from ideal-gas behavior.



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:

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

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**.



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 $0.021796 \text{ m}^3/\text{kg}$ and determine the error involved in each case.

Solution

?