Al-Mustaqbal University
Department of Biomedical Engineering
Third Stage / 2nd Course
"Thermodynamics"
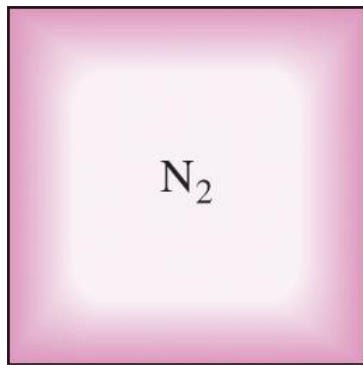*Assist. Lec. Samara Bashar Saeed*

Lec.3: PROPERTIES OF PURE SUBSTANCES
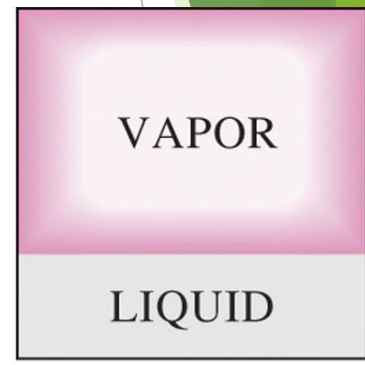
By

Assist. Lec. Samara Bashar

PURE SUBSTANCE

▶ **Pure substance**: A substance that has a fixed chemical composition throughout.

▶ Air is a mixture of several gases, but it is considered to be a pure substance.
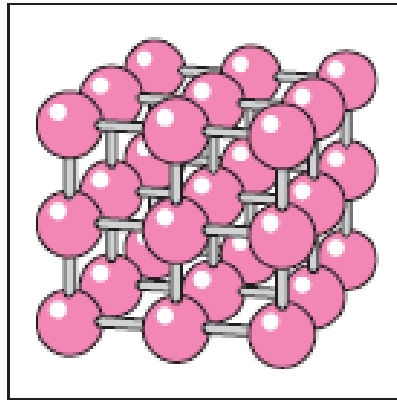

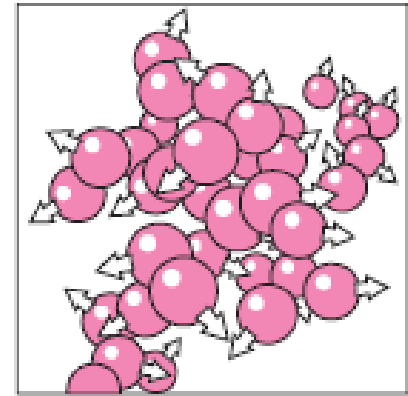Nitrogen and gaseous air are pure substances.

A mixture of liquid and gaseous water is a pure substance, but a mixture of liquid and gaseous air is not.
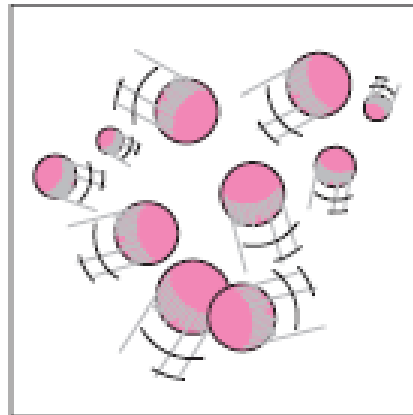
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Phases of Pure Substance

Solid

Liquid

Gaseous

Phase-change Processes of Pure Substances

▶ Consider a piston–cylinder device containing liquid water at 20°C and 1 atm pressure.

▶ 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*.

STATE 1

$P = 1$ atm
$T = 20°C$

Heat

- As more heat is transferred, the temperature keeps rising until it reaches 100°C.

- At this point water is still a liquid, but any heat addition will cause some of the liquid to vaporize.

- A liquid that is *about to vaporize* is called a **saturated liquid.**

STATE 2

$P = 1$ atm
$T = 100°C$

Heat

4
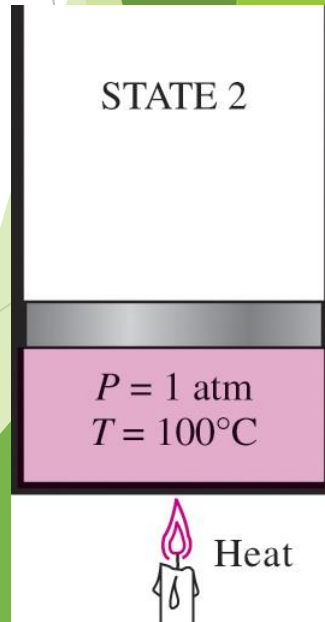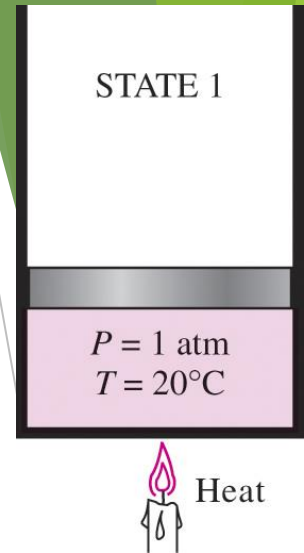
Saturated liquid–vapor mixture: The state at which the *liquid and vapor phases coexist* in equilibrium.

Saturated vapor: A vapor that is *about to condense*.

STATE 3

P = 1 atm
T = 100°C

Saturated vapor

Saturated liquid

Heat

STATE 4

P = 1 atm
T = 100°C

Heat

STATE 5

P = 1 atm
T = 300°C
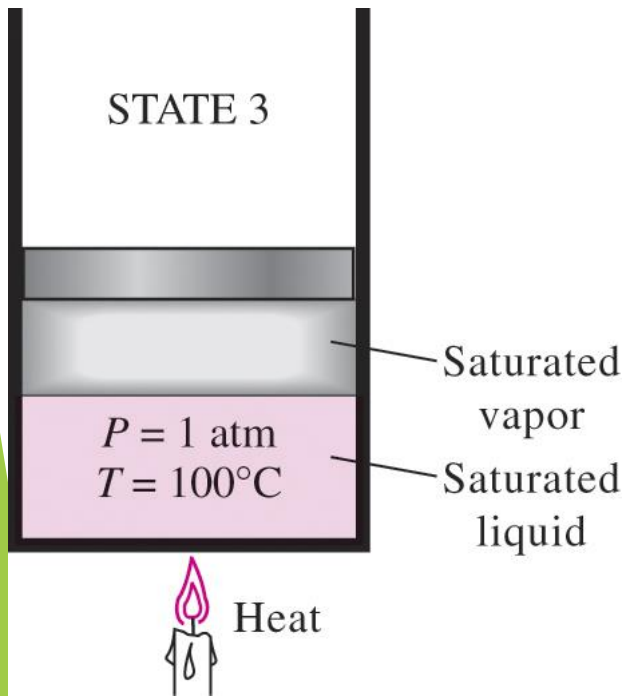
Heat

As more heat is transferred, part of the saturated liquid vaporizes (*saturated liquid–vapor mixture*).
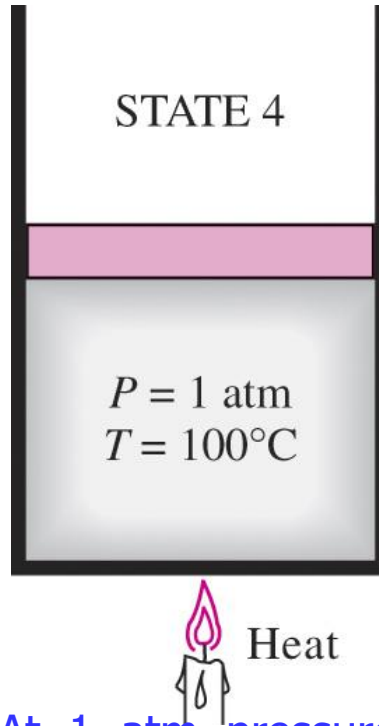
At 1 atm pressure, the temperature remains constant at 100°C until the last drop of liquid is vaporized (*saturated vapor*).
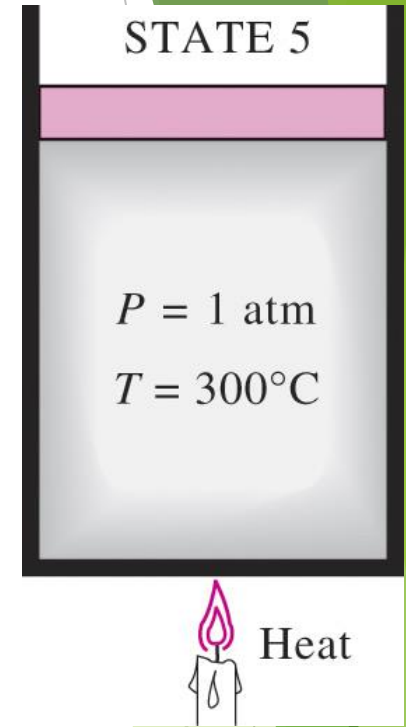
As more heat is transferred, the temperature of the vapor starts to rise (*superheated vapor*).

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Saturation Temperature and Saturation Pressure

▶ The temperature at which water starts boiling depends on the pressure; therefore, if the pressure is fixed, so is the boiling temperature.

▶ Water boils at 100°C at 1 atm pressure.

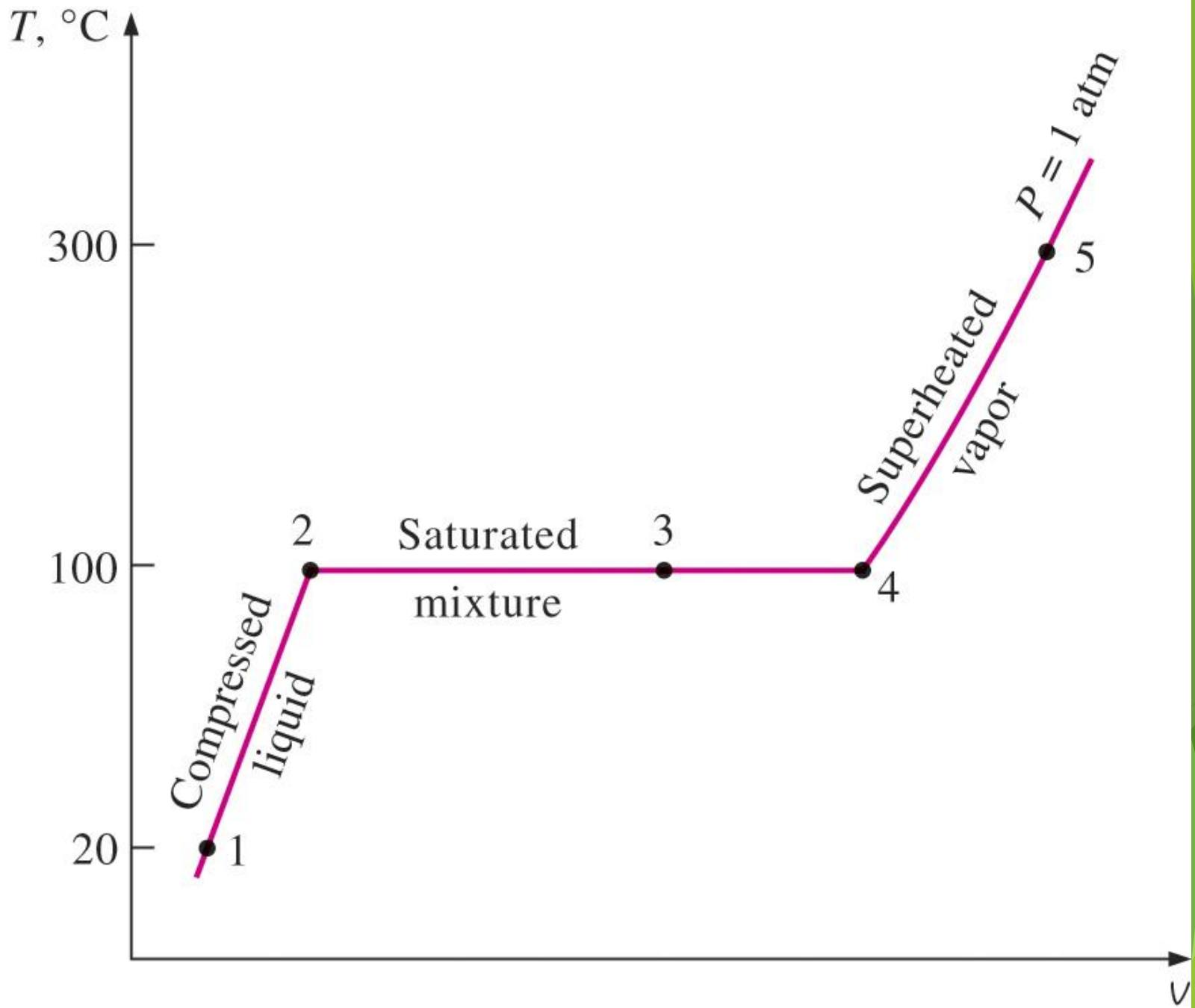▶ **Saturation temperature T_{sat}**: The temperature at which a pure substance changes phase at a given pressure.

▶ **Saturation pressure P_{sat}**: The pressure at which a pure substance changes phase at a given temperature.
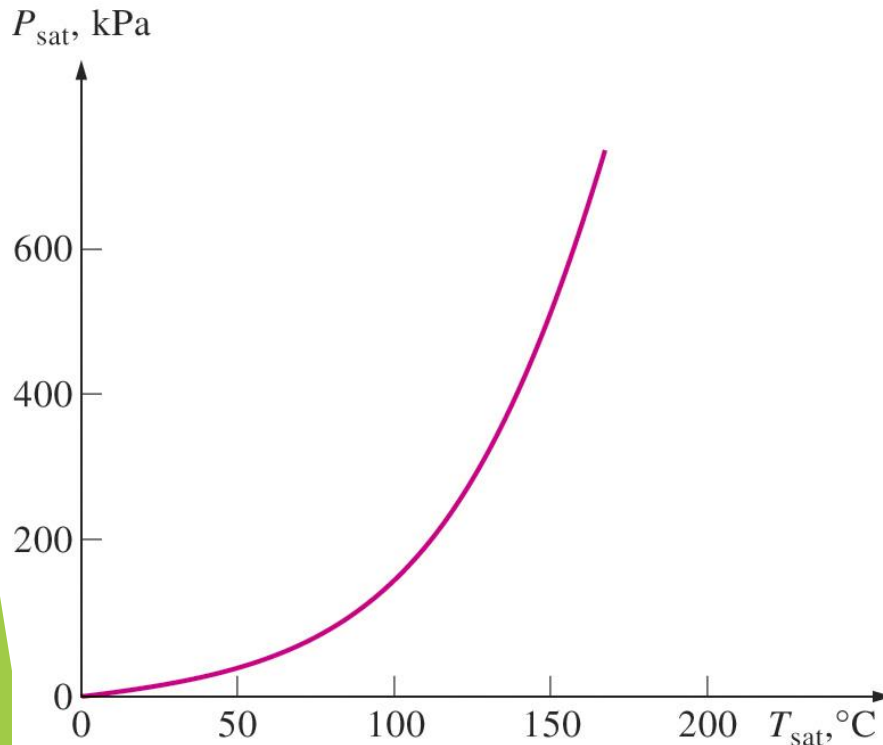
The liquid–vapor saturation curve of a pure substance (numerical values are for water).

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

- ▶ **Latent heat**: The amount of energy absorbed or released during a phase-change process.

- ▶ **Latent heat of fusion**: The amount of energy absorbed during melting. It is equivalent to the amount of energy released during freezing.

- ▶ **Latent heat of vaporization:** The amount of energy absorbed during vaporization and it 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 333.7 kJ/kg and the latent heat of vaporization is 2256.5 kJ/kg.

- ▶ The atmospheric pressure, and thus the boiling temperature of water, decreases with elevation.

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

▶ Now we repeat the previous process at different pressures to develop the *T-v* diagram..

T, °C

Critical point

$P = 25$ MPa

$P = 22.06$ MPa

$P = 15$ MPa

$P = 8$ MPa

$P = 1$ MPa

$P = 0.1$ MPa

$P = 0.01$ MPa

373.95

0.003106

Saturated liquid

Saturated vapor

v, m^3/kg

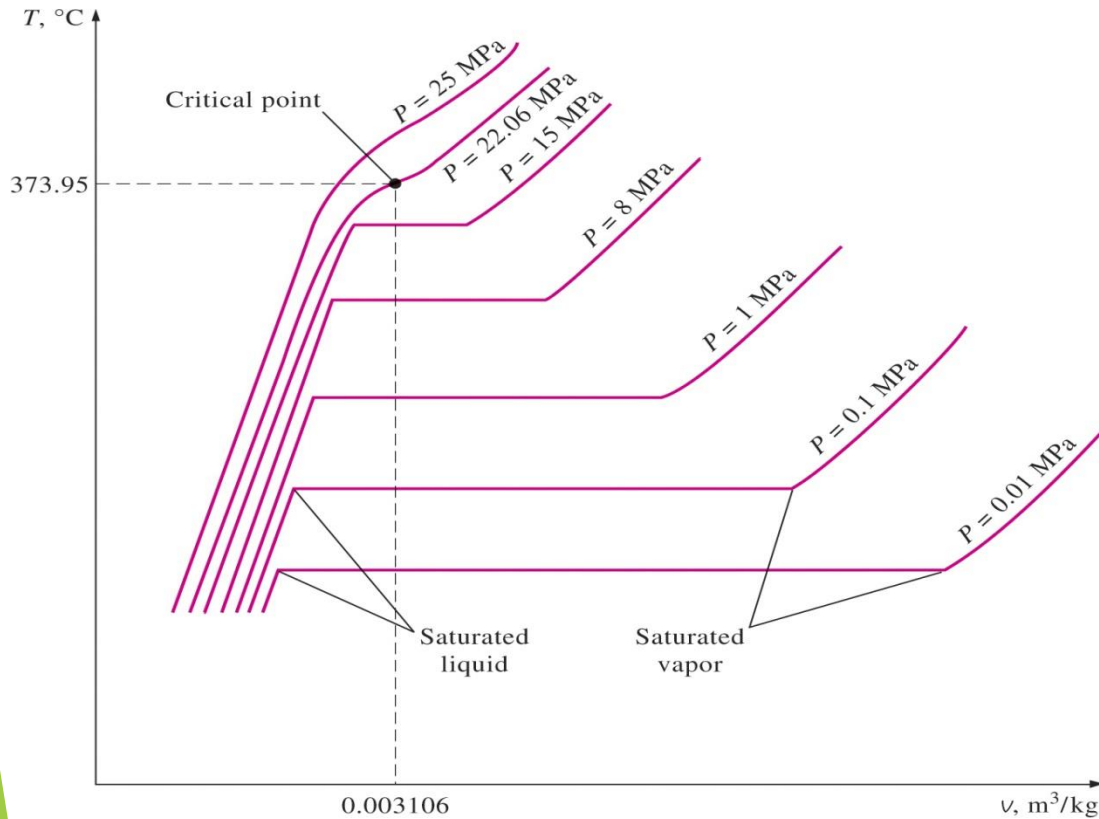*Fig. (1) T-v* diagram of constant-pressure phase-change processes of a pure substance at various pressures (numerical values are for water).

First, water starts boiling at a much higher temperature (e.g. 179.9◦C at 1 MPa) 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.

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Critical point 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}

- At pressures above the critical pressure, there is not a distinct phase change process.

- Above the critical state, there is no line that separates the compressed liquid region and the superheated vapor region.

- However, it is customary to refer to the substance as superheated vapor at temperatures above the critical temperature and as compressed liquid at temperatures below the critical temperature.
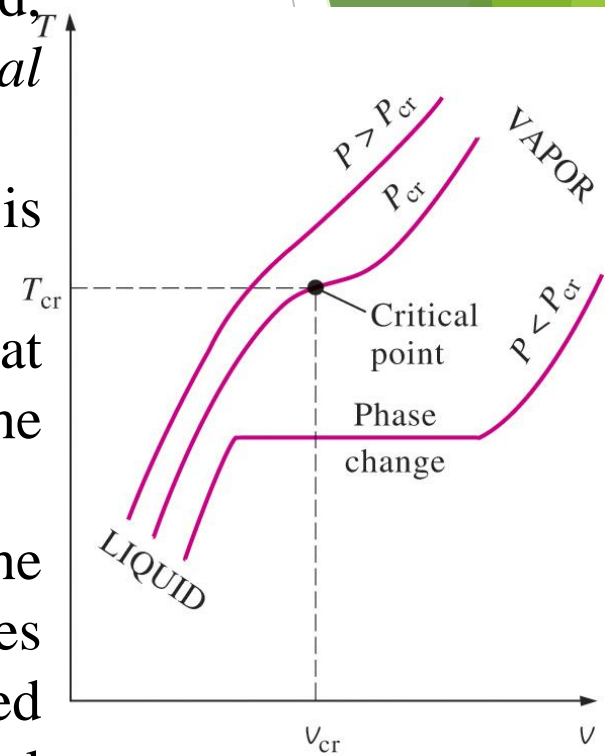
The saturated liquid states in Fig.(1) can be connected by a line called the **saturated liquid line,** and saturated vapor states in the same figure can be connected by another line, called the **saturated vapor line.** These two lines meet at the critical point, forming a dome as shown in the following Fig.

- saturated liquid line
- saturated vapor line
- compressed liquid region
- superheated vapor region
- saturated liquid-vapor mixture region (wet region)
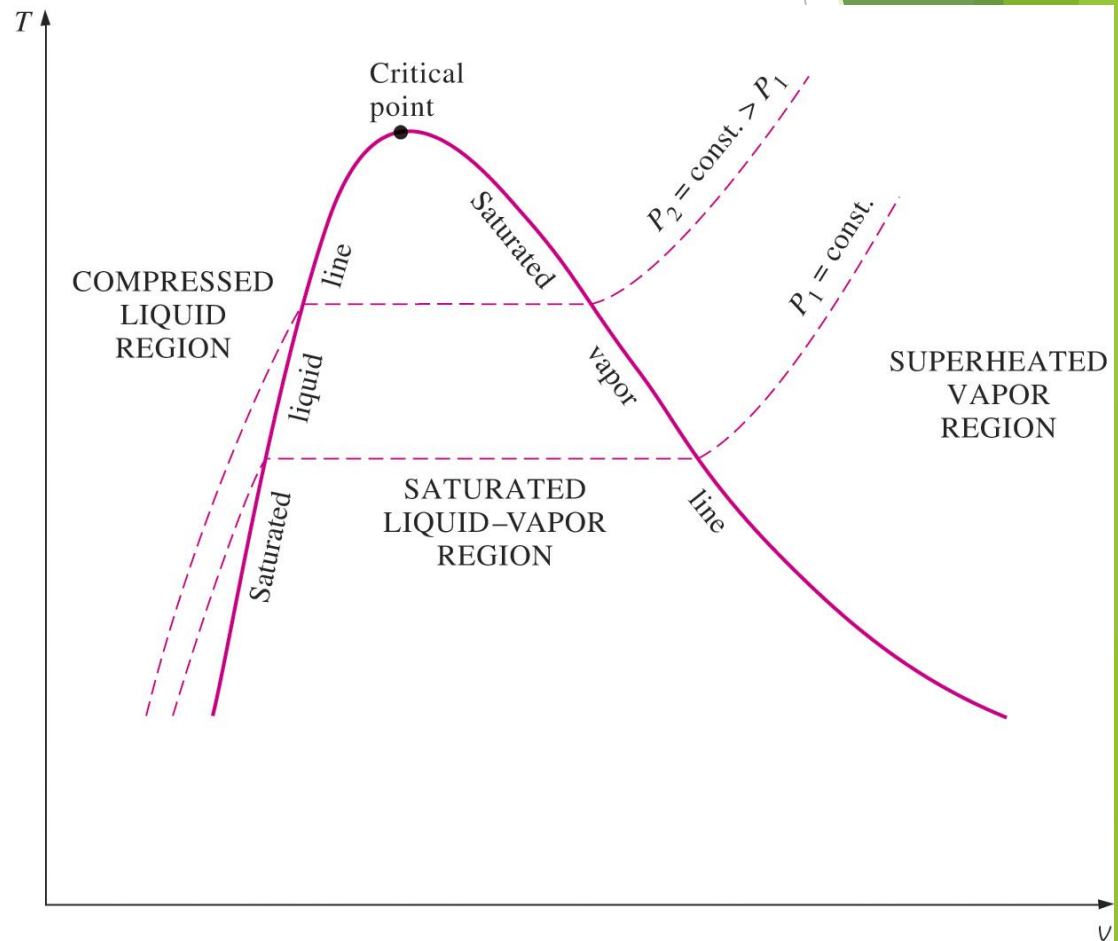
P- v diagram of a pure substance.

P

Critical
point

Saturated

line

Saturated

liquid

line

vapor

COMPRESSED
LIQUID
REGION

SUPERHEATED
VAPOR
REGION

SATURATED
LIQUID–VAPOR
REGION

Saturated

line

$T_2 = const. > T_1$

$T_1 = const.$

v

$P = 1 \text{ MPa}$
$T = 150°C$

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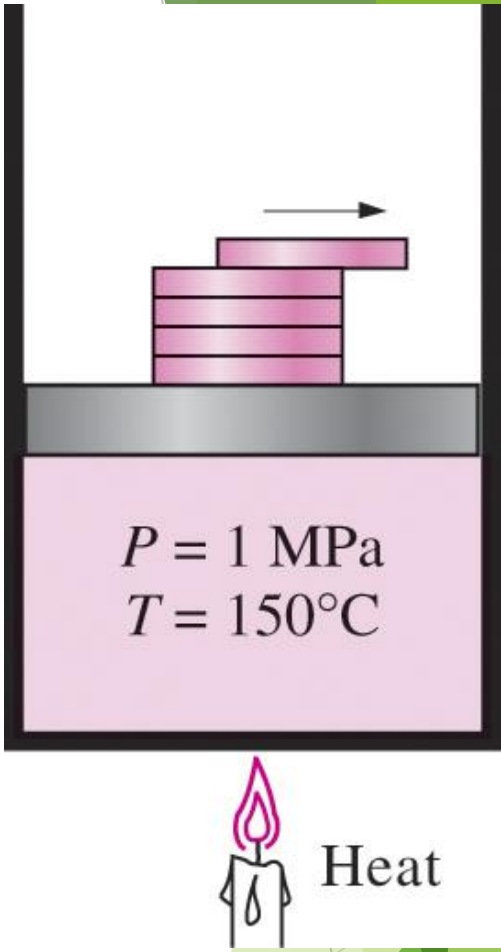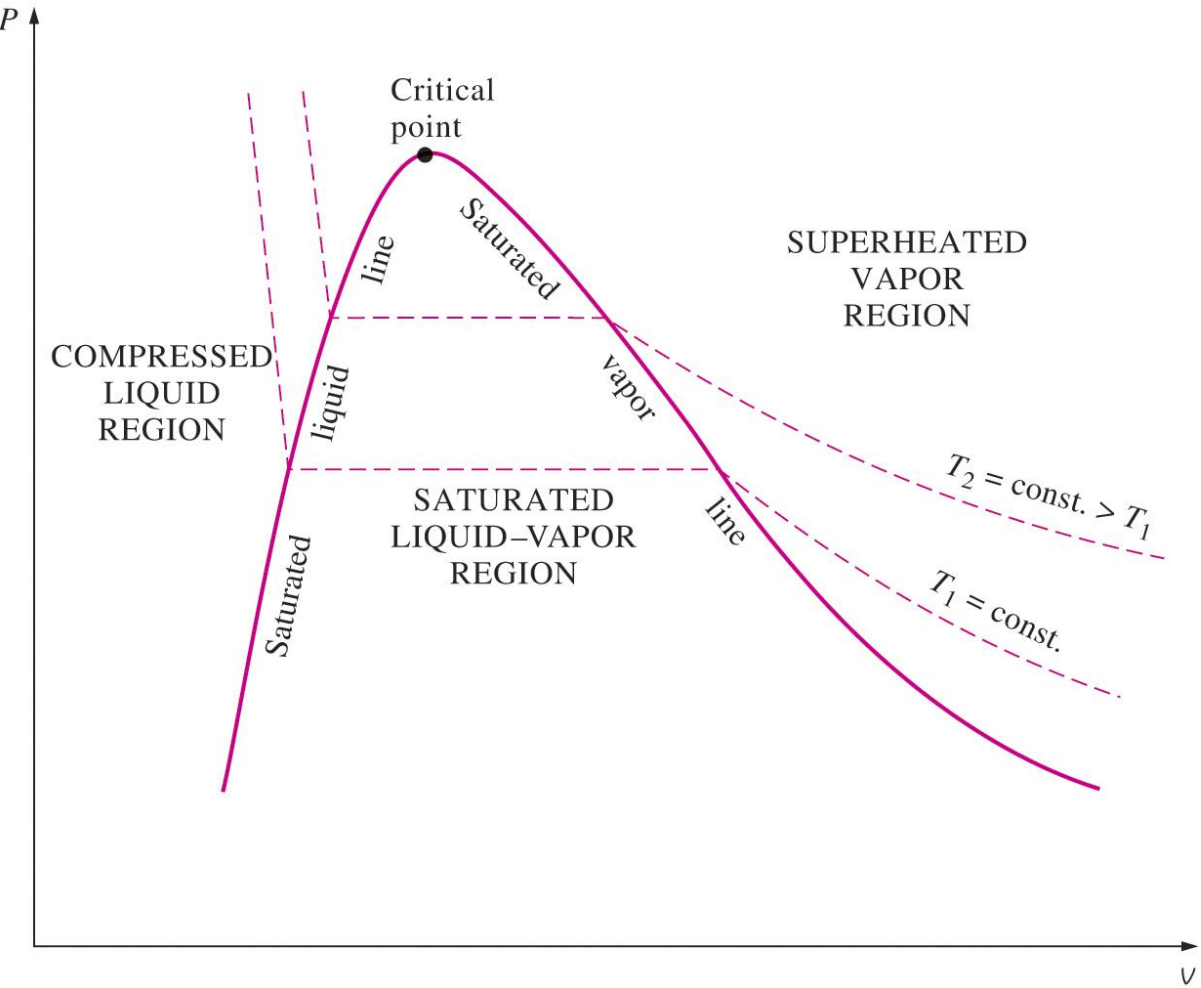
The pressure in a piston–cylinder device can be reduced by reducing the weight of the piston.

Extending the Diagrams to Include the Solid Phase

At triple-point pressure and temperature, a substance exists in three phases in equilibrium.
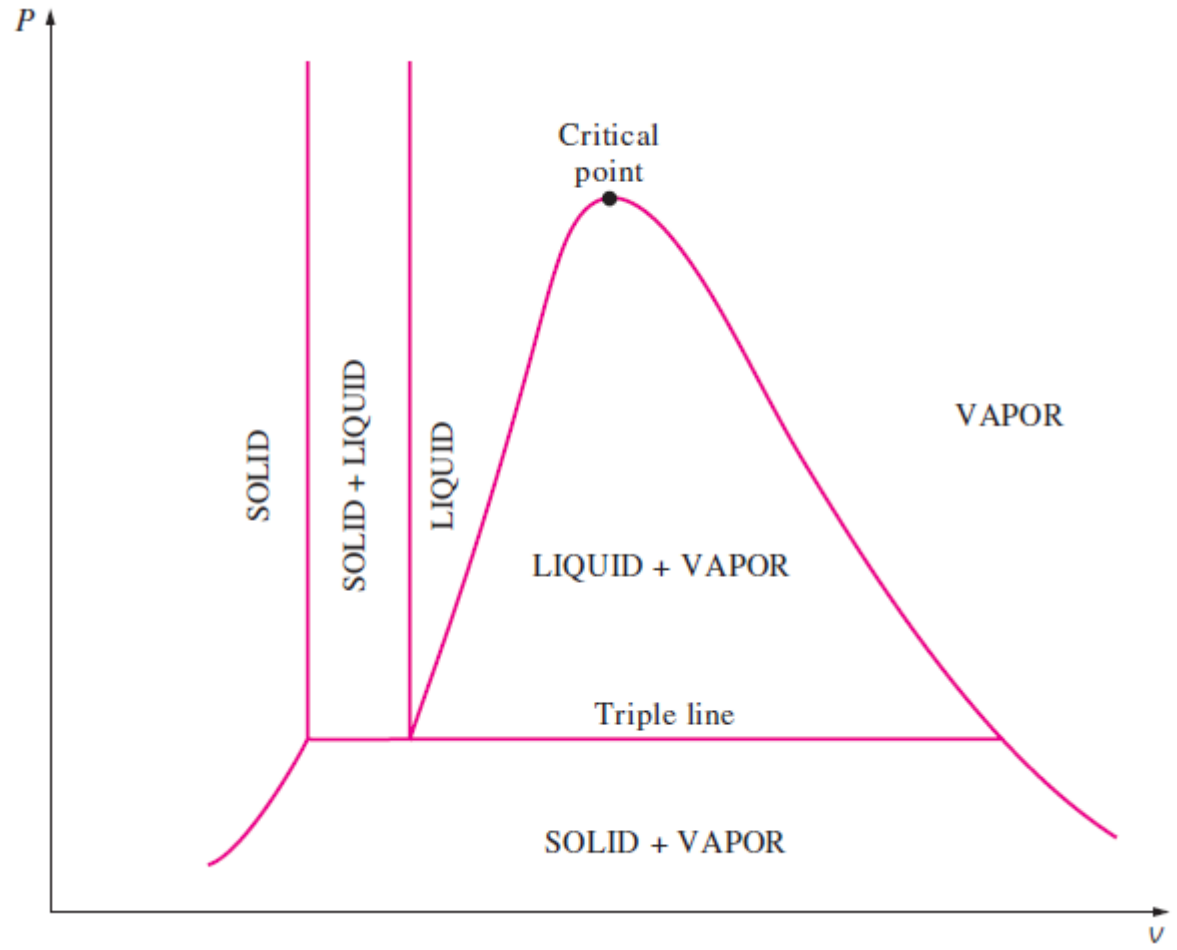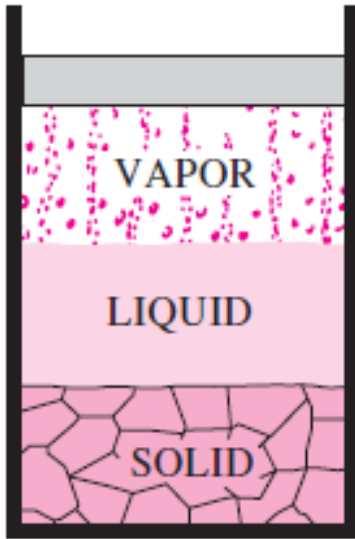
Sublimation: Passing from the solid phase directly into the vapor phase.

Equation of State

Any equation relates the P, T, v of substance. The simplest and best known is the ideal- gas equation of state. Its predict the P-V-T behavior of a gas.

Ideal Gas Law

Combination of Boyle's and Charles' laws for gases at low P result in the equation of state for the ideal gas as

$$P = R\left(\frac{T}{v}\right) \qquad or \qquad Pv = RT$$

where R is **gas constant** and takes on a different value for each gas

$$R = \frac{R_u}{M}$$

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

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

P = **absolute pressure**
v = specific volume
T = **absolute temperature** in K

The molar mass, M: mass of one mole of a substance in grams or the mass of one kmol

$$M_{air} = 28.97 \frac{g}{gmol} = 28.97 \frac{kg}{kmol} = 28.97 \frac{lbm}{lbmol}$$

The ideal gas equation of state may be written in several ways

$$PV = mRT$$

$$PV = \frac{m}{M}(MR)T$$

$$PV = NR_u T$$

$$P\frac{V}{N} = R_u T$$

$$P\overline{v} = R_u T$$

$\overline{v}$ = molar specific volume

The properties of an ideal gas at two different states are related by

$$m_1 = m_2$$

$$\frac{P_1 V_1}{RT_1} = \frac{P_2 V_2}{RT_2}$$

$$\therefore \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Compressibility Factor—a Measure of Deviation From Ideal-gas Behavior

Compressibility factor Z : A factor that accounts for the deviation of real gases from ideal-gas behavior at a given temperature and pressure.

$$Pv = ZRT$$

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

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

IDEAL GAS

$Z = 1$

REAL GASES

$Z \begin{cases} > 1 \\ = 1 \\ < 1 \end{cases}$

Gases behave as an ideal gas at low densities (i.e., low pressure, high temperature).

Question: What is the criteria for low pressure and high temperature?

Answer: The pressure or temperature of a gas is high or low relative to its critical temperature or pressure.

REAL GAS

as $P \rightarrow 0$
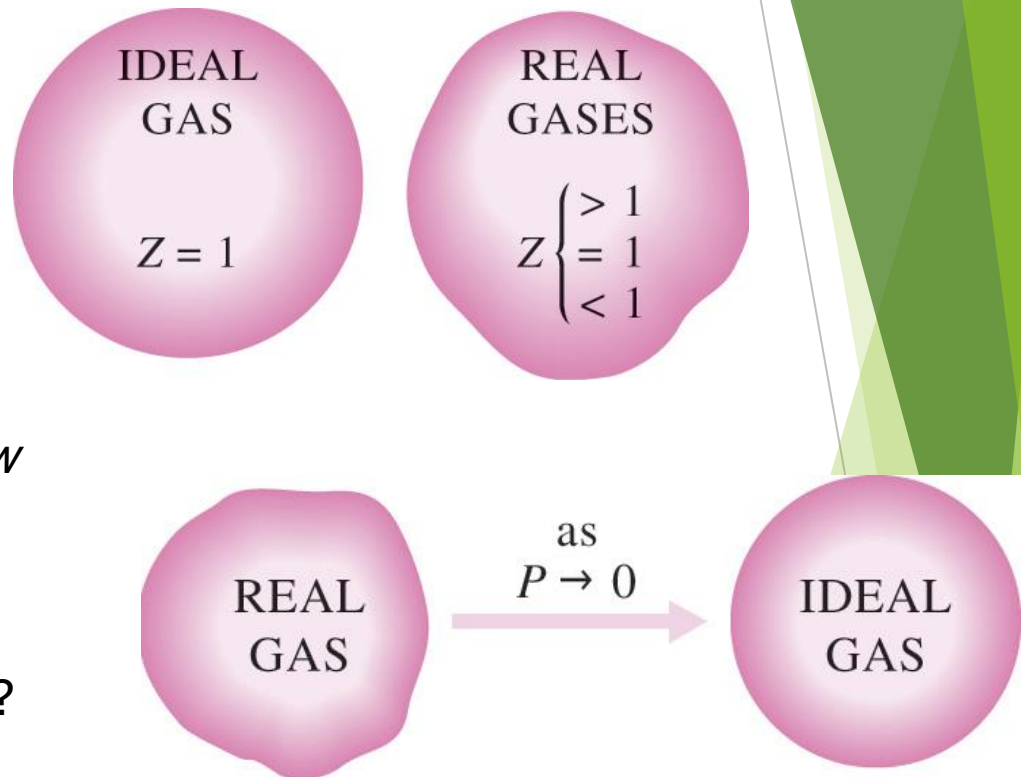
IDEAL GAS

At very low pressures, all gases approach ideal-gas behavior (regardless of their temperature).

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Z: a function of the reduced pressure and the reduced temperature. The *Z* factor is approximately the same for all gases at the same *reduced temperature* and *reduced pressure*, which are defined as

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

where P_R= reduced pressure

T_R= reduced temperature

The critical constant data for various substances are given in Table A-1.

When either *P* or *T* is unknown, *Z* can be determined from the compressibility chart with the help of the **pseudo-reduced specific volume**, defined as

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

Figure A-15 (book) presents the generalized compressibility chart based on data for a large number of gases.

OTHER EQUATIONS OF STATE

Several equations have been proposed to represent the *P-v-T* behavior of substances accurately over a larger region with no limitations.

van der Waals

Berthelet

Redlich-Kwang

Beattie-Bridgeman

Benedict-Webb-Rubin

Strobridge

Virial

Van der Waals Equation of State

$$\left(P + \frac{a}{v^2} \right) (v - b) = RT$$

$$a = \frac{27R^2T_{cr}^2}{64P_{cr}} \qquad b = \frac{RT_{cr}}{8P_{cr}}$$

Critical isotherm of a pure substance has an inflection point at the critical state.

$$\left(\frac{\partial P}{\partial v} \right)_{T=T_{cr}=\text{const}} = 0$$

$$\left(\frac{\partial^2 P}{\partial v^2} \right)_{T=T_{cr}=\text{const}} = 0$$

Critical point

$T_{cr} = constant$

This model includes two effects not considered in the ideal-gas model: the *intermolecular attraction forces* and the *volume occupied by the molecules themselves*. The accuracy of the van der Waals equation of state is often inadequate.
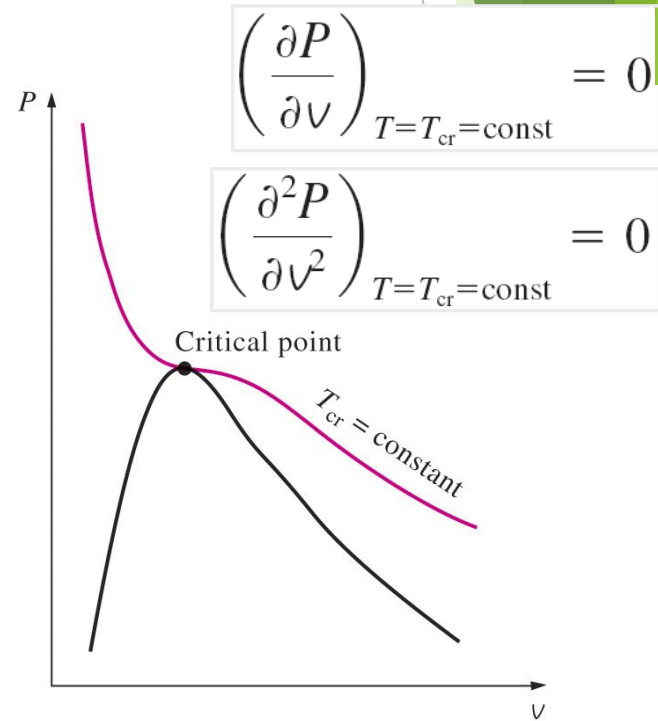
Beattie-Bridgeman Equation of State

$$P = \frac{R_u T}{\bar{v}^2}\left(1 - \frac{c}{\bar{v}T^3}\right)(\bar{v} + B) - \frac{A}{\bar{v}^2}$$

The constants are given in Table 3–4 for various substances. It is known to be reasonably accurate for densities up to about $0.8\rho_{cr}$

$$A = A_0\left(1 - \frac{a}{\bar{v}}\right) \quad B = B_0\left(1 - \frac{b}{\bar{v}}\right)$$

Benedict-Webb-Rubin Equation of State

$$P = \frac{R_u T}{\bar{v}} + \left(B_0 R_u T - A_0 - \frac{C_0}{T^2}\right)\frac{1}{\bar{v}^2} + \frac{bR_u T - a}{\bar{v}^3} + \frac{a\alpha}{\bar{v}^6} + \frac{c}{\bar{v}^3 T^2}\left(1 + \frac{\gamma}{\bar{v}^2}\right)e^{-\gamma/\bar{v}^2}$$

The constants are given in Table 3–4. This equation can handle substances at densities up to about 2.5 ρ_{cr}

Virial Equation of State

$$P = \frac{RT}{\bar{v}} + \frac{a(T)}{\bar{v}^2} + \frac{b(T)}{\bar{v}^3} + \frac{c(T)}{\bar{v}^4} + \frac{d(T)}{\bar{v}^5} + \cdots$$

The coefficients $a(T)$, $b(T)$, $c(T)$, and so on, that are functions of temperature alone are called *virial coefficients*.

Example (1)

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

Example (2)

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.

Example (3)

Determine the pressure of water vapor at 350°C and 0.035262 m3/kg, using (*a*) the steam tables, (*b*) the ideal-gas equation, and (*c*) the generalized compressibility chart.