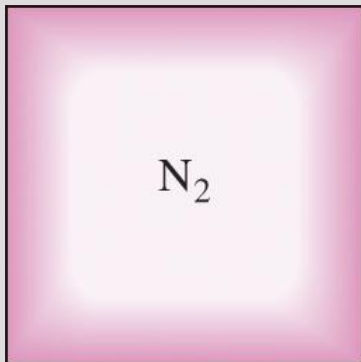


Chapter 3

PROPERTIES OF PURE SUBSTANCES

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.

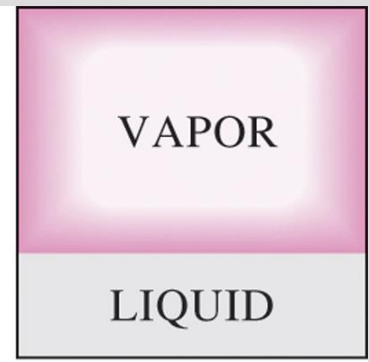


Nitrogen and gaseous air are pure substances.



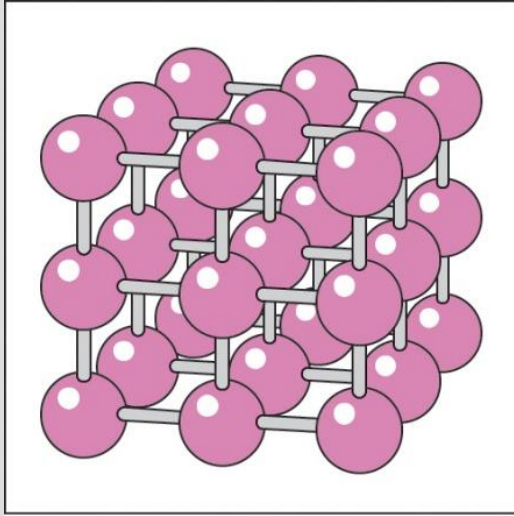
(a) H_2O

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

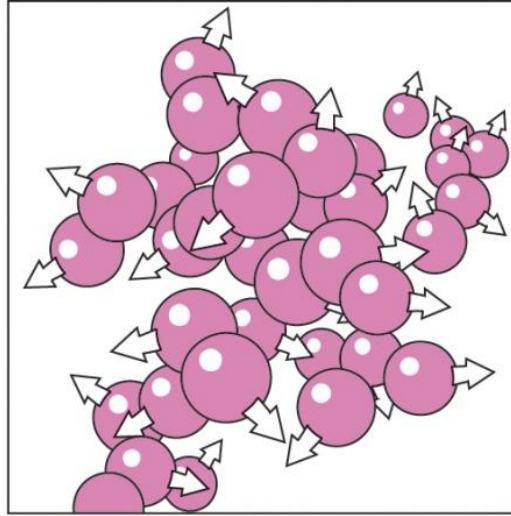


(b) AIR

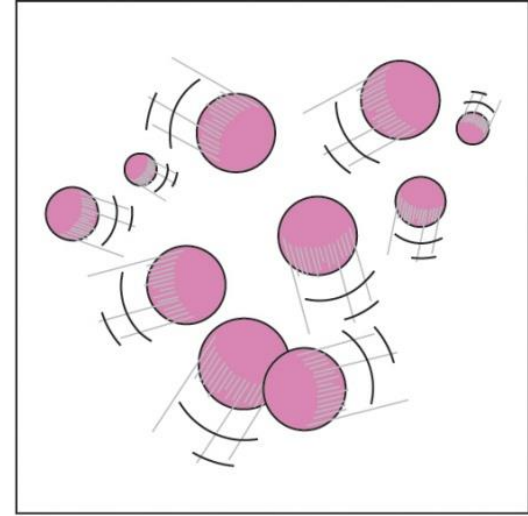
PHASES OF A PURE SUBSTANCE



(a)



(b)



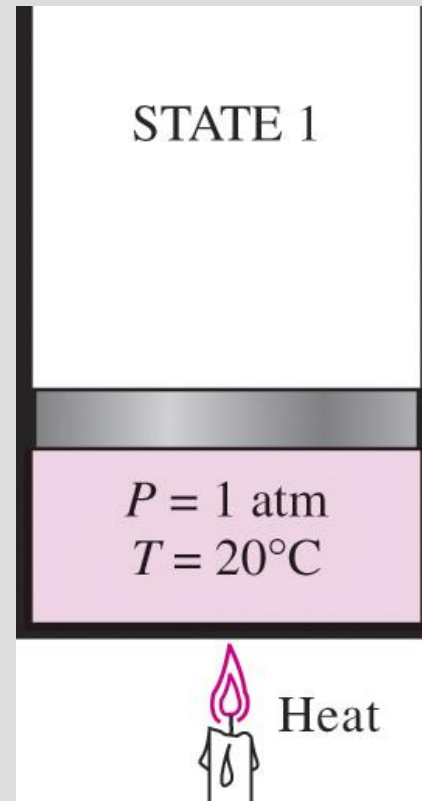
(c)

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

- **Compressed liquid (subcooled liquid):** A substance that is *not about to vaporize*.

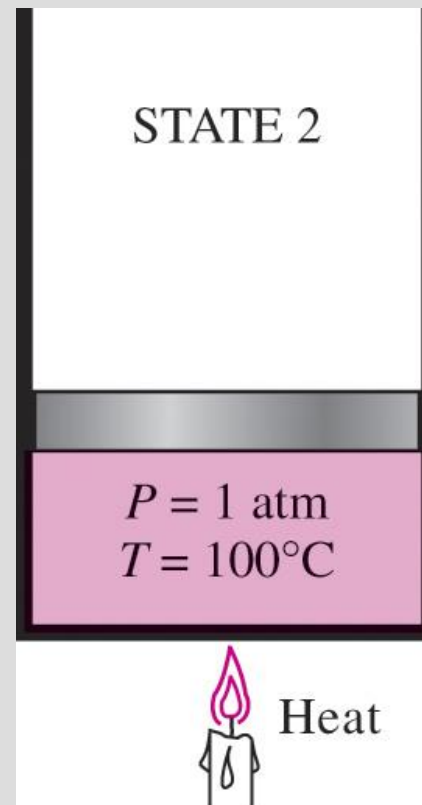
At 1 atm and 20°C,
water exists in the
liquid phase
(***compressed liquid***).



PHASE-CHANGE PROCESSES OF PURE SUBSTANCES

- **Saturated liquid:** A liquid that is *about to vaporize*.

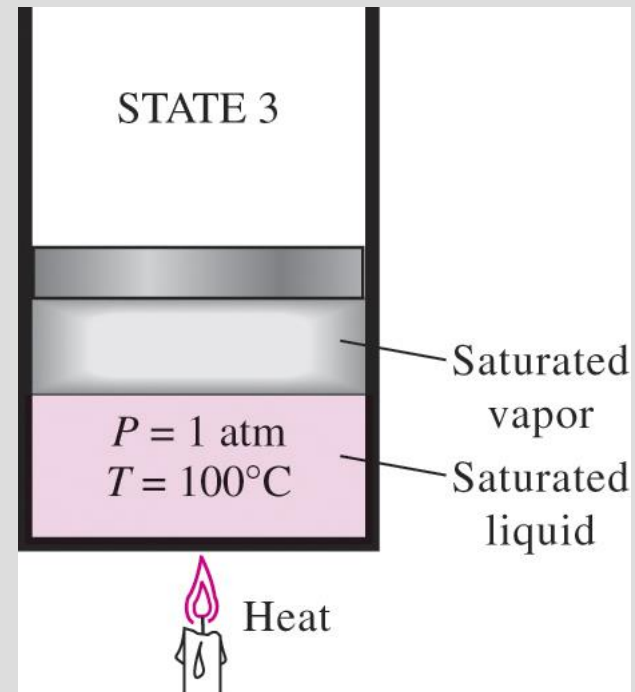
At 1 atm pressure and 100°C, water exists as a liquid that is ready to vaporize (*saturated liquid*).



PHASE-CHANGE PROCESSES OF PURE SUBSTANCES

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

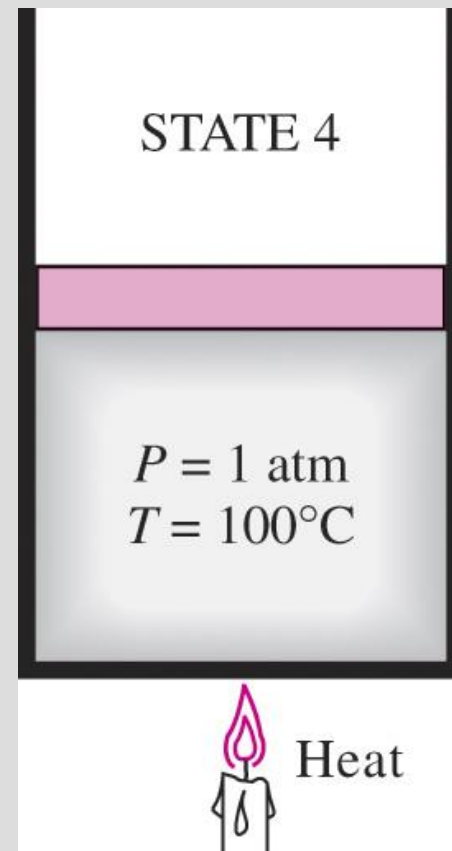
As more heat is transferred, part of the saturated liquid vaporizes (***saturated liquid–vapor mixture***).



PHASE-CHANGE PROCESSES OF PURE SUBSTANCES

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

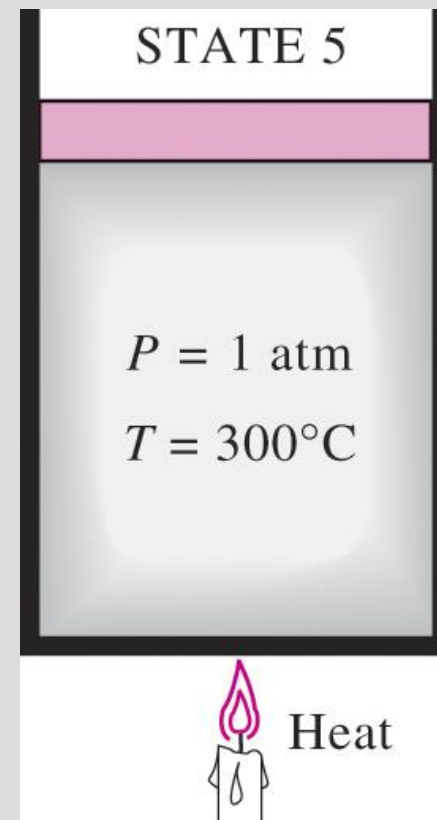
At 1 atm pressure, the temperature remains constant at 100°C until the last drop of liquid is vaporized (***saturated vapor***).

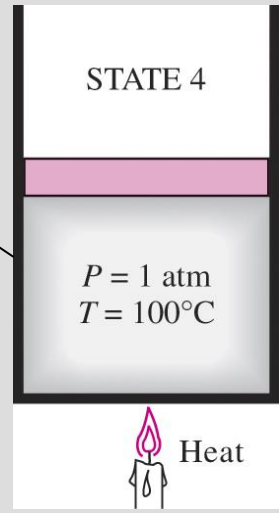
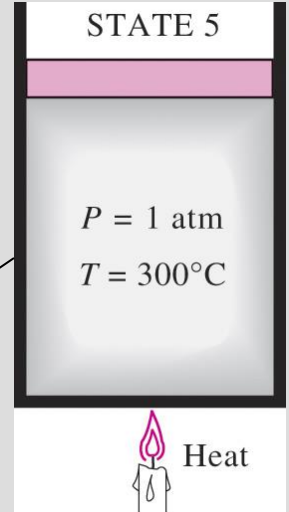
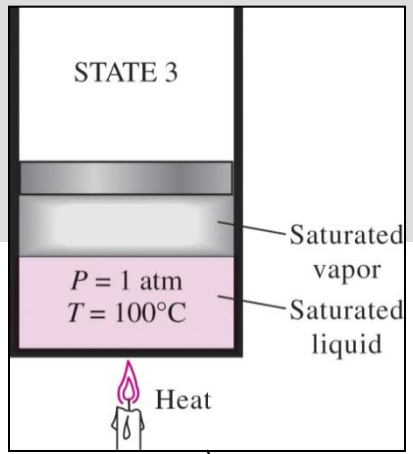
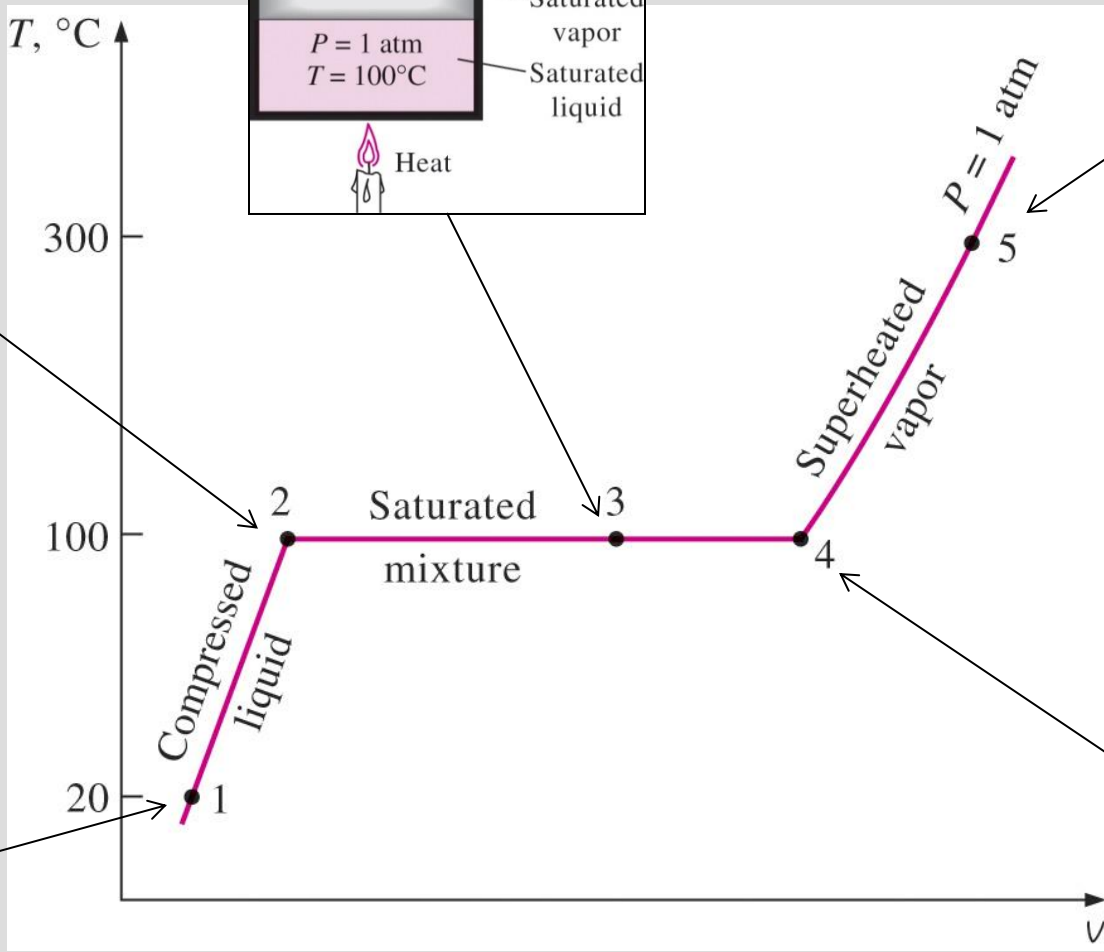
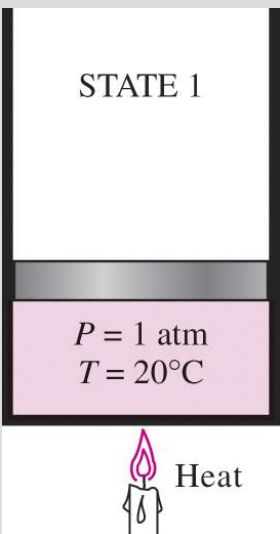
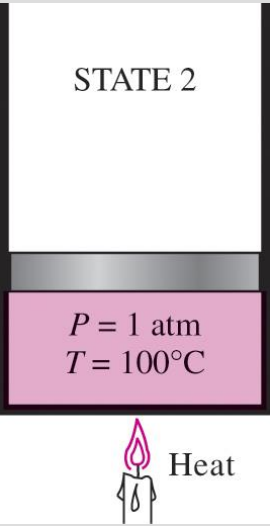


PHASE-CHANGE PROCESSES OF PURE SUBSTANCES

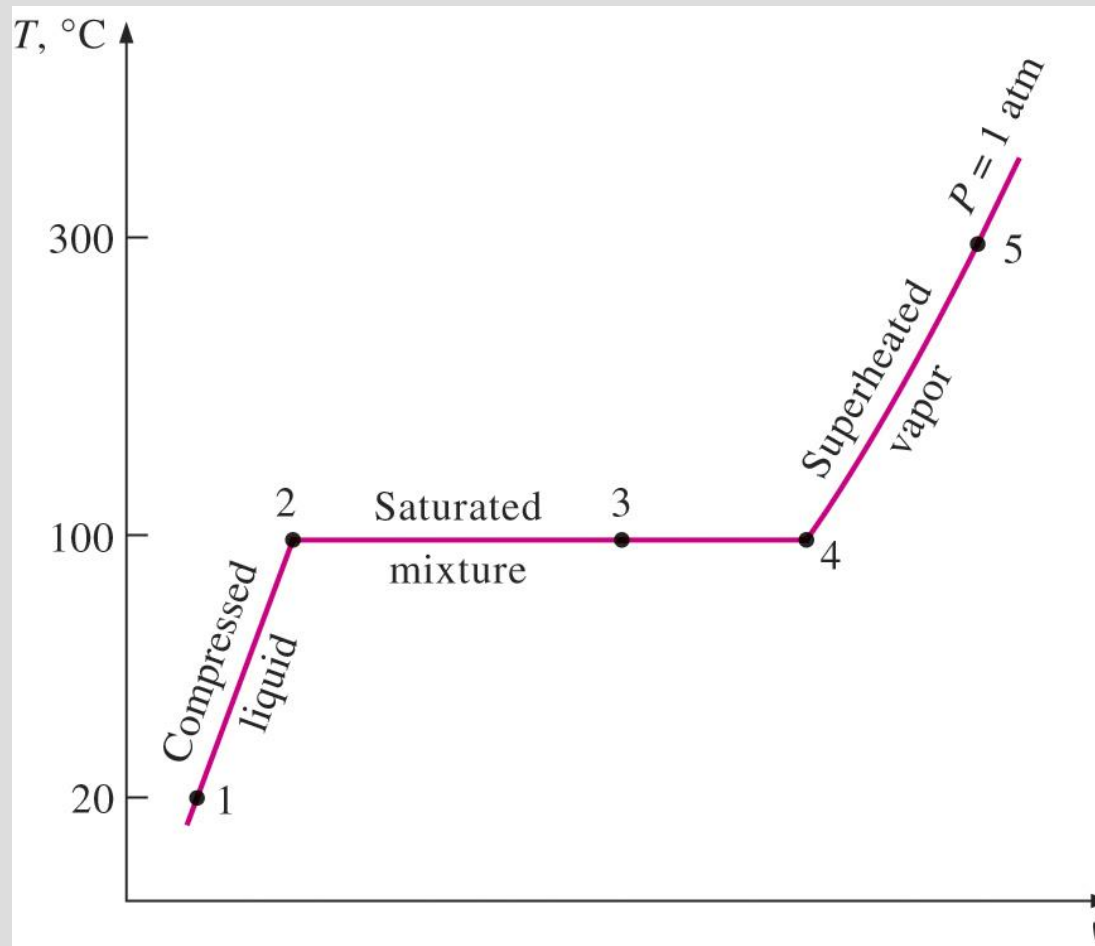
Superheated vapor: A vapor that is *not about to condense* (i.e., not a saturated vapor).

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



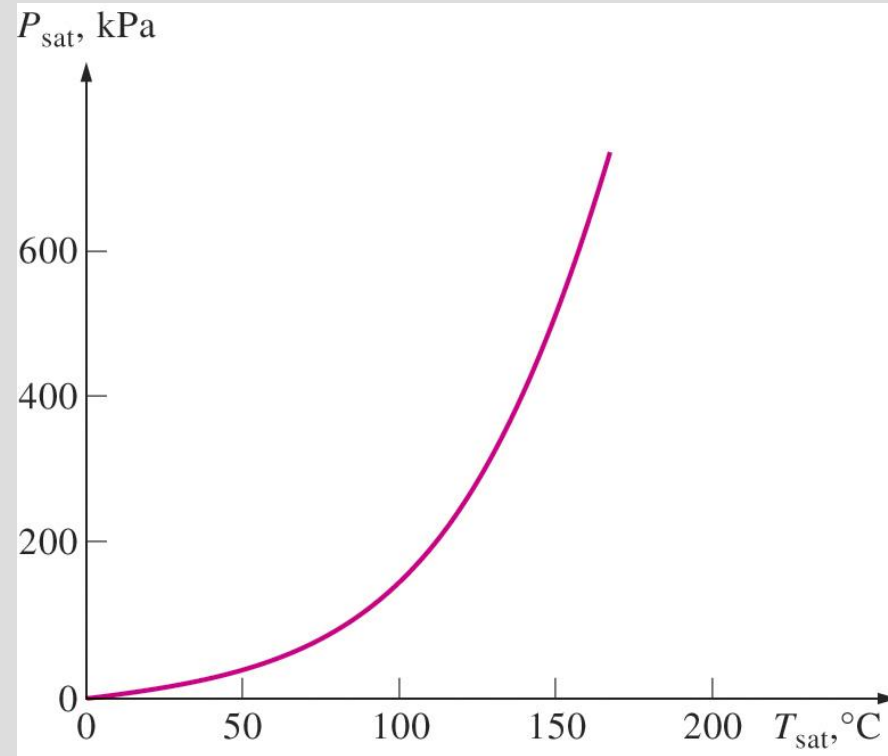


If the entire process between state 1 and 5 described in the figure is reversed by cooling the water while maintaining the pressure at the same value, the water will go back to state 1, retracing the same path, and in so doing, the amount of heat released will exactly match the amount of heat added during the heating process.



Saturation Temperature and Saturation Pressure

- The temperature at which water starts boiling depends on the pressure
- If the pressure is fixed, so is the boiling temperature.
- Water boils at 100°C at 1 atm.
- **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.



Saturation Temperature and 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

TABLE 3–2

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

Elevation, m	Atmospheric pressure, kPa	Boiling tempera- ture, °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

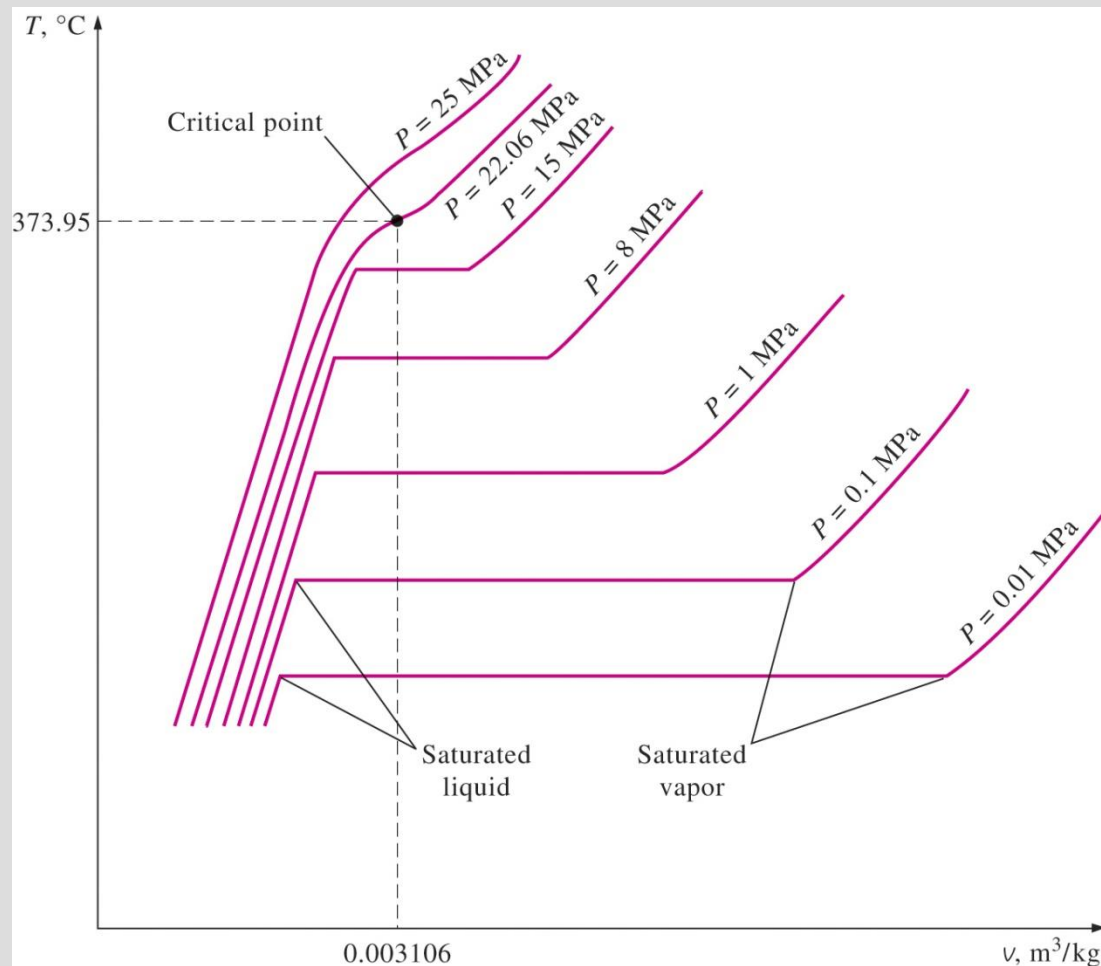
The atmospheric pressure, and thus the boiling temperature of water, decreases with elevation.

Latent Heat

- **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.

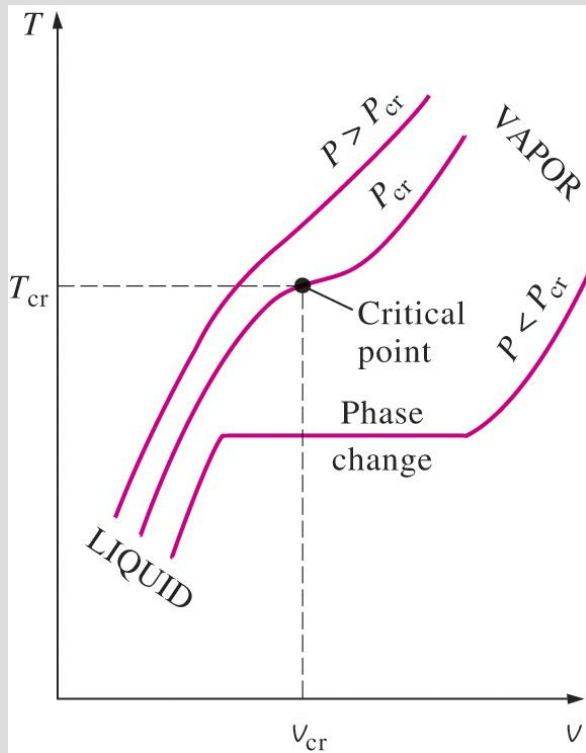
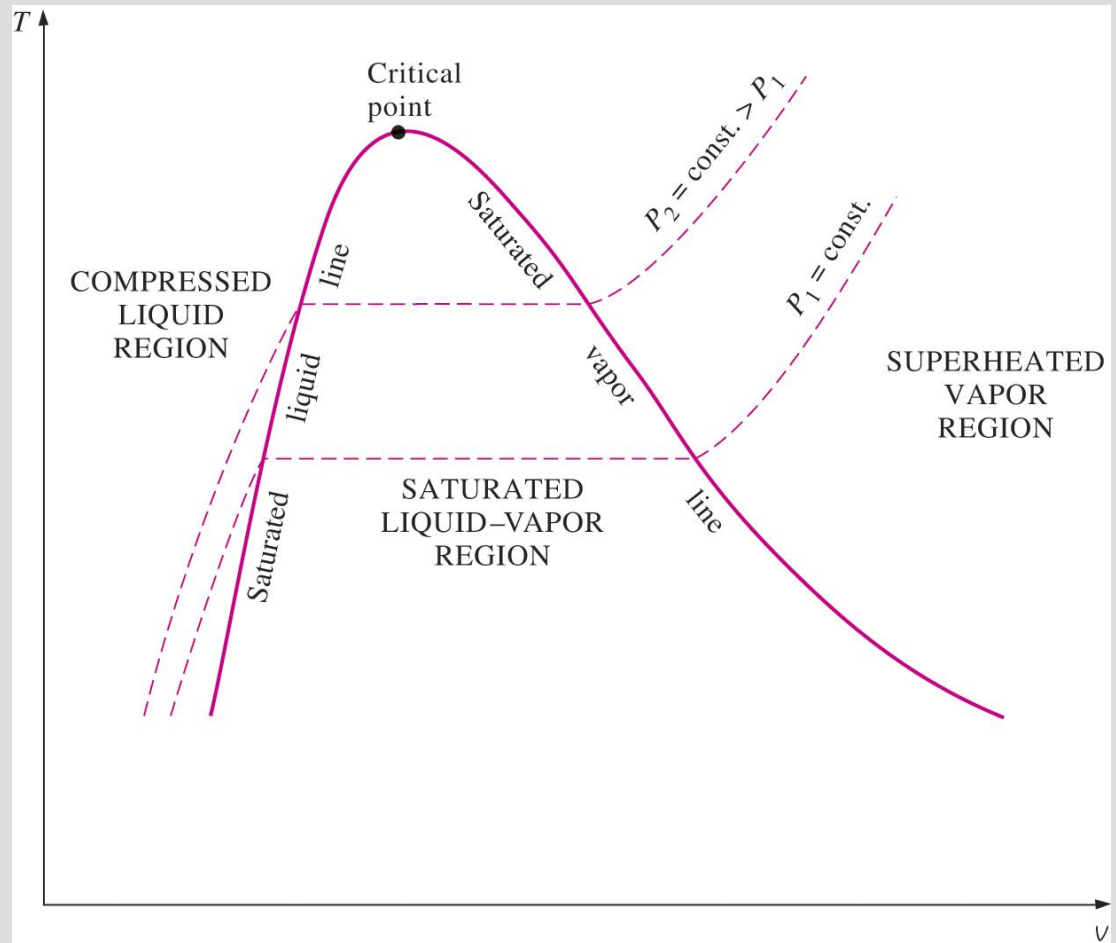
PROPERTY DIAGRAMS FOR PHASE-CHANGE PROCESSES

- The variations of properties during phase-change processes are best studied and understood with the help of property diagrams such as the T - v , P - v , and P - T diagrams for pure substances.



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

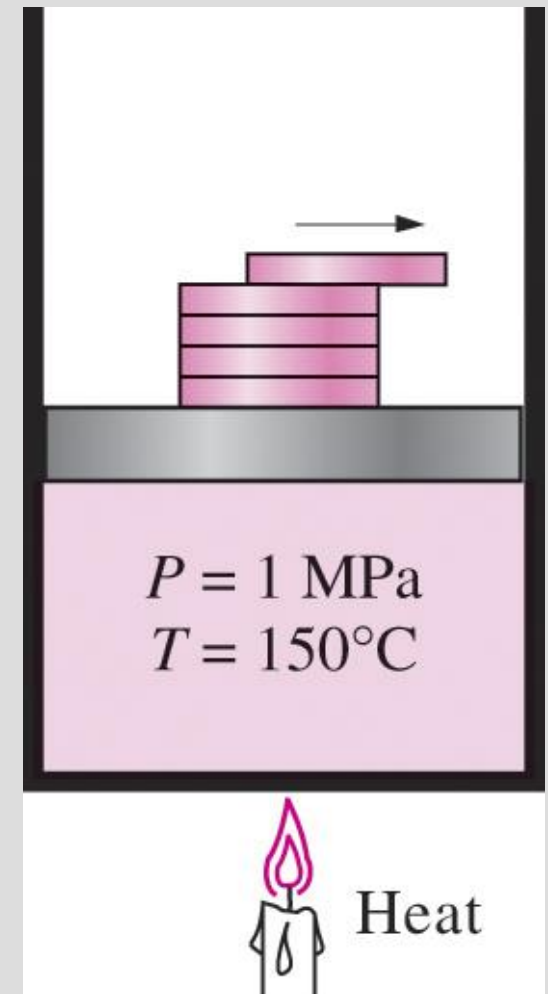
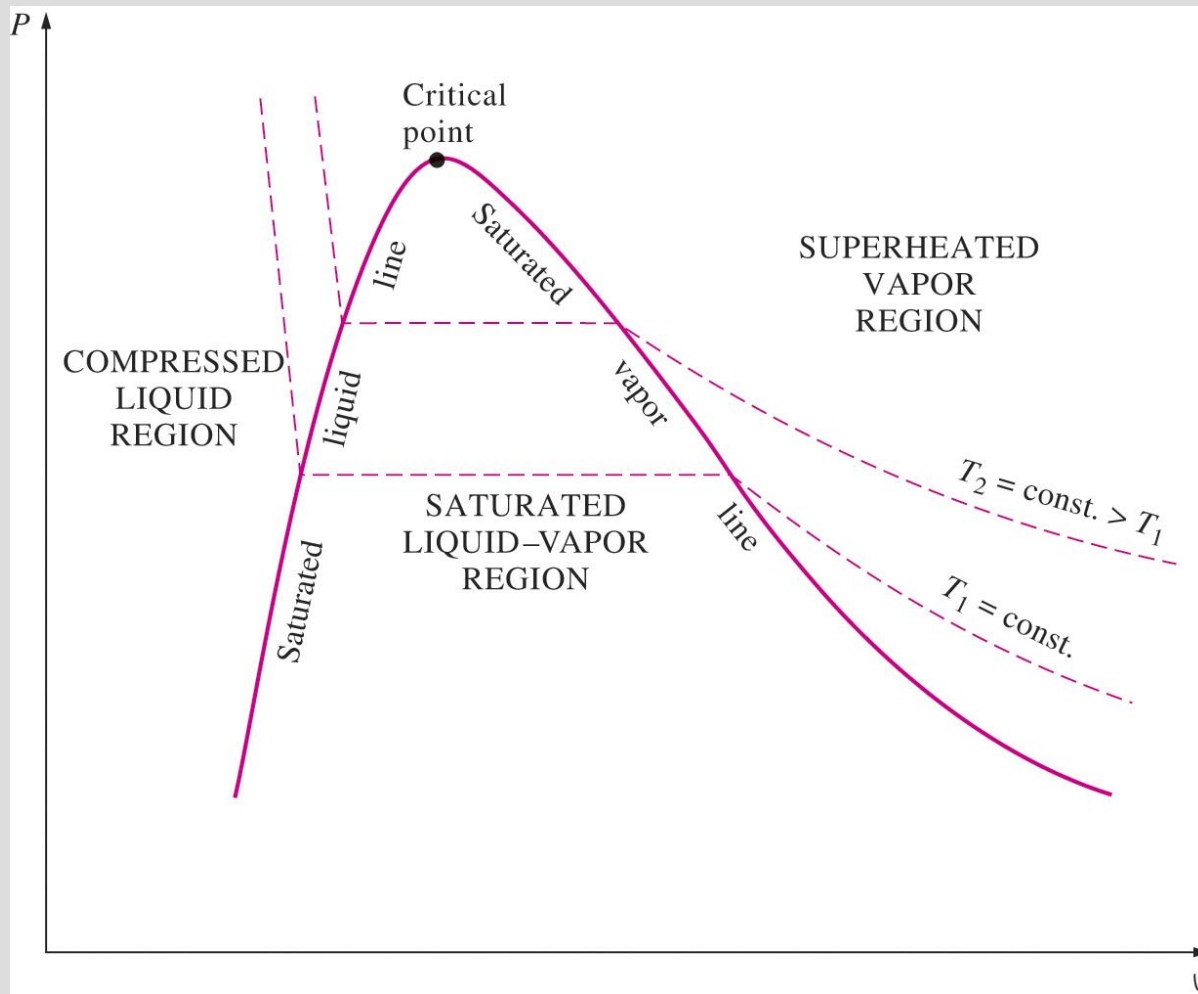
- saturated liquid line
- saturated vapor line
- compressed liquid region
- superheated vapor region
- saturated liquid–vapor mixture region (wet region)



At supercritical pressures ($P > P_{cr}$), there is no distinct phase-change (boiling) process.

T - v diagram of a pure substance.

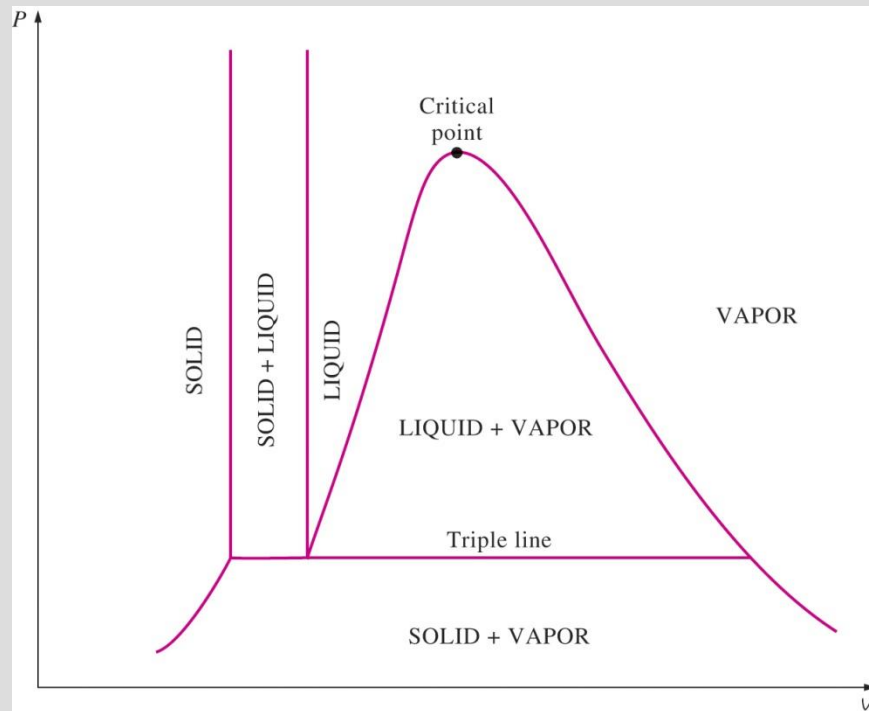
Critical point: The point at which the saturated liquid and saturated vapor states are identical.



P - v diagram of a pure substance.

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

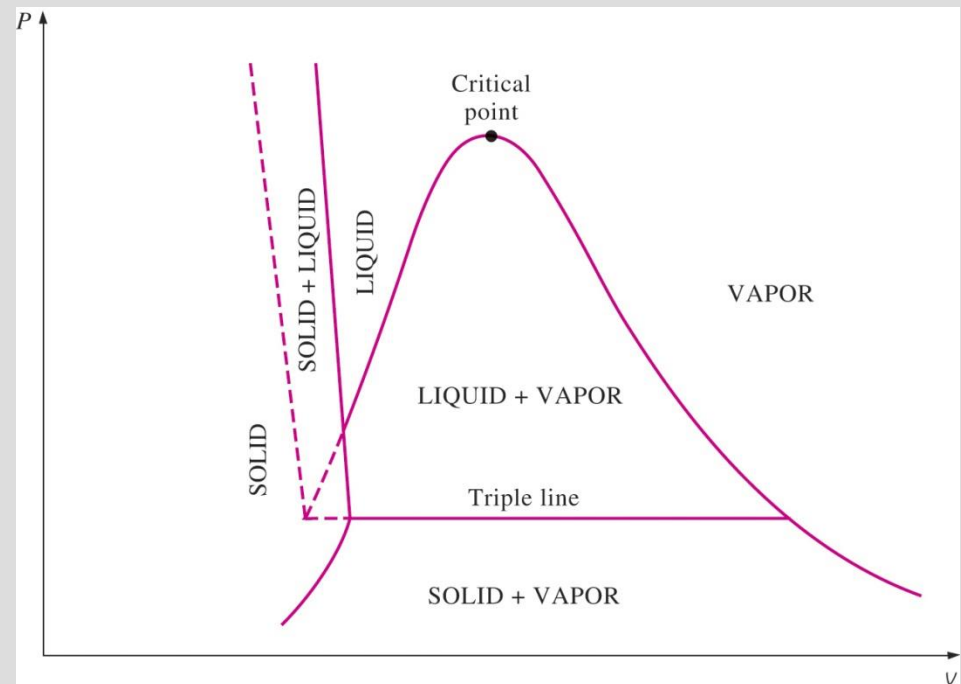
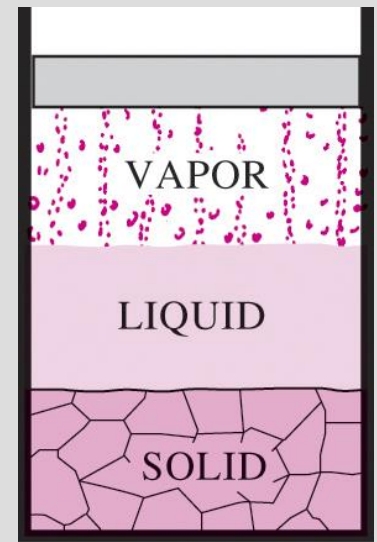
Extending the Diagrams to Include the Solid Phase



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

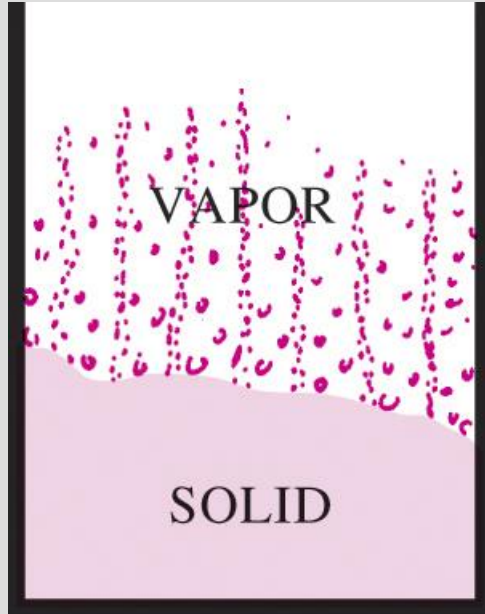
For water,
 $T_{tp} = 0.01^\circ\text{C}$
 $P_{tp} = 0.6117 \text{ kPa}$

At triple-point pressure and temperature, a substance exists in three phases in equilibrium.



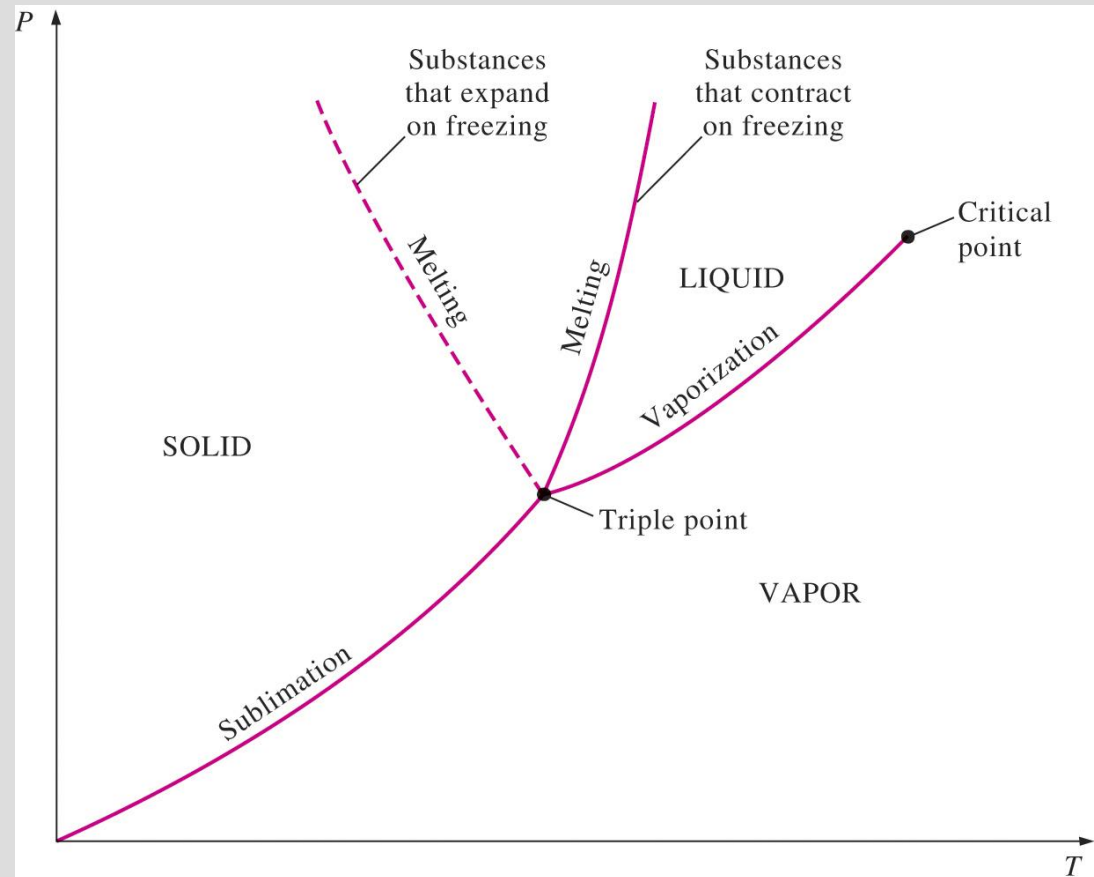
P - v diagram of a substance that expands on freezing (such as water).

Sublimation: Passing from the solid phase directly into the vapor phase.



At low pressures (below the triple-point value), solids evaporate without melting first (*sublimation*).

Phase Diagram



P-T diagram of pure substances.

PROPERTY TABLES

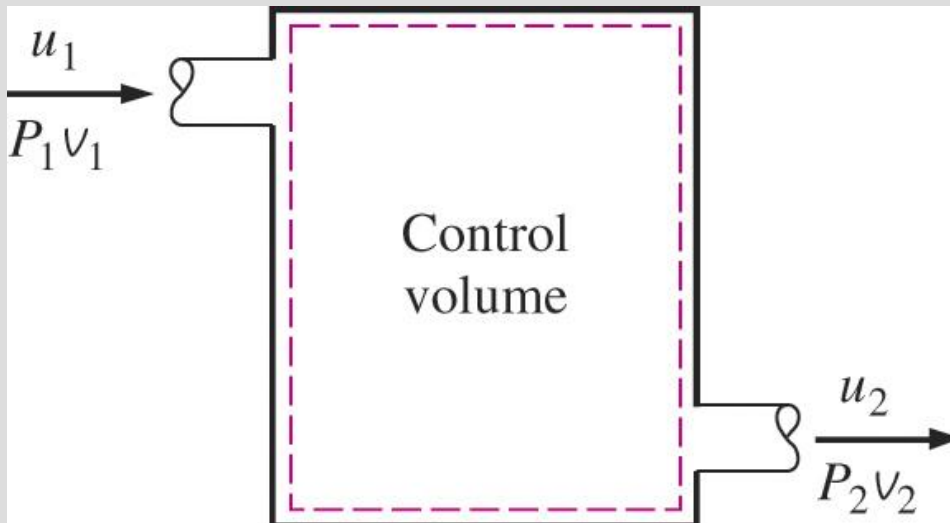
- For most substances, the relationships among thermodynamic properties are too complex to be expressed by simple equations.
- Therefore, properties are frequently presented in the form of tables.
- Some thermodynamic properties can be measured easily, but others cannot and are calculated by using the relations between them and measurable properties.
- The results of these measurements and calculations are presented in tables in a convenient format.

ENTHALPY

- Property tables contain a property called **Enthalpy**
- Enthalpy is a combination property

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

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



The combination $u + Pv$ is frequently encountered in the analysis of control volumes.

Saturated Liquid and Saturated Vapor States

- **Table A–4:** Saturation properties of water under temperature.
- **Table A–5:** Saturation properties of water under pressure.

A partial list of Table A–4.

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

Specific temperature

Corresponding saturation pressure

Specific volume of saturated liquid

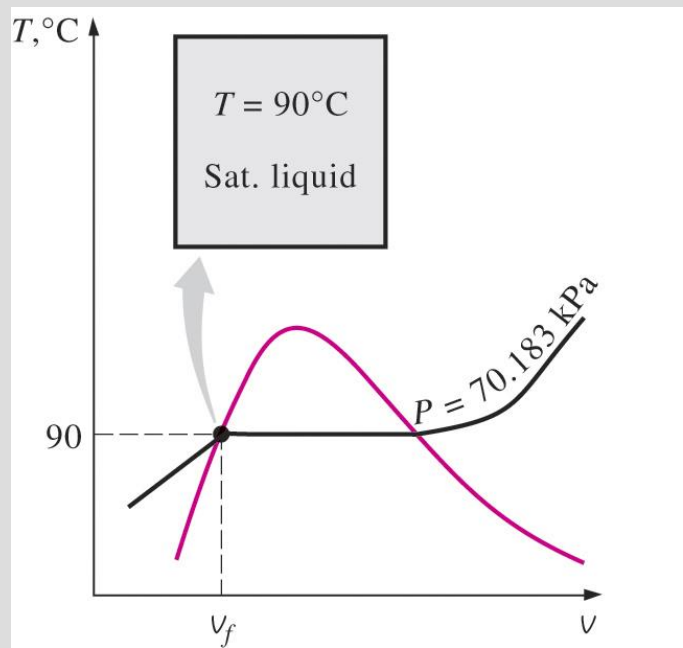
Specific volume of saturated vapor

ν_f = specific volume of saturated liquid

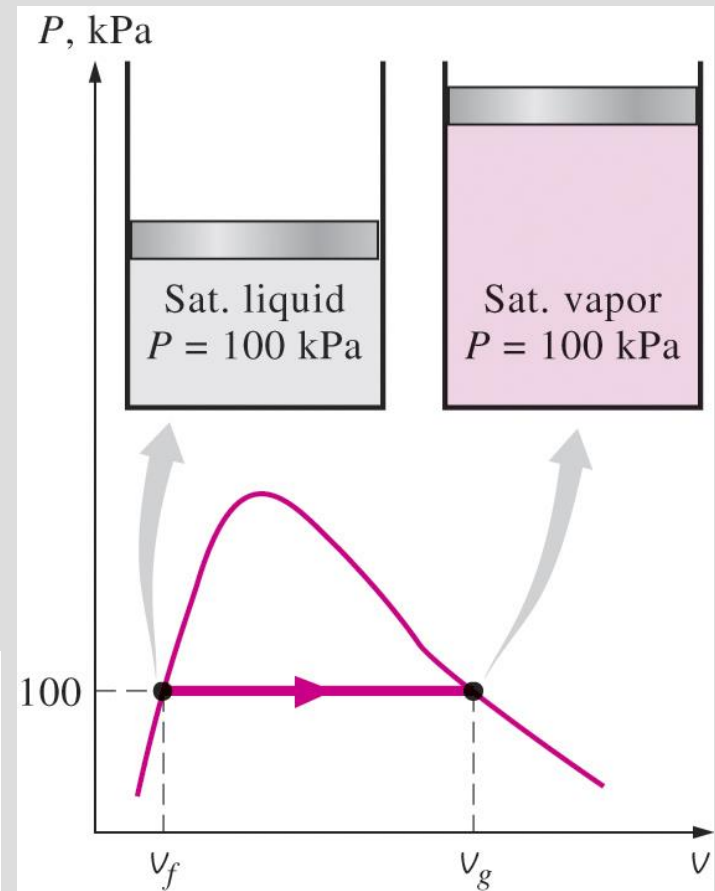
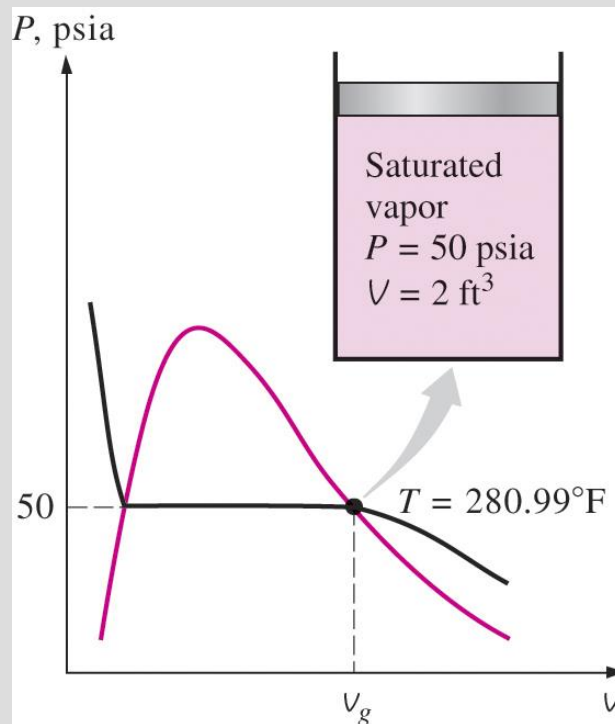
ν_g = specific volume of saturated vapor

ν_{fg} = difference between ν_g and ν_f (that is, $\nu_{fg} = \nu_g - \nu_f$)

Enthalpy of vaporization, h_{fg} (Latent heat of vaporization): The amount of energy needed to vaporize a unit mass of saturated liquid at a given temperature or pressure.



Examples:
Saturated liquid
and saturated
vapor states of
water on T - v and
 P - v diagrams.



Saturated Liquid–Vapor Mixture

Quality, x : The ratio of the mass of vapor to the total mass of the mixture.

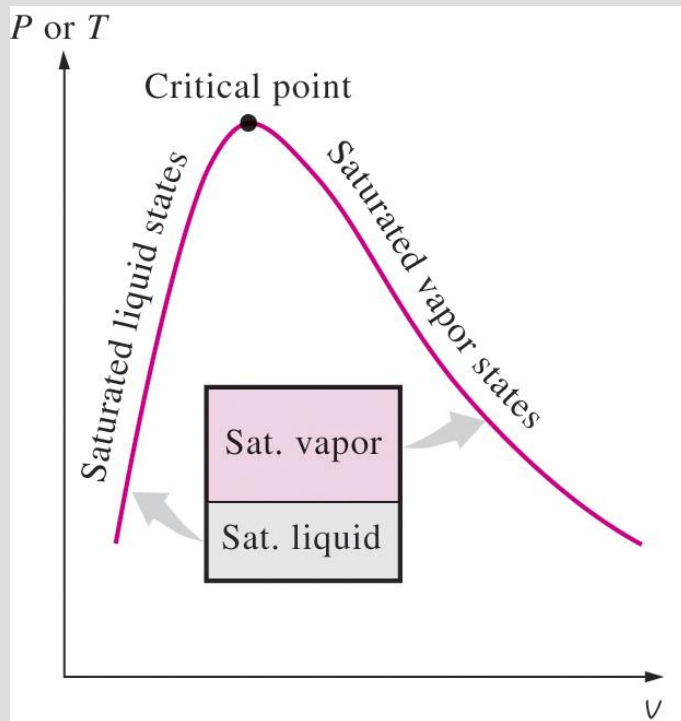
Quality is between 0 and 1 \rightarrow 0: sat. liquid, 1: sat. vapor.

The properties of the saturated liquid are the same whether it exists alone or in a mixture with saturated vapor.

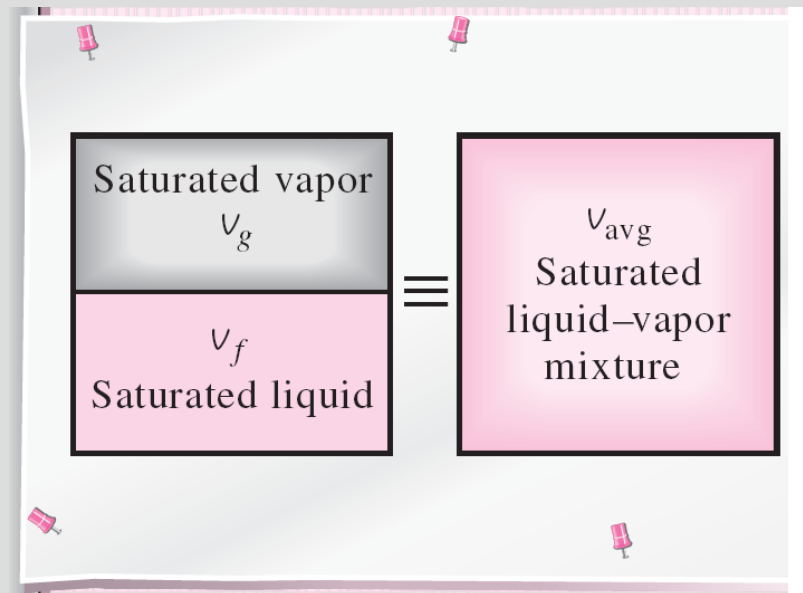
$$x = \frac{m_{\text{vapor}}}{m_{\text{total}}}$$

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

Temperature and pressure are dependent properties for a mixture.



The relative amounts of liquid and vapor phases in a saturated mixture are specified by the **quality x** .



A two-phase system can be treated as a homogeneous mixture for convenience.

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

$$x = m_g/m_t$$

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

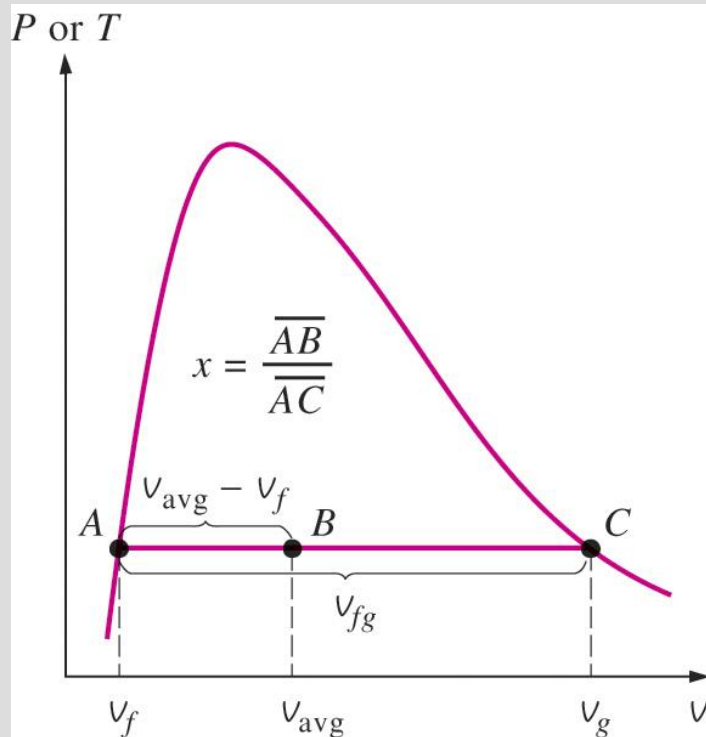
$$u_{\text{avg}} = u_f + x u_{fg} \quad (\text{kJ/kg})$$

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

$y \rightarrow v, u, \text{ or } h.$

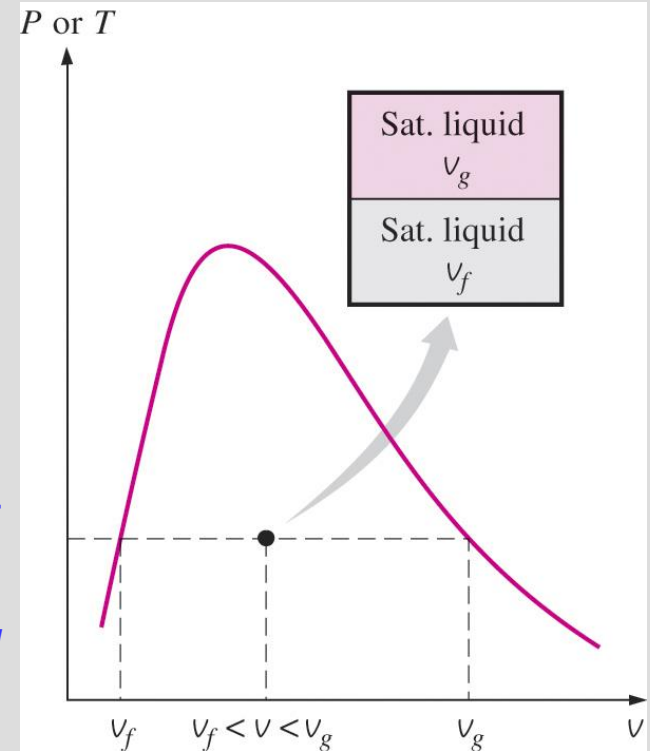
$$y_{\text{avg}} = y_f + x y_{fg}$$

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

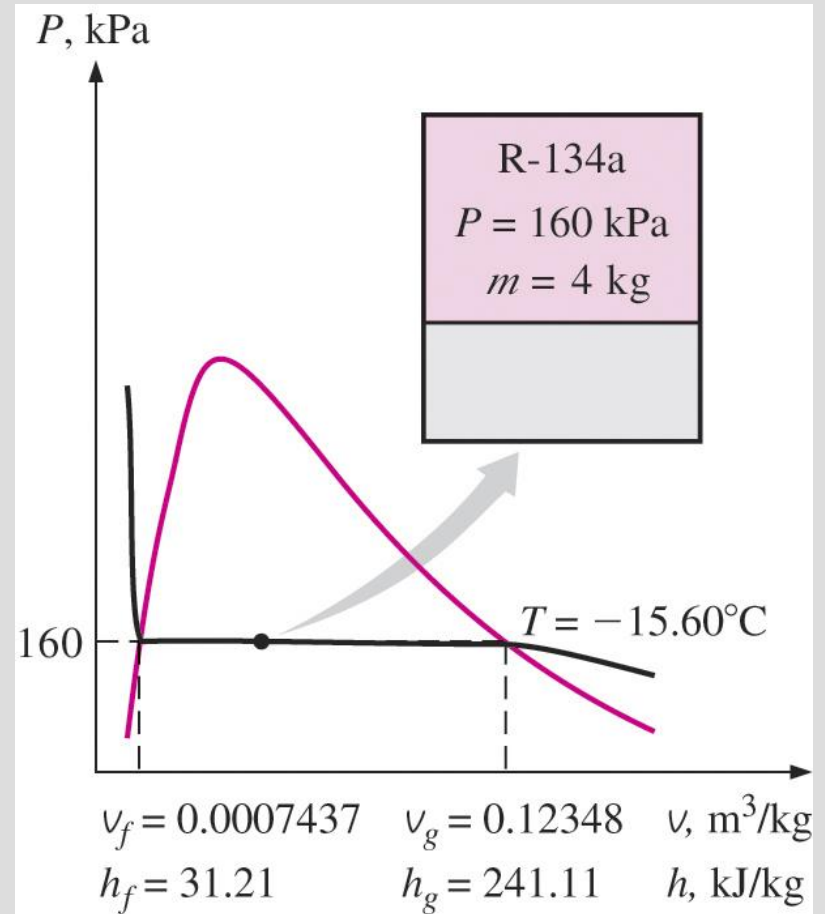
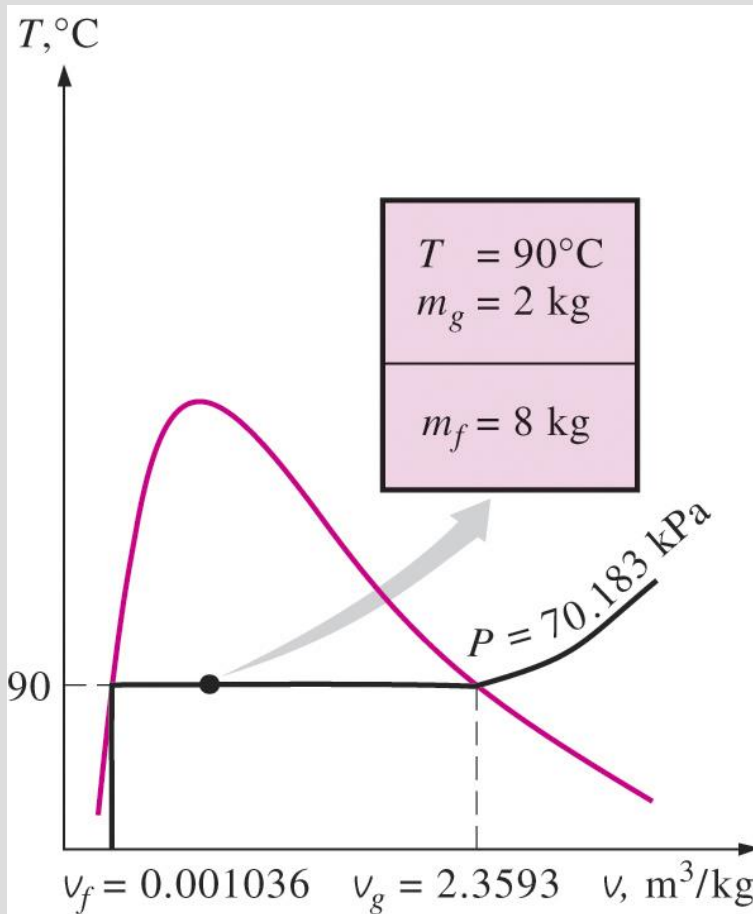


Quality is related to the horizontal distances on P - v and T - v diagrams.

The v value of a saturated liquid-vapor mixture lies between the v_f and v_g values at the specified T or P .



Examples: Saturated liquid-vapor mixture states on T - v and P - v diagrams.



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 this region, temperature and pressure are independent properties.

$T, ^\circ\text{C}$	ν m^3/kg	u kJ/kg	h kJ/kg
$P = 0.1 \text{ MPa } (99.61^\circ\text{C})$			
Sat.	1.6941	2505.6	2675.0
100	1.6959	2506.2	2675.8
150	1.9367	2582.9	2776.6
\vdots	\vdots	\vdots	\vdots
1300	7.2605	4687.2	5413.3
$P = 0.5 \text{ MPa } (151.83^\circ\text{C})$			
Sat.	0.37483	2560.7	2748.1
200	0.42503	2643.3	2855.8
250	0.47443	2723.8	2961.0

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)

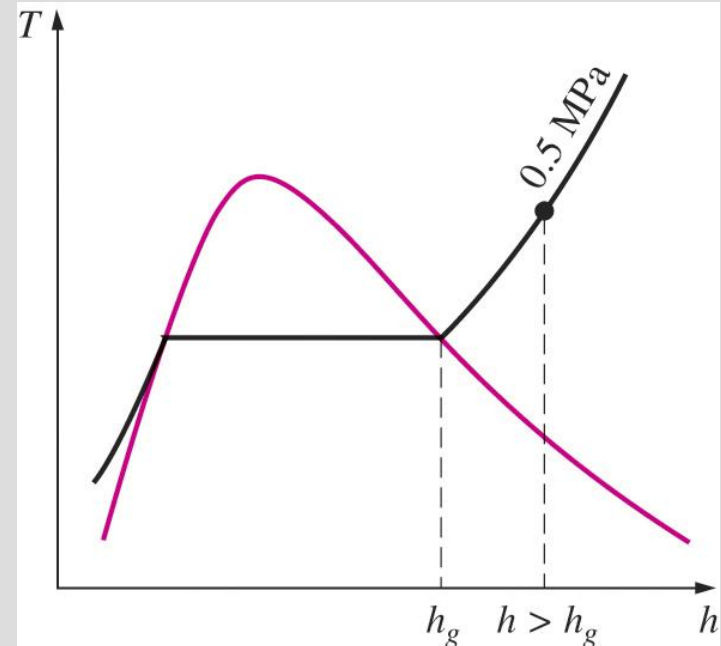
Higher specific volumes ($\nu > \nu_g$ at a given P or T)

Higher internal energies ($u > u_g$ at a given P or T)

Higher enthalpies ($h > h_g$ at a given P or T)

At a specified P , superheated vapor exists at a higher h than the saturated vapor.

A partial listing of Table A-6.



The compressed liquid properties depend on temperature much more strongly than they do on pressure.

$$y \cong y_f @ T \quad y \rightarrow v, u, \text{ or } h$$

A more accurate relation for h

$$h \cong h_f @ T + v_{f@T} (P - P_{\text{sat}} @ T)$$

Given: P and T

$$v \cong v_f @ T$$

$$u \cong u_f @ T$$

$$h \cong h_f @ T$$

A compressed liquid may be approximated as a saturated liquid at the given temperature.

At a given P and T , a pure substance will exist as a compressed liquid if

$$T < T_{\text{sat}} @ P$$

Compressed Liquid

Compressed liquid is characterized by

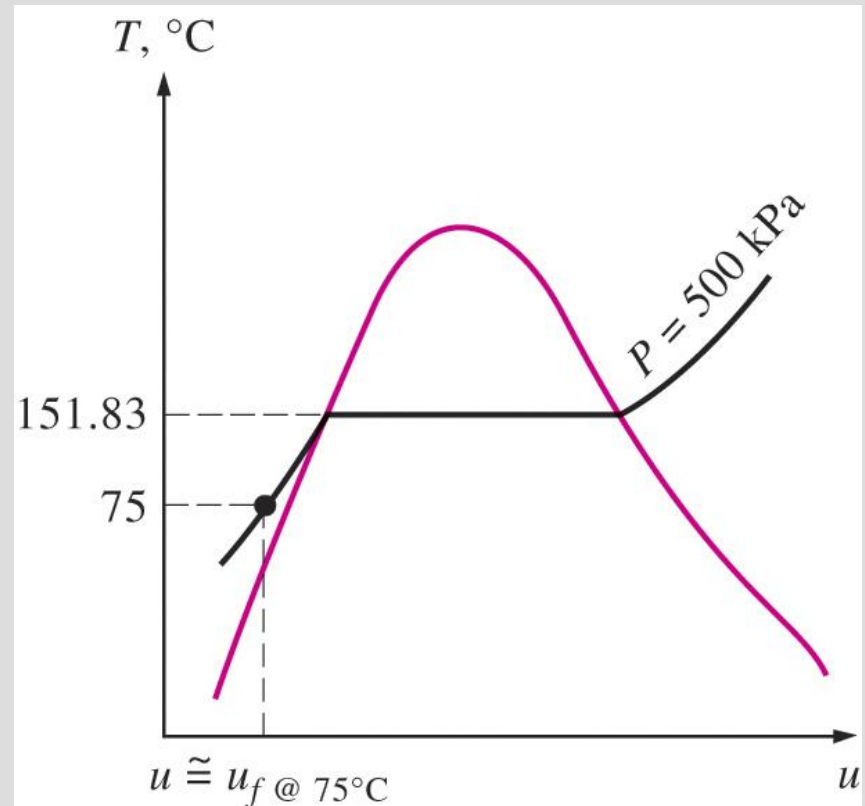
Higher pressures ($P > P_{\text{sat}}$ at a given T)

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)



THE IDEAL-GAS EQUATION OF STATE

- **Equation of state**: Any equation that relates the pressure, temperature, and specific volume of a substance.
- The simplest and best-known equation of state for substances in the gas phase is the ideal-gas equation of state.

$$Pv = RT \longrightarrow \frac{P_1 v_1}{T_1} = \frac{P_2 v_2}{T_2}$$

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

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

THE GAS CONSTANT

$$Pv = RT$$

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

R : gas constant

M : molar mass (kg/kmol)

R_u : universal gas constant

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

OTHER EXPRESSIONS OF THE IDEAL-GAS EQUATION OF STATE

$$V = mV \longrightarrow PV = mRT$$

Mass = Molar mass \times Mole number

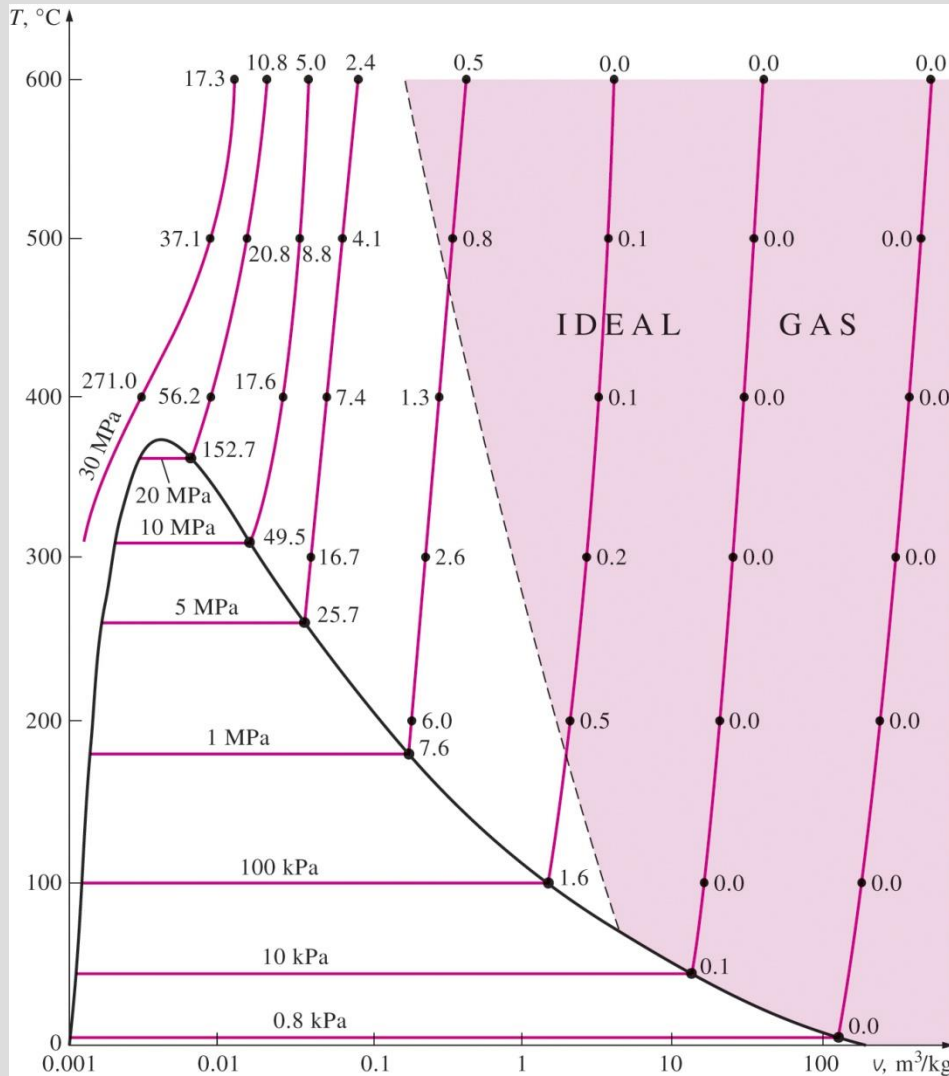
$$m = MN \quad (\text{kg})$$

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

IS THE IDEAL-GAS EQUATION OF STATE ALWAYS VALID?

- Real gases behave as an ideal gas at low densities (i.e., low pressure, high temperature).
- The ideal-gas relation often is **NOT** applicable to real gases
- Care should be taken when using it.

Is Water Vapor an Ideal Gas?



- 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).
- At higher pressures, however, the ideal gas assumption yields unacceptable errors, particularly in the vicinity of the critical point and the saturated vapor line.
- In air-conditioning applications, the water vapor in the air can be treated as an ideal gas. Why?
- In steam power plant applications, however, the pressures involved are usually very high; therefore, ideal-gas relations should not be used.

Percentage of error ($[(v_{\text{table}} - v_{\text{ideal}})/v_{\text{table}}] \times 100$) involved in assuming steam to be an ideal gas, and the region where steam can be treated as an ideal gas with less than 1 percent error.

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.

$$PV = ZRT$$

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

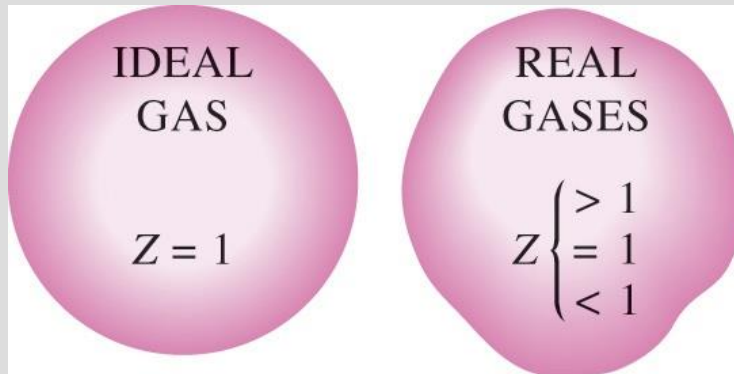
$$Z = \frac{V_{\text{actual}}}{V_{\text{ideal}}}$$

The farther away Z is from unity, the more the gas deviates from ideal-gas behavior.

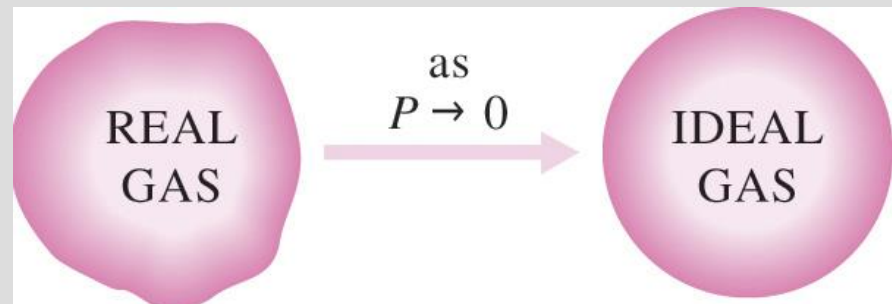
Gases behave as an ideal gas at low densities (i.e., low pressure, high temperature).

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.



The compressibility factor is unity for ideal gases.



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

$$P_R = \frac{P}{P_{cr}}$$

Reduced
pressure

$$T_R = \frac{T}{T_{cr}}$$

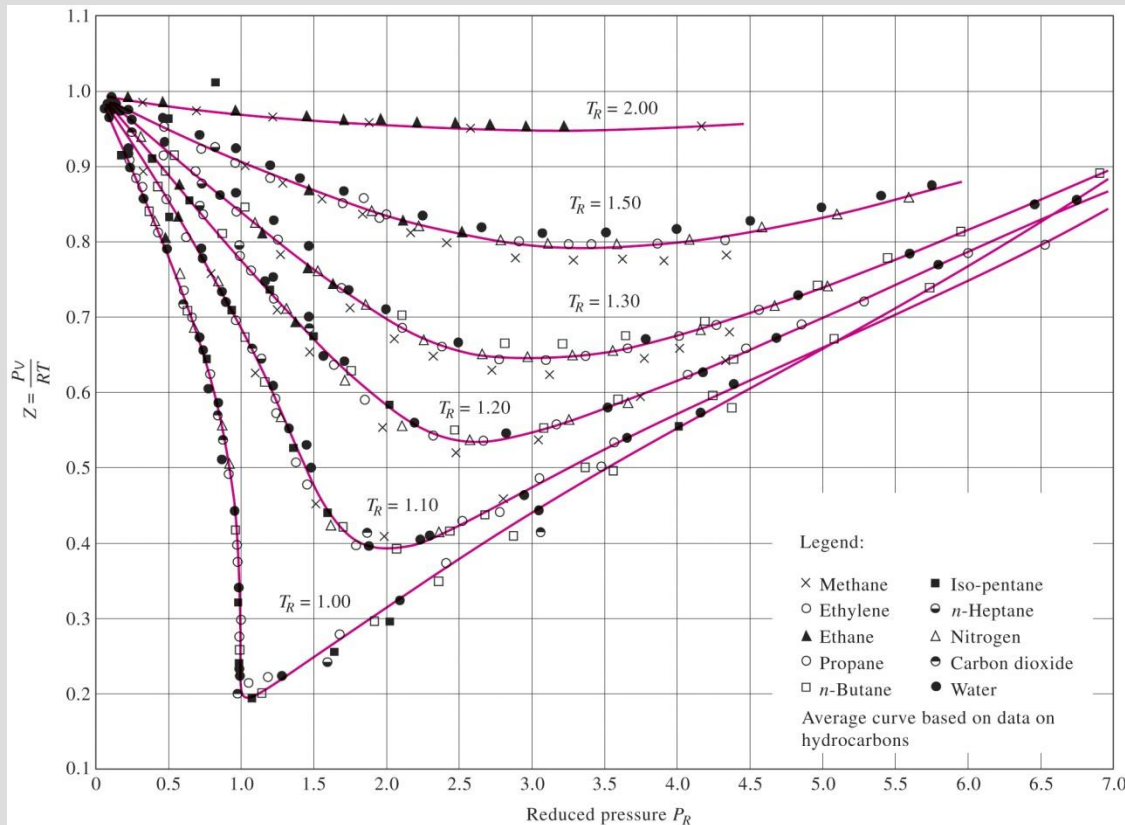
Reduced
temperature

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

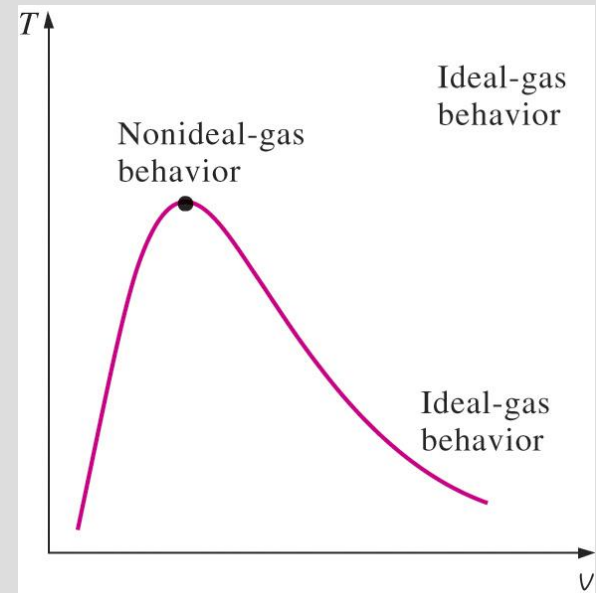
Pseudo-reduced
specific volume

$$\left. \begin{aligned} P_R &= \frac{P}{P_{cr}} \\ v_R &= \frac{v}{RT_{cr}/P_{cr}} \end{aligned} \right\} Z = \dots \quad (\text{Fig. A-15})$$

Z can also be determined from
a knowledge of P_R and v_R .



Comparison of Z factors for various gases.



Gases deviate from the
ideal-gas behavior the
most in the neighborhood
of the critical point.

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 Equation of State

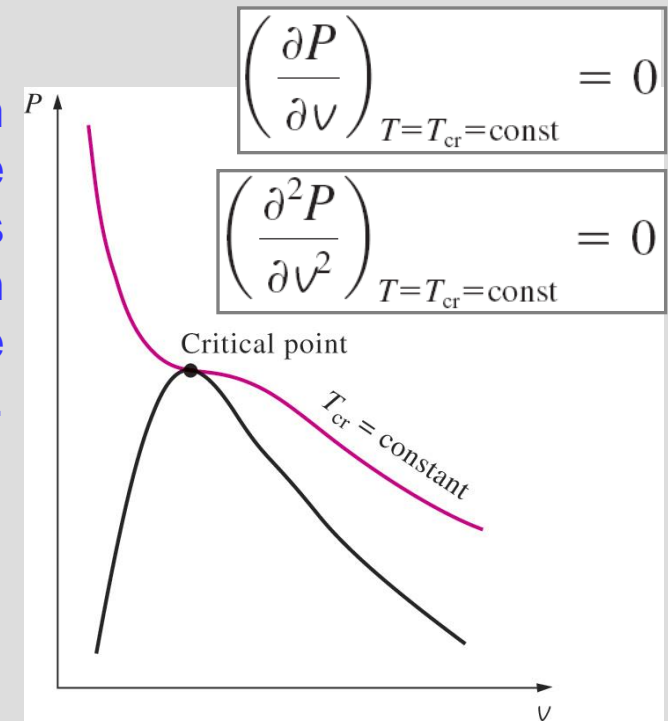
$$\left(P + \frac{a}{v^2}\right)(v - b) = RT$$

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

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.



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



Beattie-Bridgeman Equation of State

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

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

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

Benedict-Webb-Rubin Equation of State

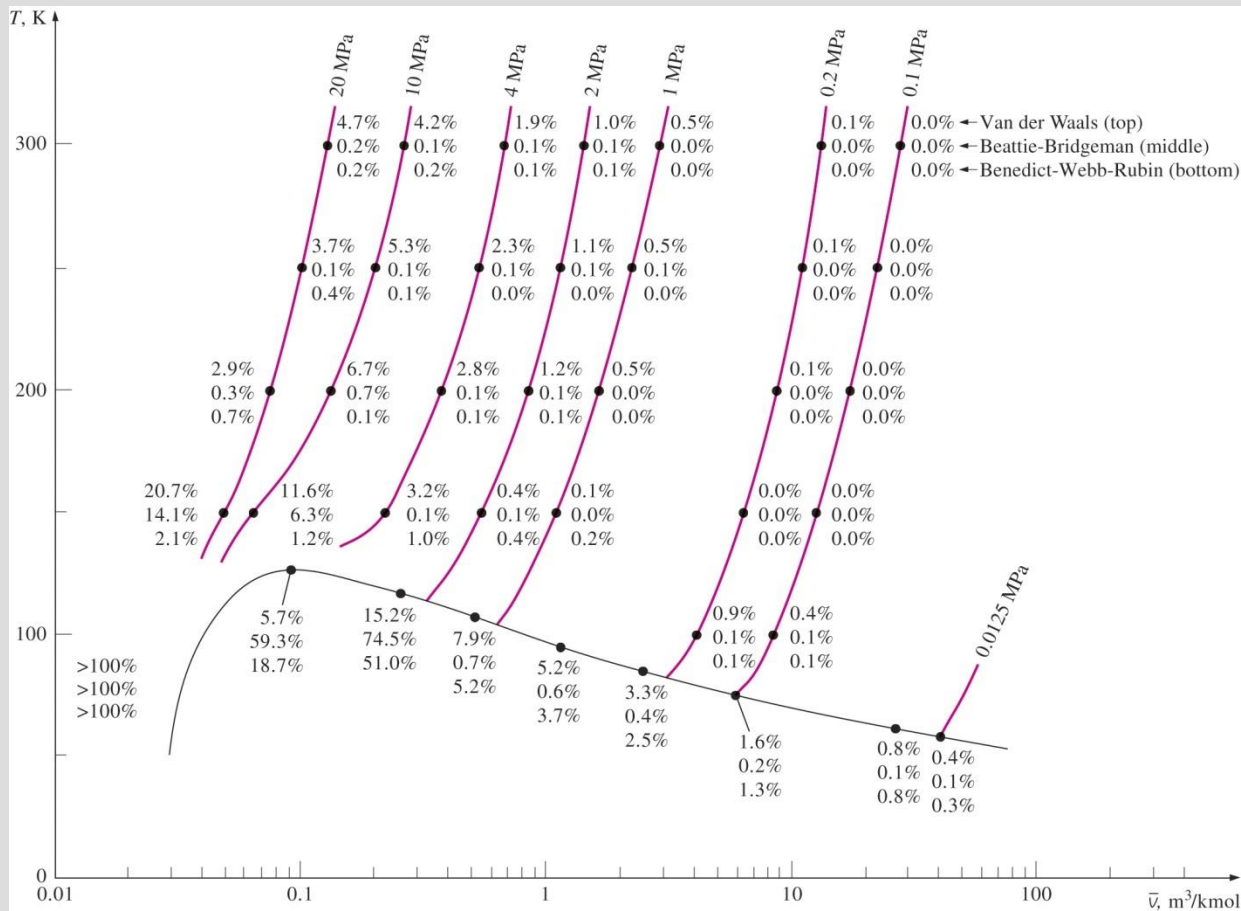
$$P = \frac{R_u T}{\bar{V}} + \left(B_0 R_u T - A_0 - \frac{C_0}{T^2} \right) \frac{1}{\bar{V}^2} + \frac{b R_u T - a}{\bar{V}^3} + \frac{a\alpha}{\bar{V}^6} + \frac{c}{\bar{V}^3 T^2} \left(1 + \frac{\gamma}{\bar{V}^2} \right) e^{-\gamma/\bar{V}^2}$$

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

Virial Equation of State

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

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



van der Waals: 2 constants.
Accurate over a limited range.

Beattie-Bridgeman: 5 constants.
Accurate for $\rho \leq 0.8\rho_{\text{cr}}$.

Benedict-Webb-Rubin: 8 constants.
Accurate for $\rho \leq 2.5\rho_{\text{cr}}$.

Strobridge: 16 constants.
More suitable for
computer calculations.

Virial: may vary.
Accuracy depends on the
number of terms used.

Complex equations of
state represent the P - v - T
behavior of gases
more accurately over a
wider range.