Chapter 3

PROPERTIES OF PURE SUBSTANCES

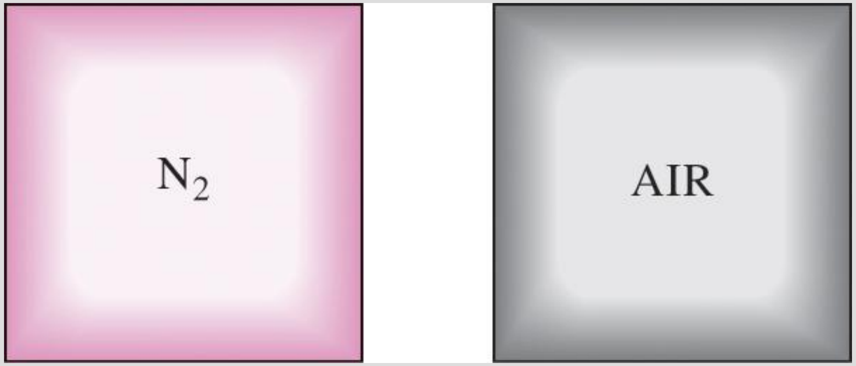
Thermodynamics: An Engineering Approach, 6th Edition
Yunus A. Cengel, Michael A. Boles
McGraw-Hill, 2008

Objectives

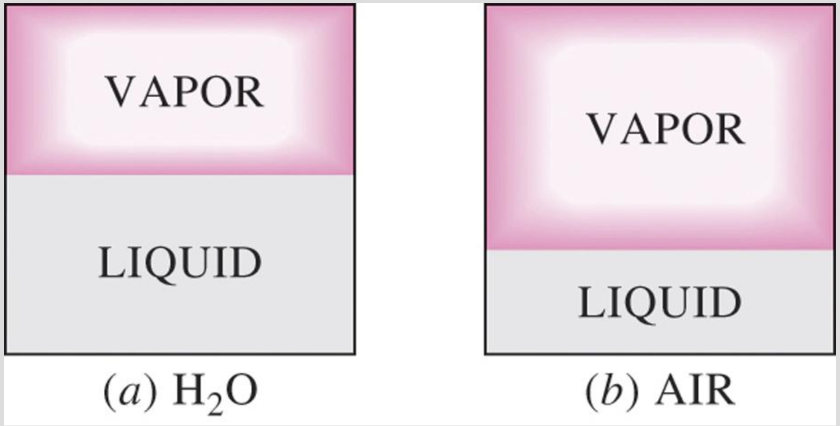
- Introduce the concept of a pure substance.
- Discuss the physics of phase-change processes.
- Illustrate the *P*-*v*, *T*-*v*, and *P*-*T* property diagrams and *P*-*v*-*T* surfaces of pure substances.
- Demonstrate the procedures for determining thermodynamic properties of pure substances from tables 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.
- Present some of the best-known equations of state.

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 (as along as it in the same phase).



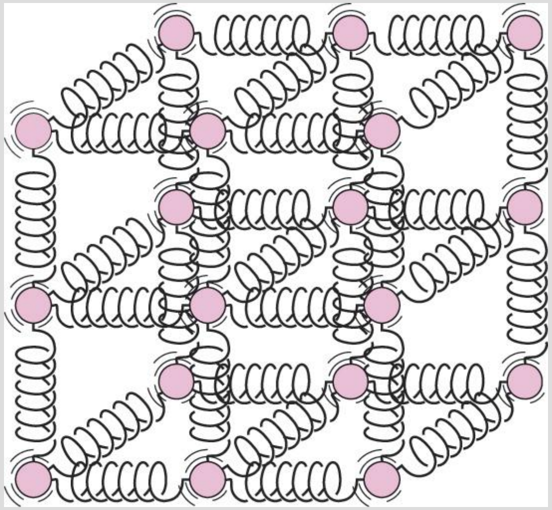
Nitrogen and gaseous air are pure substances.



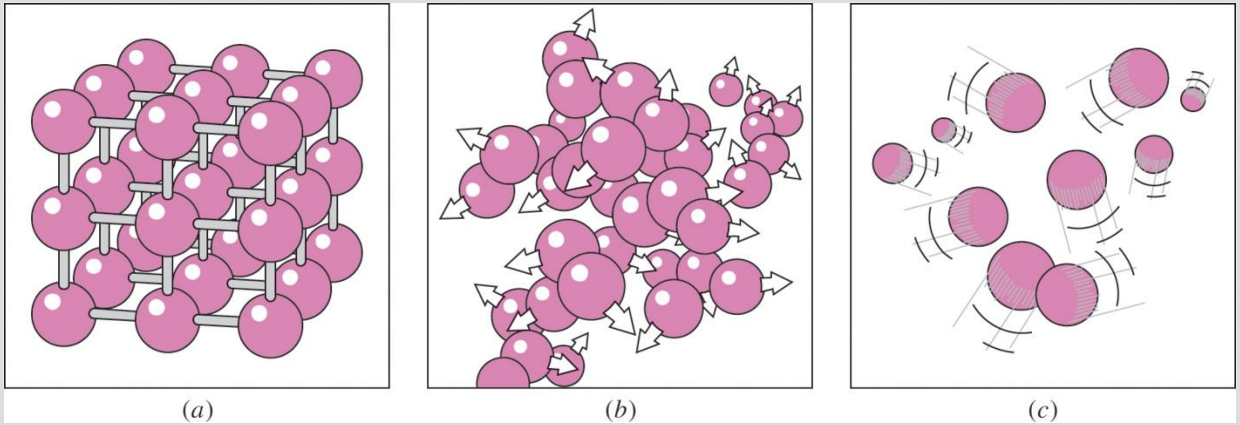
(*a*) H_2O (*b*) AIR

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

PHASES OF A PURE SUBSTANCE



The molecules in a solid are kept at their positions by the large springlike inter-molecular forces.



(*a*) (*b*) (*c*)

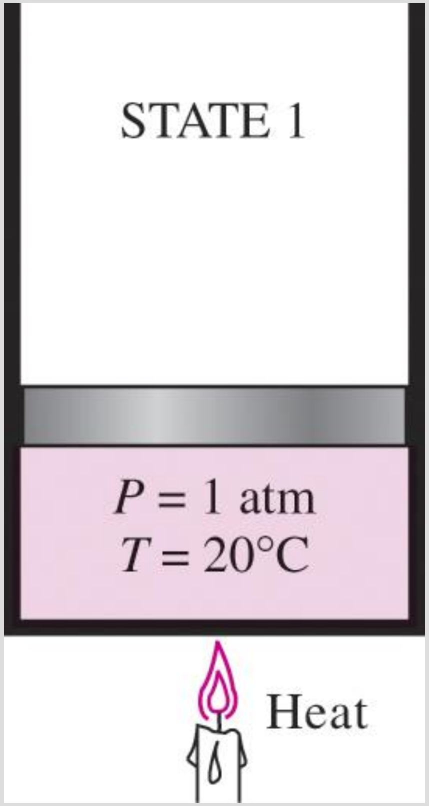
The arrangement of atoms in different phases: (*a*) molecules are at relatively fixed positions in a solid, (*b*) groups of molecules move about each other in the liquid phase, and (*c*) molecules move about at random in the gas phase.

PURE SUBSTANCE PROPERTIES DIAGRAM

- To study the phase change process for a pure substance, we take water as an example.
- Water, in liquid phase is filled in a piston cylinder without any weight on the piston.

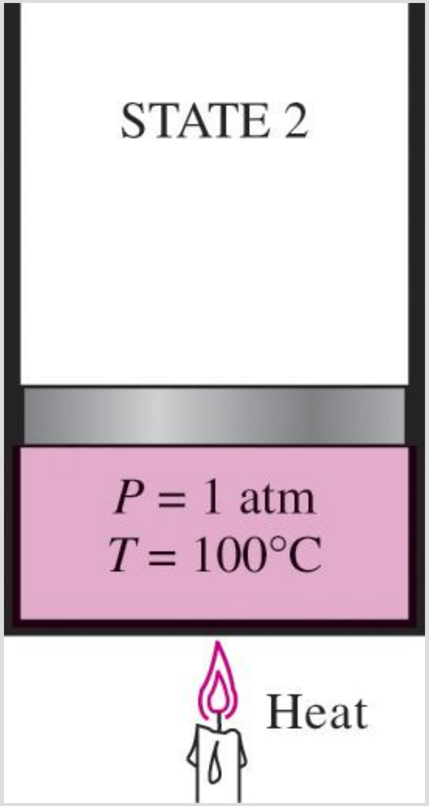
PHASE-CHANGE PROCESSES OF PURE SUBSTANCES

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

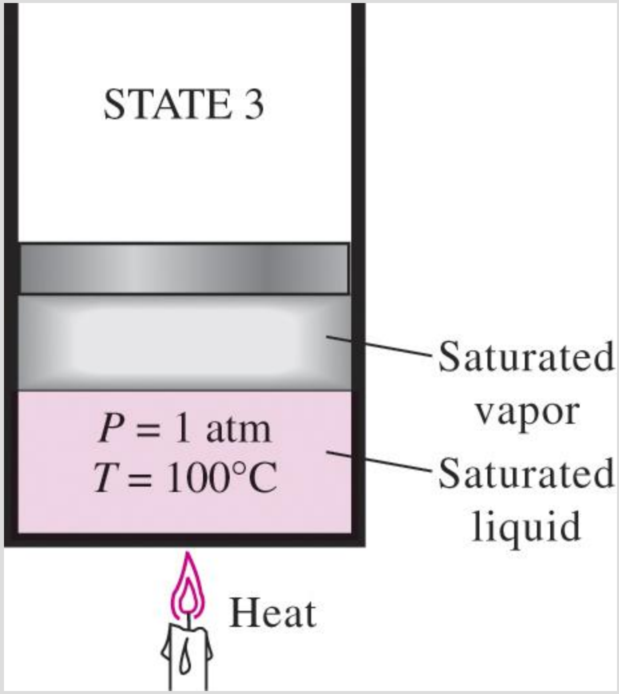


At 1 atm(≈1bar) and 20°C, water exists in the liquid phase (***compressed liquid***).

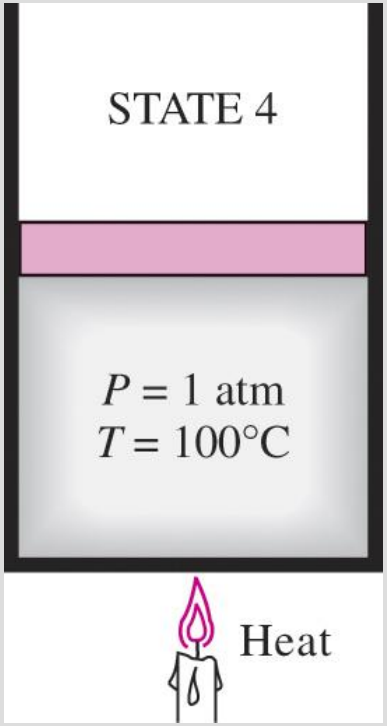
At 1 atm pressure and 100°C, water exists as a liquid that is ready to vaporize (***saturated liquid***).



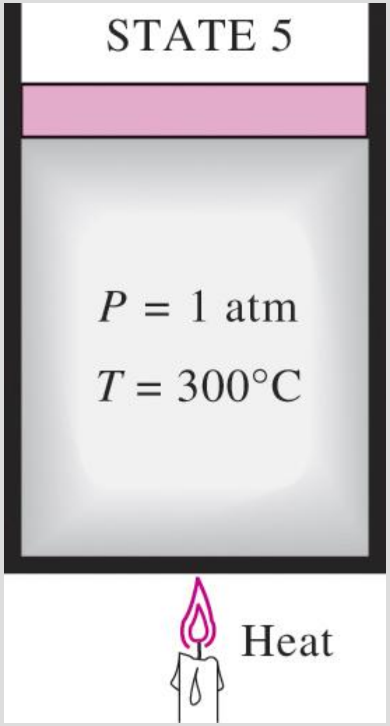
- **Saturated vapor**: A vapor that is *about to condense.*
- **Saturated liquid–vapor mixture**: The state at which the *liquid and vapor phases coexist* in equilibrium.
- **Superheated vapor**: A vapor that is *not about to condense* (i.e., not a saturated vapor).



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

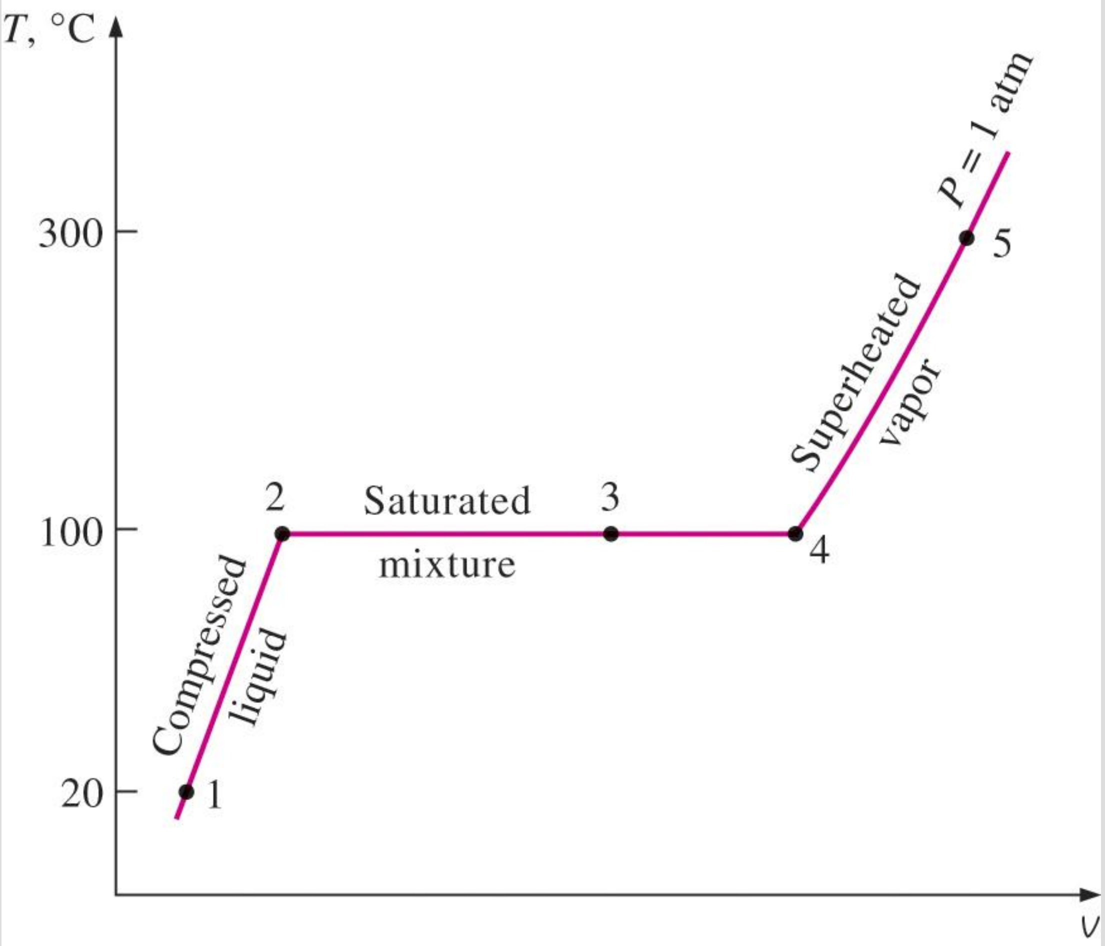


At 1 atm pressure, the temperature remains constant at 100°C until the last drop of liquid is vaporized (***saturated vapor***).



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

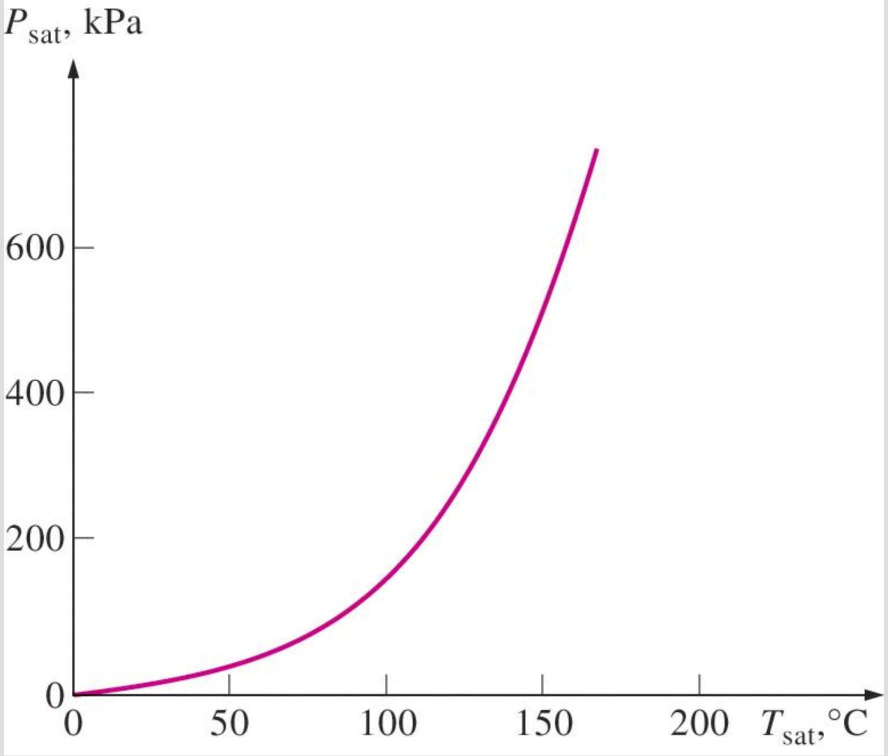
If the entire process between state 1 and 5 described in the figure is reversed by cooling the water while maintaining the pressure at the same value, the water will go back to state 1, retracing the same path, and in so doing, the amount of heat released will exactly match the amount of heat added during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



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

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).

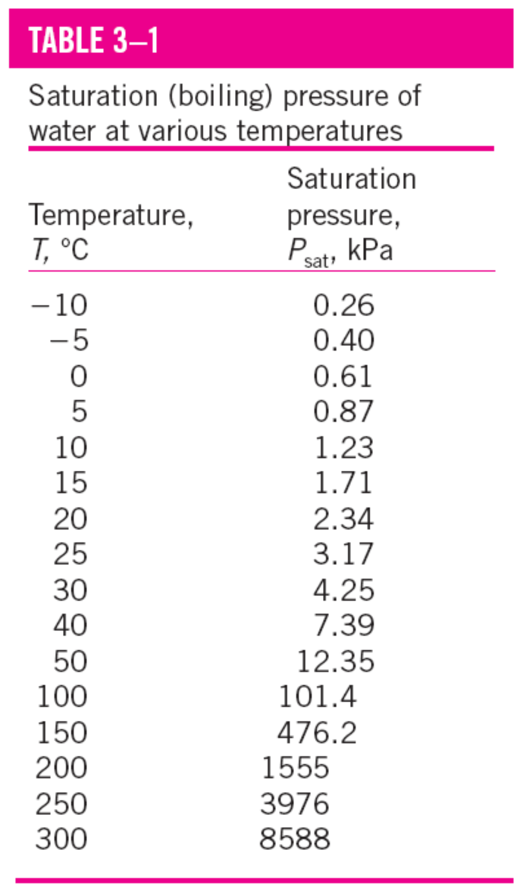


TABLE 3–1

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.

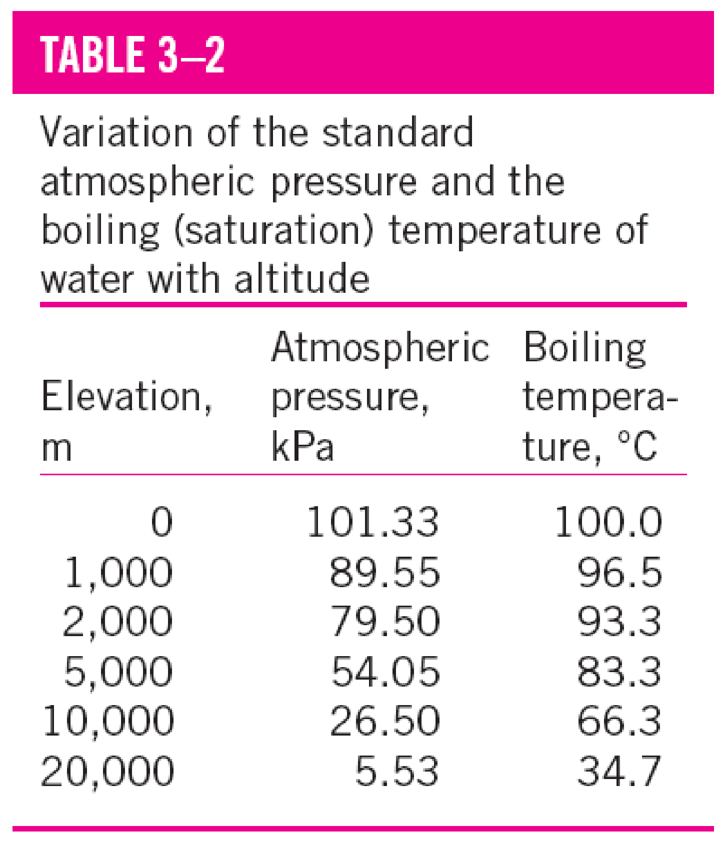


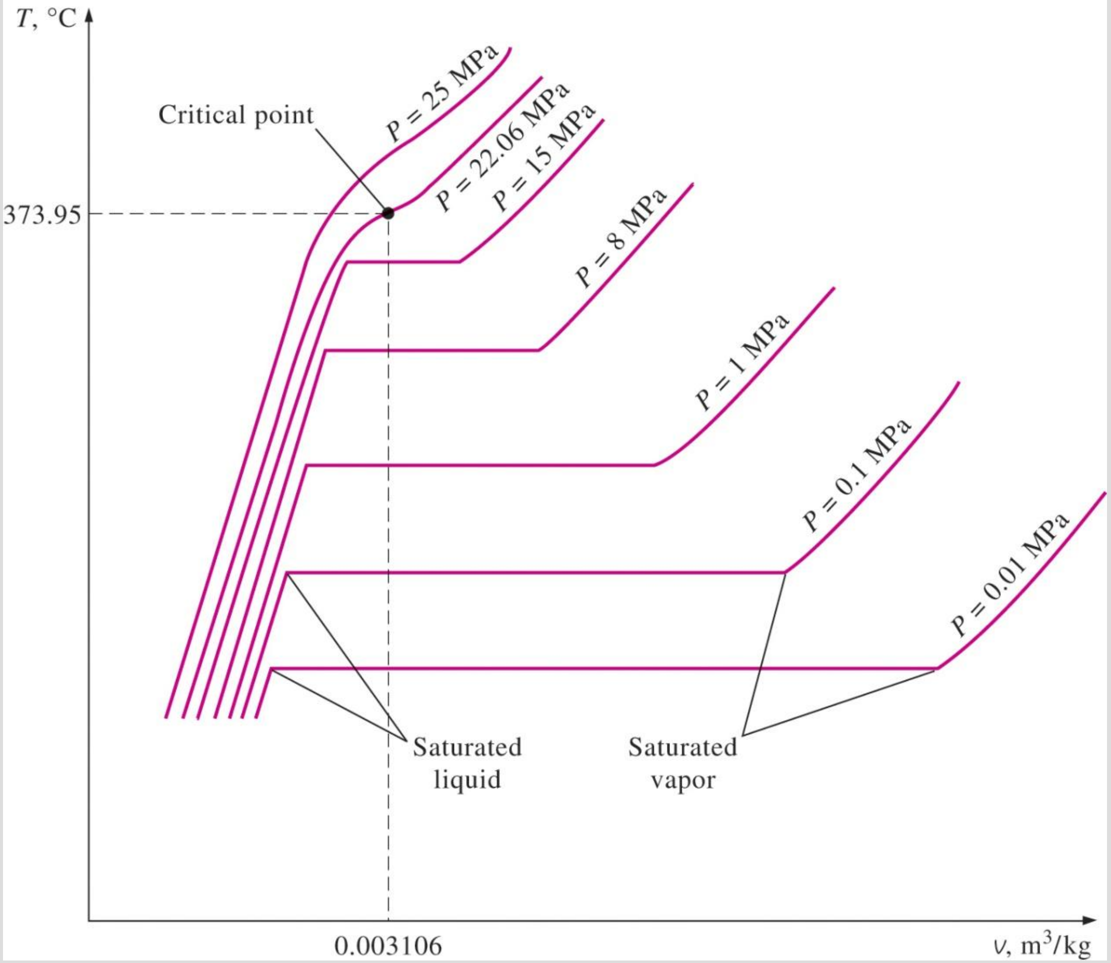
TABLE 3–2

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

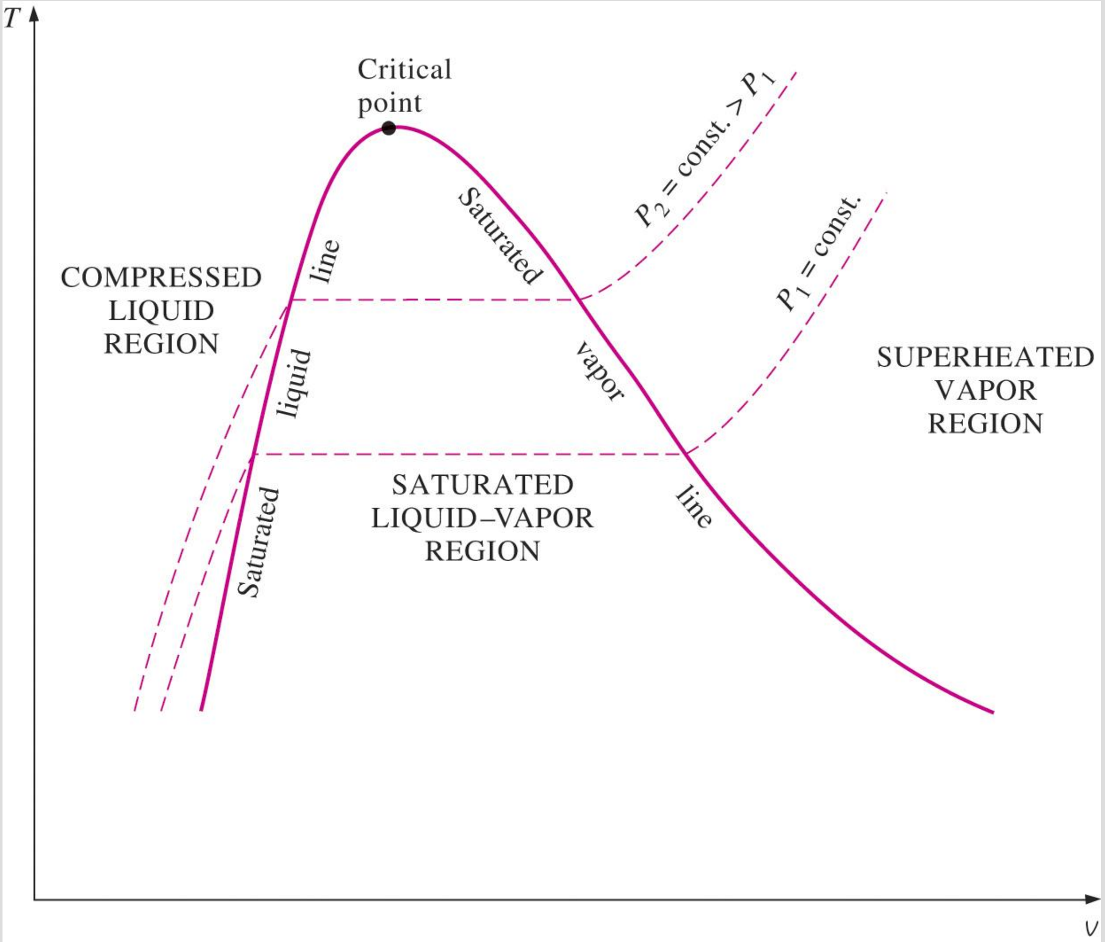
PROPERTY DIAGRAMS FOR PHASE-CHANGE PROCESSES

- 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.

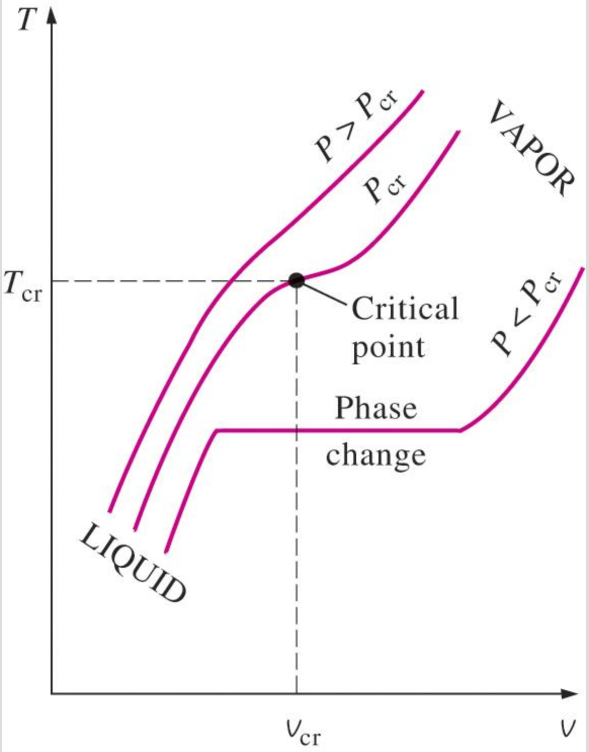


T-*v* diagram of constant-pressure phase-change processes of a pure substance at various pressures (numerical values are for water).

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

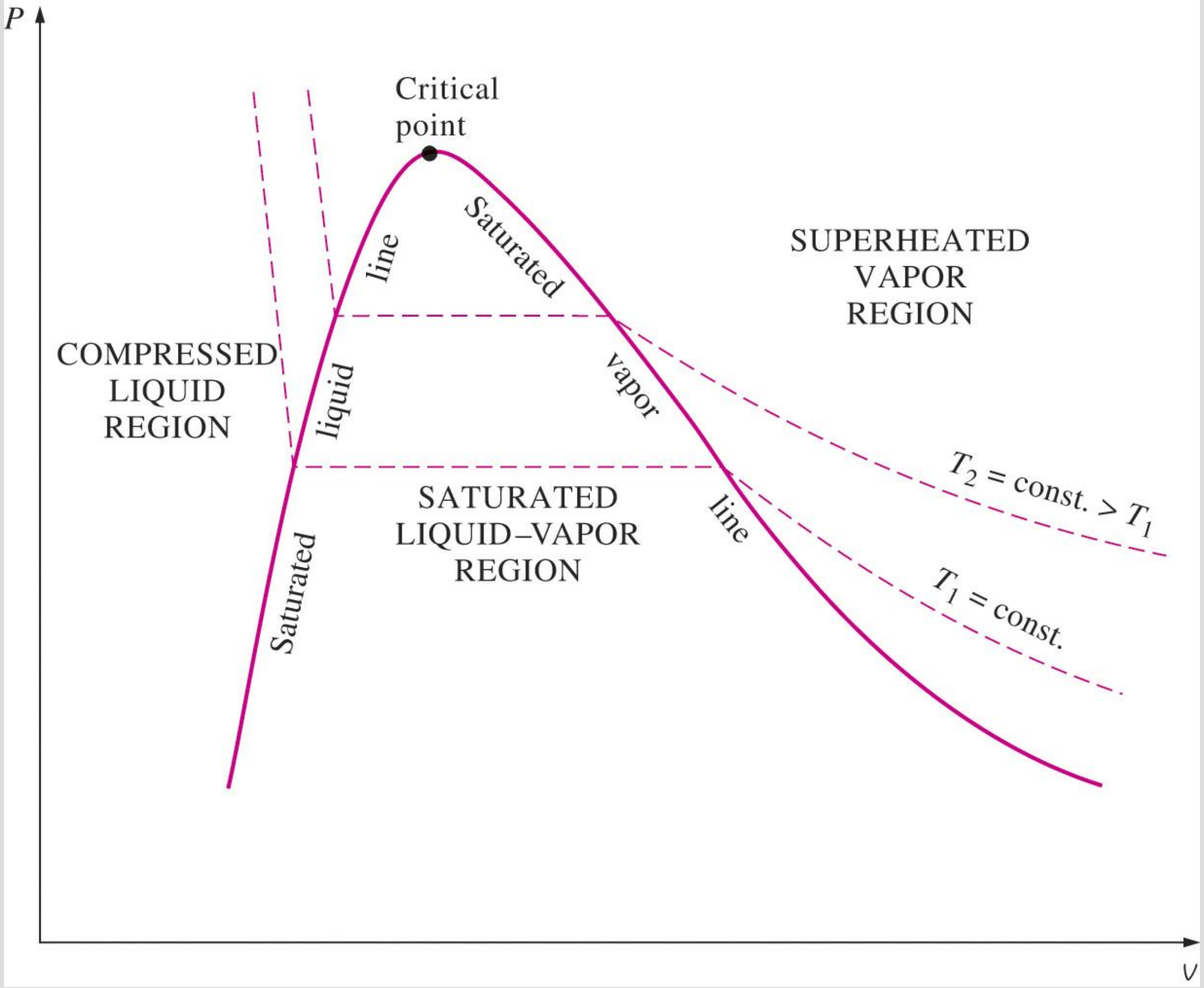


T-*v* diagram of a pure substance.

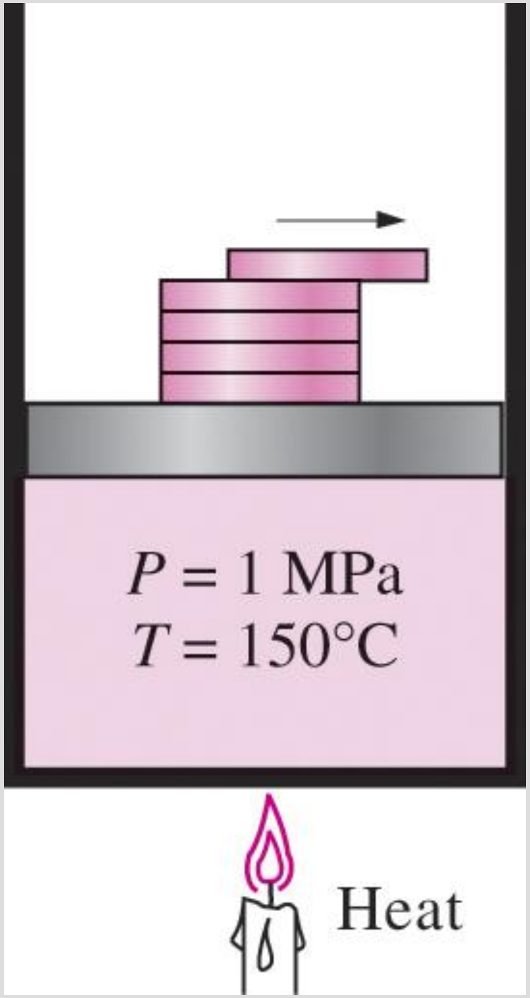


At supercritical pressures ($P > P_{cr}$), there is no distinct phase-change (boiling) process.

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



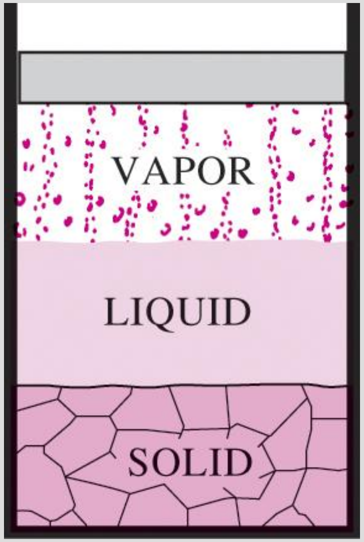
P-*v* diagram of a pure substance.



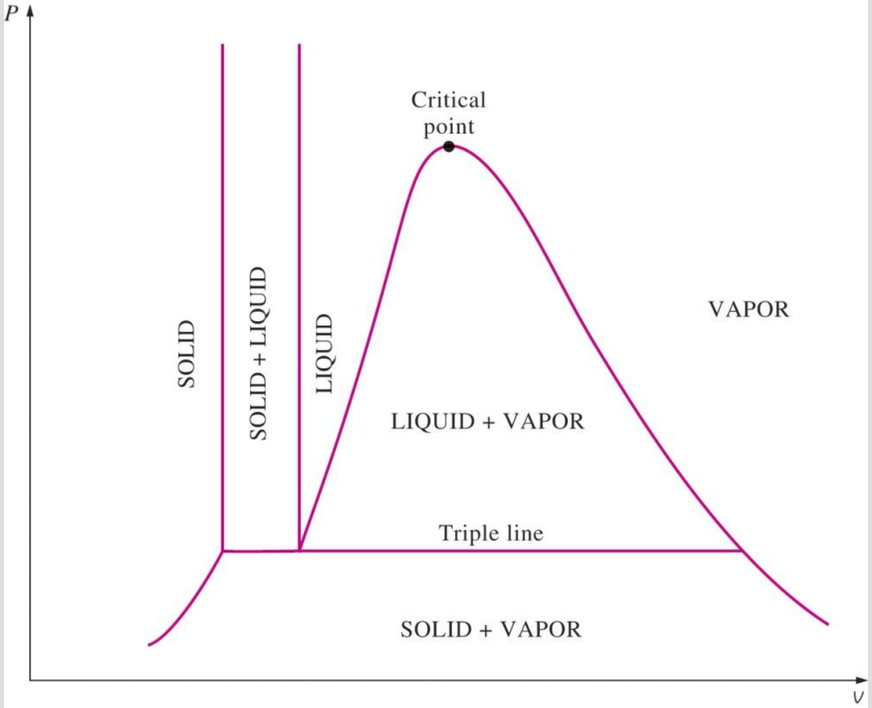
The pressure in a piston–cylinder device can be reduced by reducing the weight of the piston.

Extending the Diagrams to Include the Solid Phase

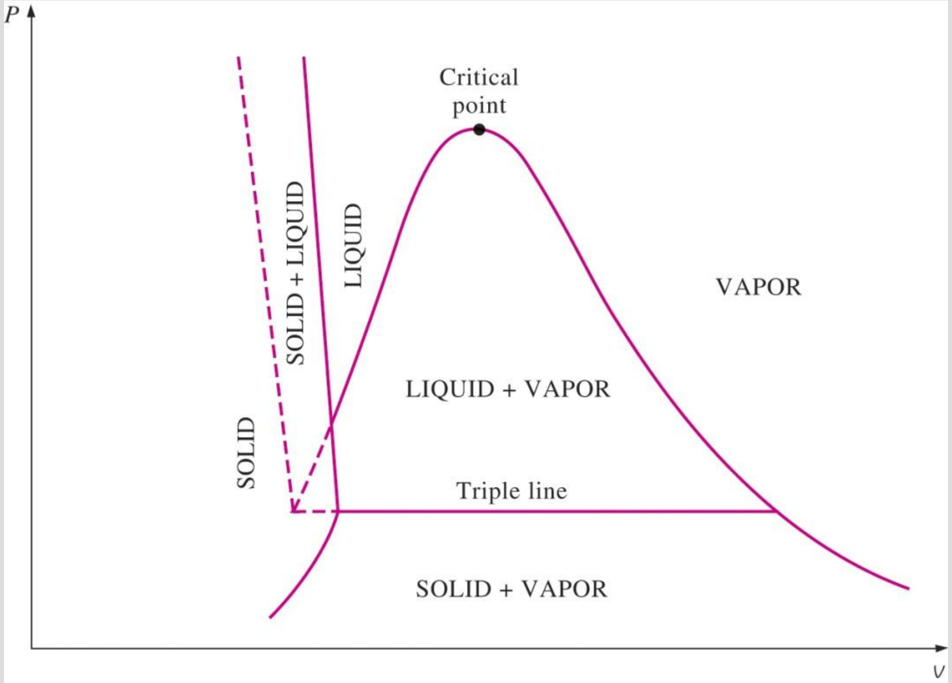
For water,
$T_{tp} = 0.01°C$
$P_{tp} = 0.6117$ kPa



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



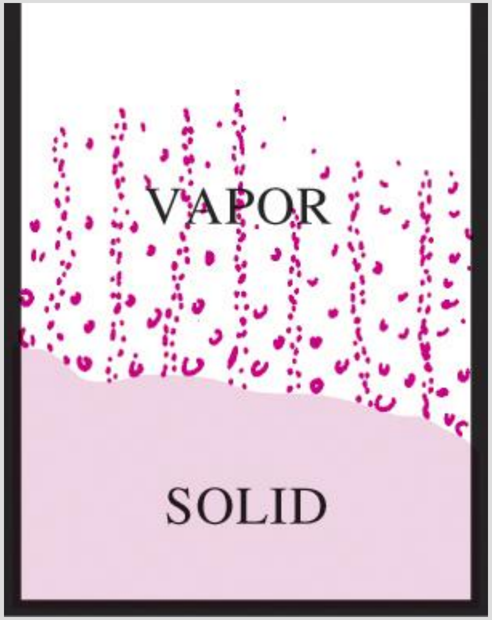
P-*v* diagram of a substance that contracts on freezing.



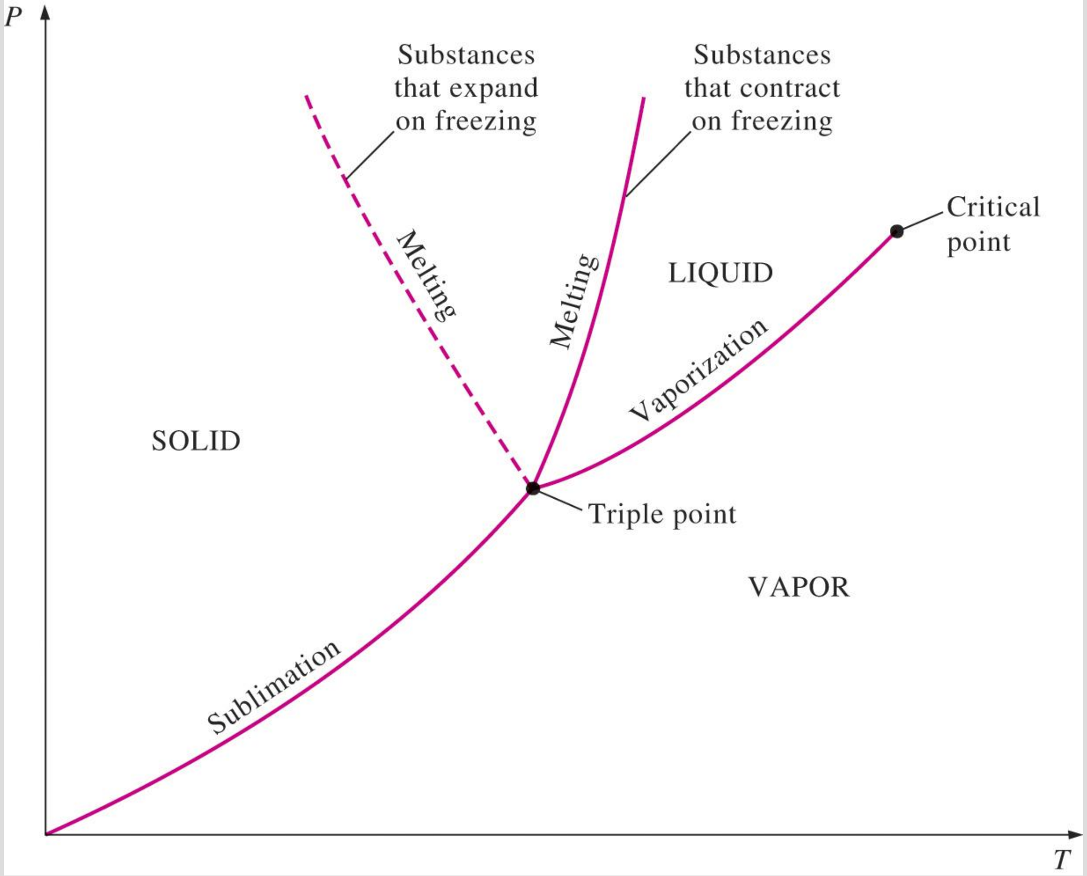
P-*v* diagram of a substance that expands on freezing (such as water).

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

Phase Diagram

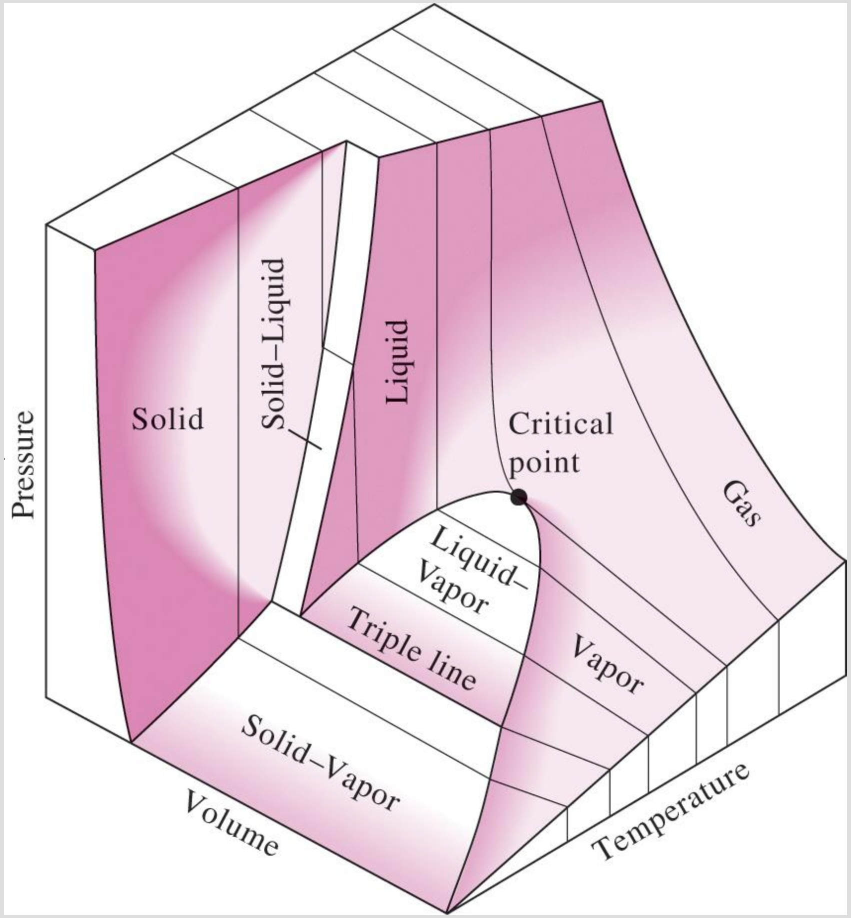


At low pressures (below the triple-point value), solids evaporate without melting first (*sublimation*).

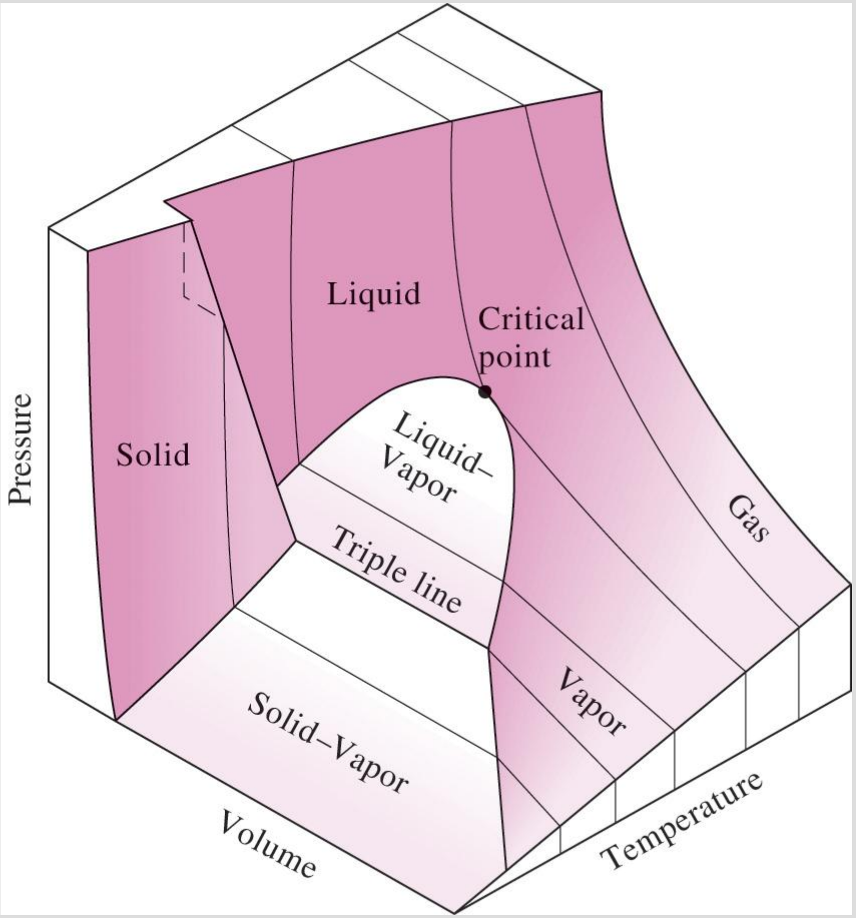


P-T diagram of pure substances.

The *P*-*v*-*T* surfaces present a great deal of information at once, but in a thermodynamic analysis it is more convenient to work with two-dimensional diagrams, such as the *P*-*v* and *T*-*v* diagrams.



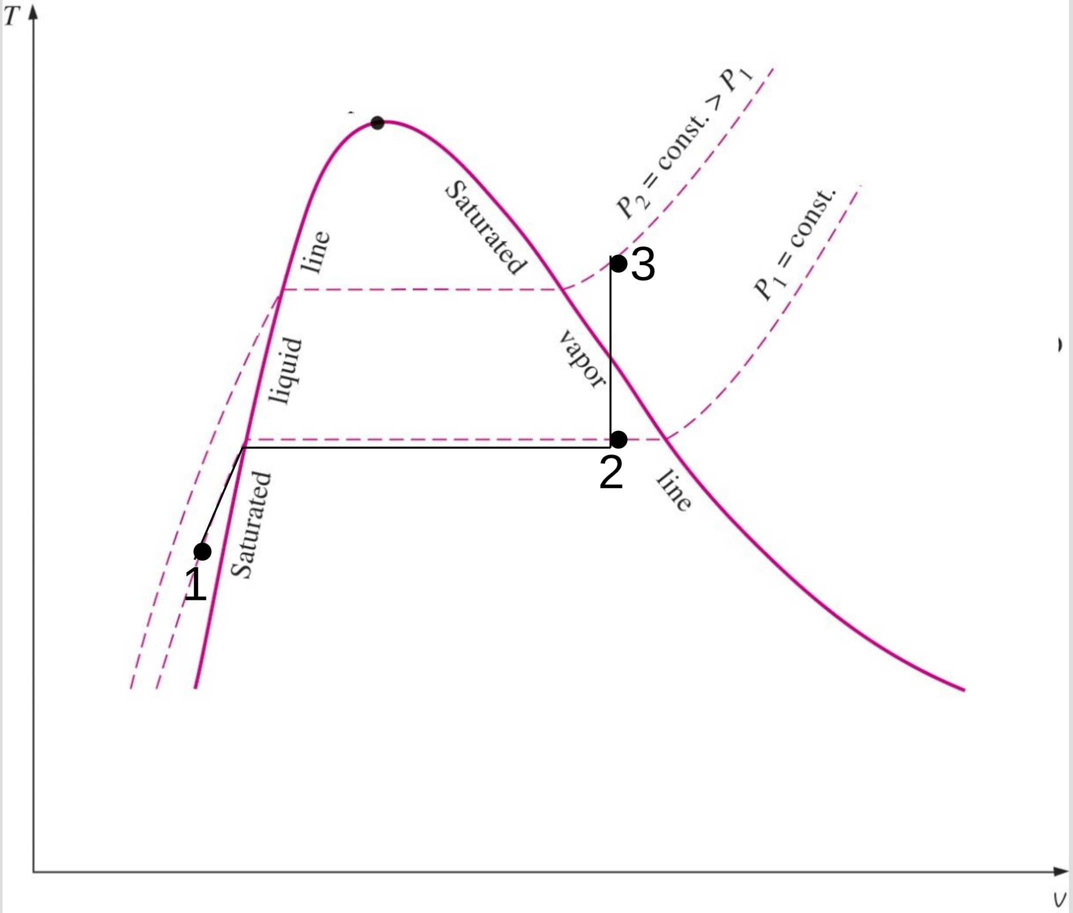
P-*v*-*T* surface of a substance that *contracts* on freezing.



P-*v*-*T* surface of a substance that *expands* on freezing (like water).

Why properties diagrams are important?

- From the diagram we can show any process that a system go through.
- For example: 1kg water is heated in constant pressure from state 1 to state 2. Then the system is heated in constant volume until state 3.
- The above process can be shown in Pv diagram or Tv diagram
- The value of a system characteristics are also can be defined at each state involved in the process



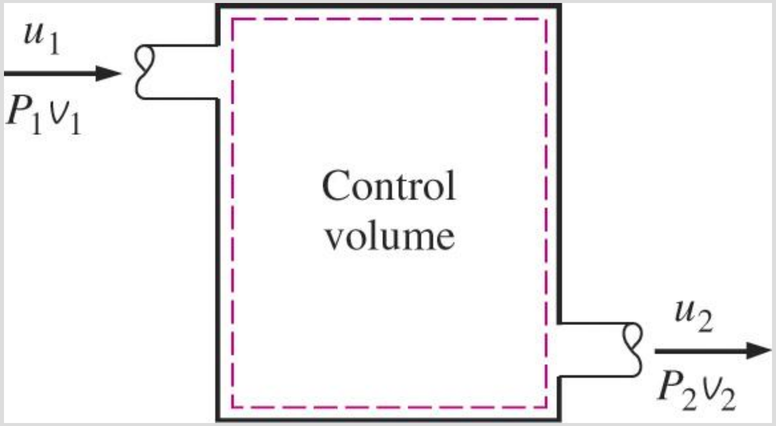
PROPERTY TABLES

- 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—A Combination Property

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

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



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

$$\text{kPa} \cdot \text{m}^3 \equiv \text{kJ}$$

$$\text{kPa} \cdot \text{m}^3/\text{kg} \equiv \text{kJ/kg}$$

$$\text{bar} \cdot \text{m}^3 \equiv 100\ \text{kJ}$$

$$\text{MPa} \cdot \text{m}^3 \equiv 1000\ \text{kJ}$$

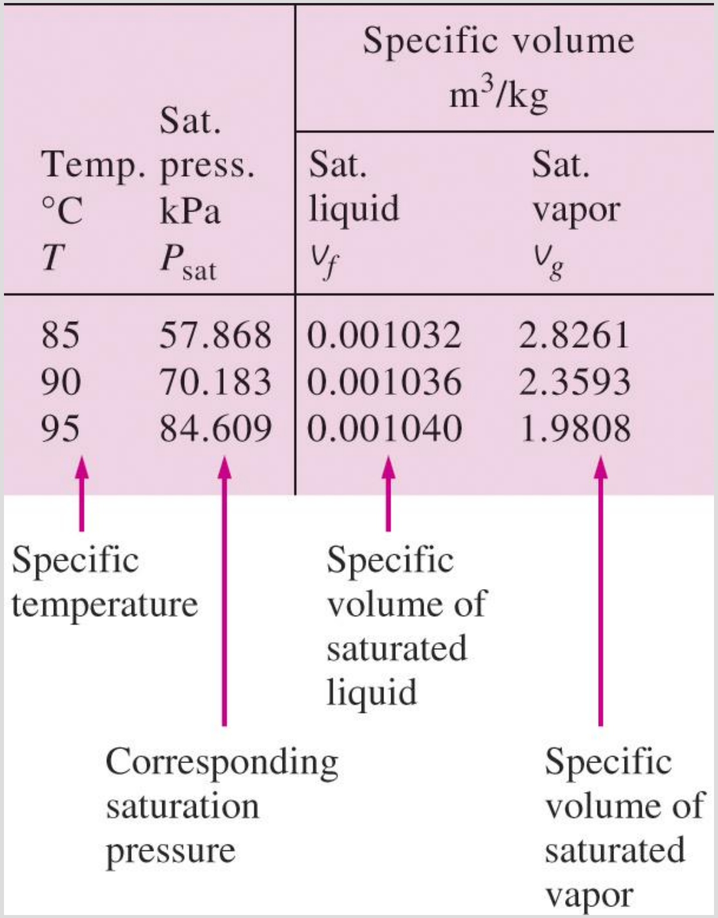
$$\text{psi} \cdot \text{ft}^3 \equiv 0.18505\ \text{Btu}$$

The product *pressure* × *volume* has energy units.

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.



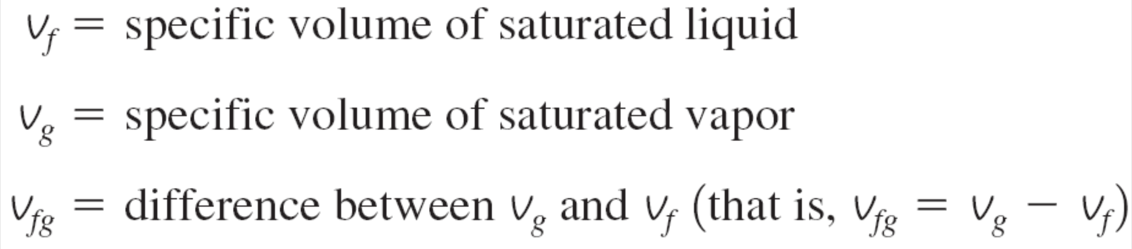
Temp. °C T	Sat. press. kPa P_{sat}	Specific volume m^3/kg Sat. liquid v_f	 Sat. vapor v_g
85	57.868	0.001032	2.8261
90	70.183	0.001036	2.3593
95	84.609	0.001040	1.9808

Specific temperature

Corresponding saturation pressure

Specific volume of saturated liquid

Specific volume of saturated vapor



v_f = specific volume of saturated liquid

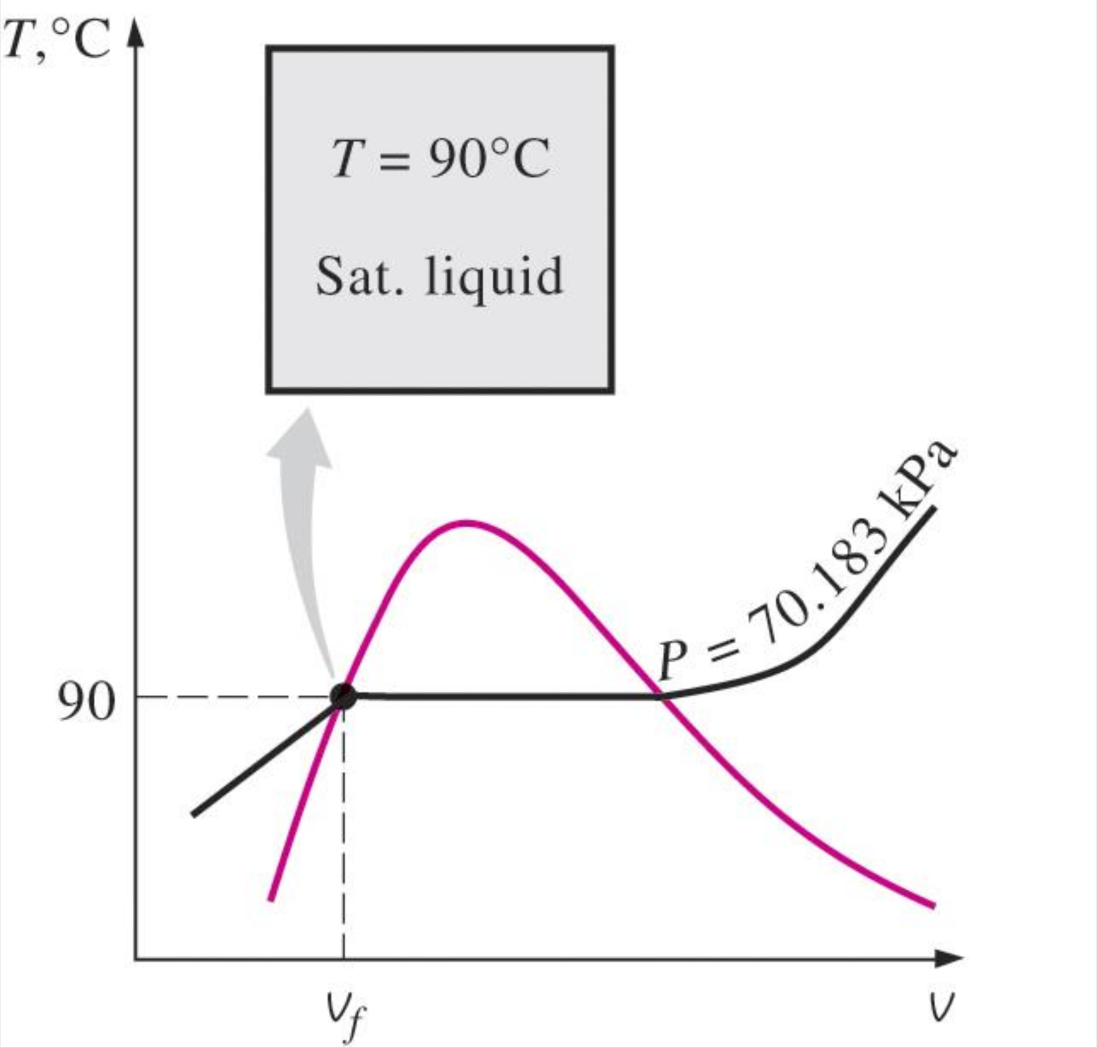
v_g = specific volume of saturated vapor

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

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 Pressure of saturated liquid

A rigid tank contains 50kg of saturated liquid water at 90ºc. Determine the pressure in the tank and the volume of the tank.


T,°C
T = 90°C
Sat. liquid
P = 70.183 kPa
90
v_f
v

Example: Temperature of saturated vapor

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

Saturated Liquid–Vapor Mixture

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

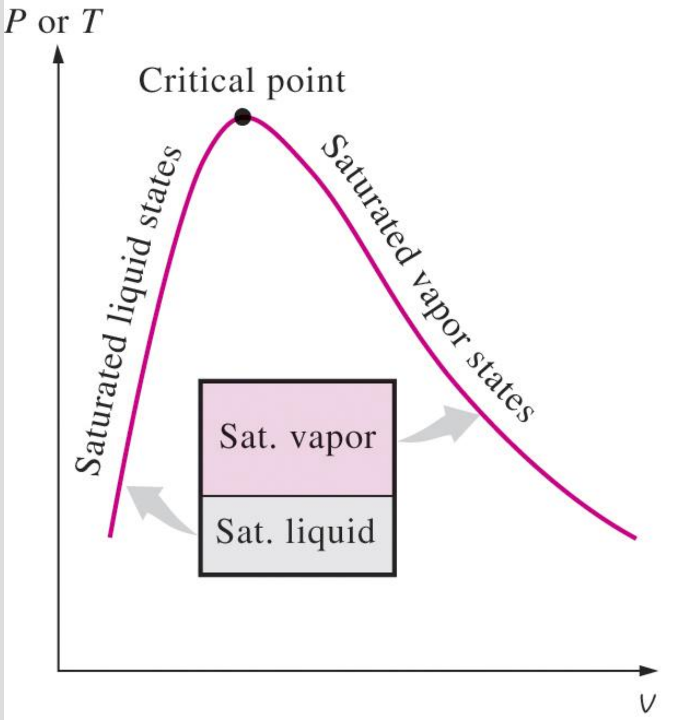
Quality is between 0 and 1 → 0: sat. liquid, 1: sat. vapor

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

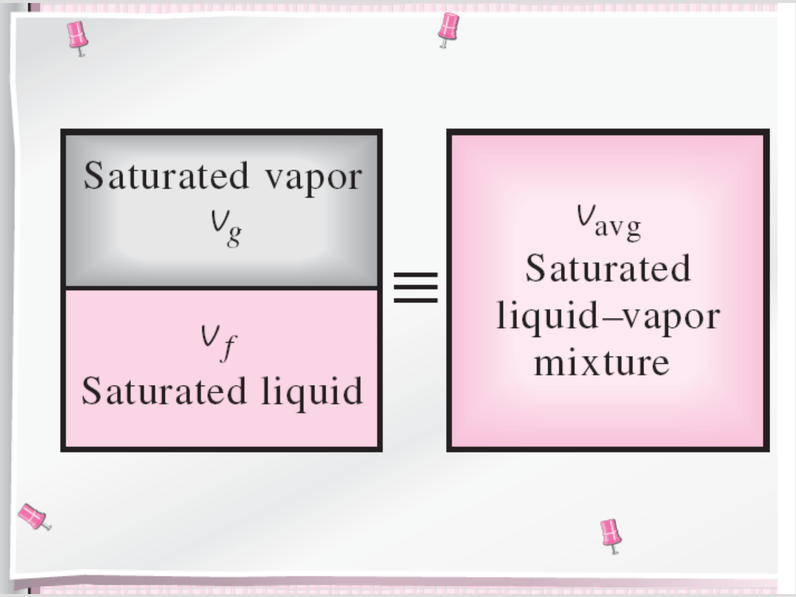
$$m_{\text{total}} = m_{\text{liquid}} + m_{\text{vapor}} = m_f + m_g$$

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

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.

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

$$x = m_g/m_t$$

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

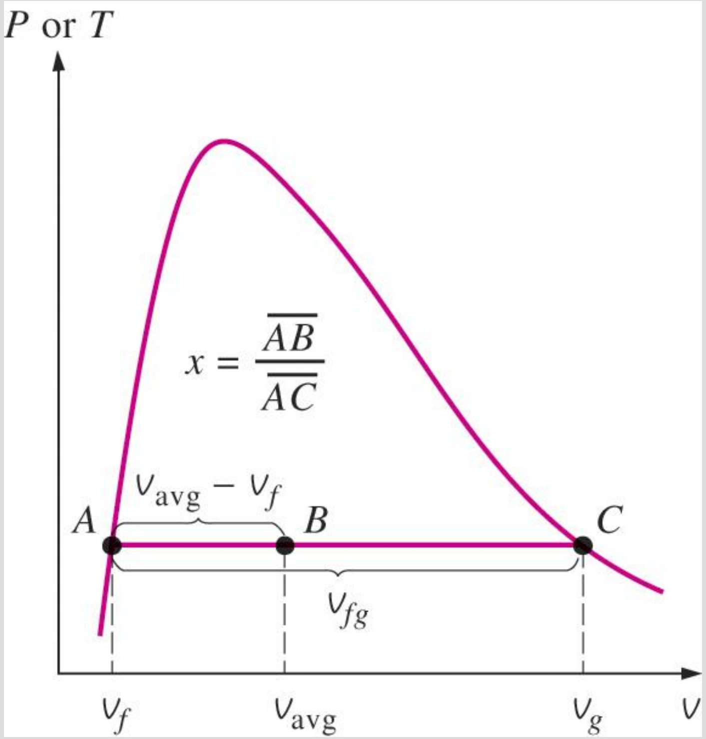
$$u_{\text{avg}} = u_f + x u_{fg} \qquad (\text{kJ/kg})$$

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

y → *v*, *u*, or *h*.

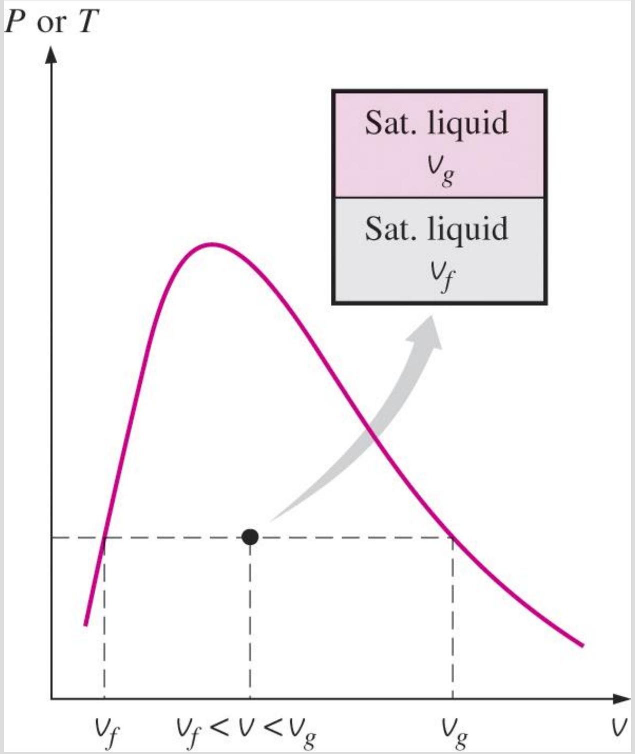
$$y_{\text{avg}} = y_f + x y_{fg}$$

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



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

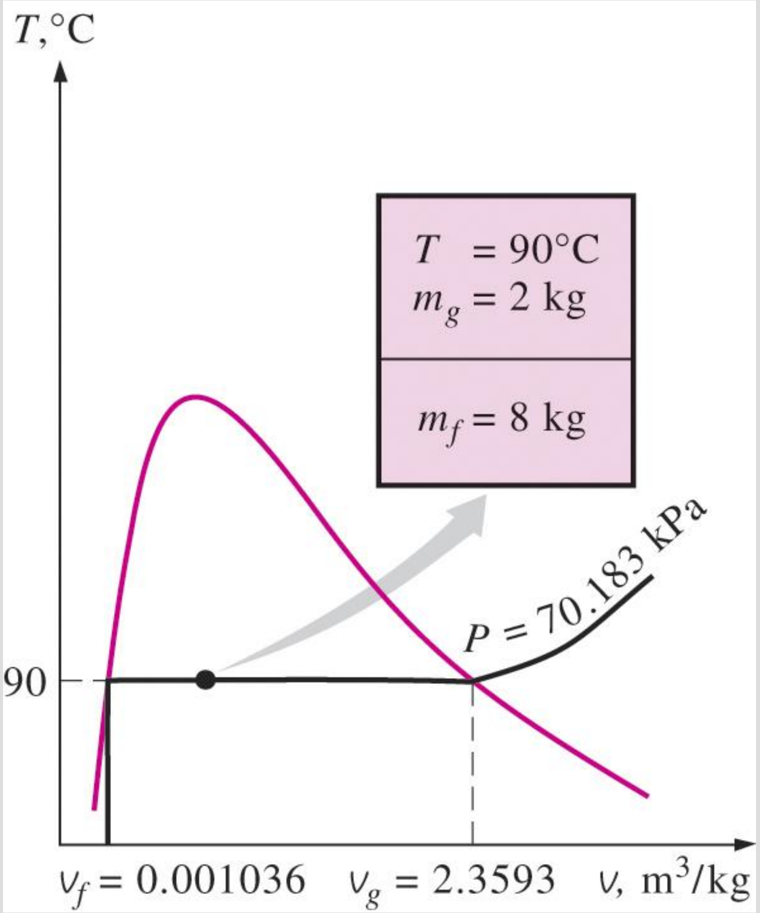
The *v* value of a saturated liquid–vapor mixture lies between the v_f and v_g values at the specified *T* or *P*.

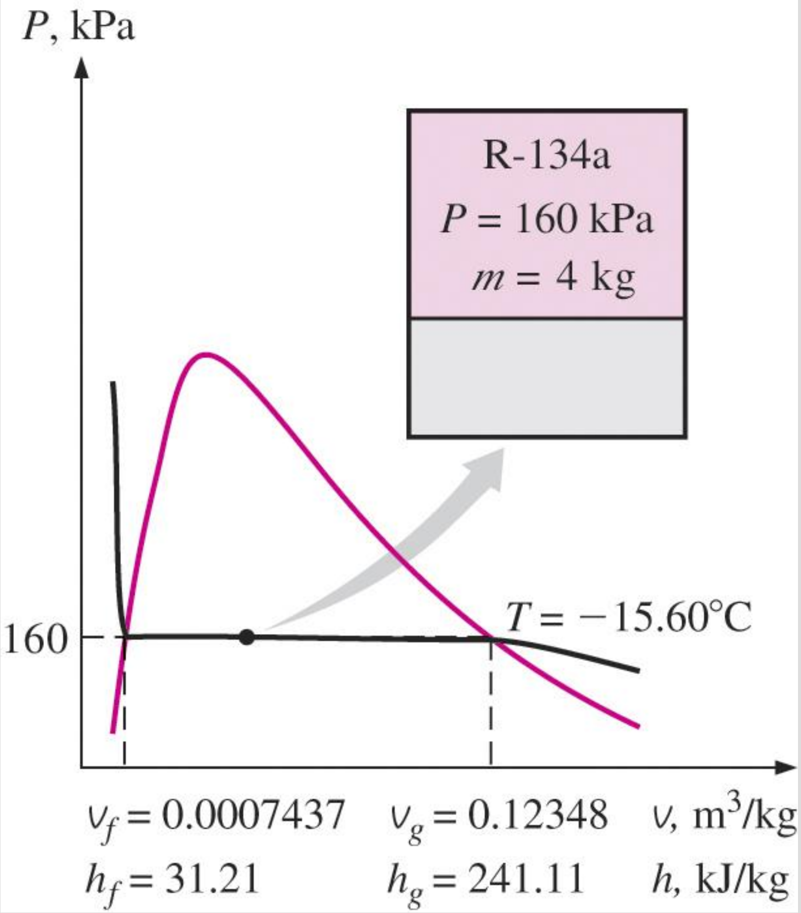


PRESSURE AND VOLUME OF SATURATED MIXTURE

- A rigid tank contains 10kg of water at 90oC. If 8kg 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

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

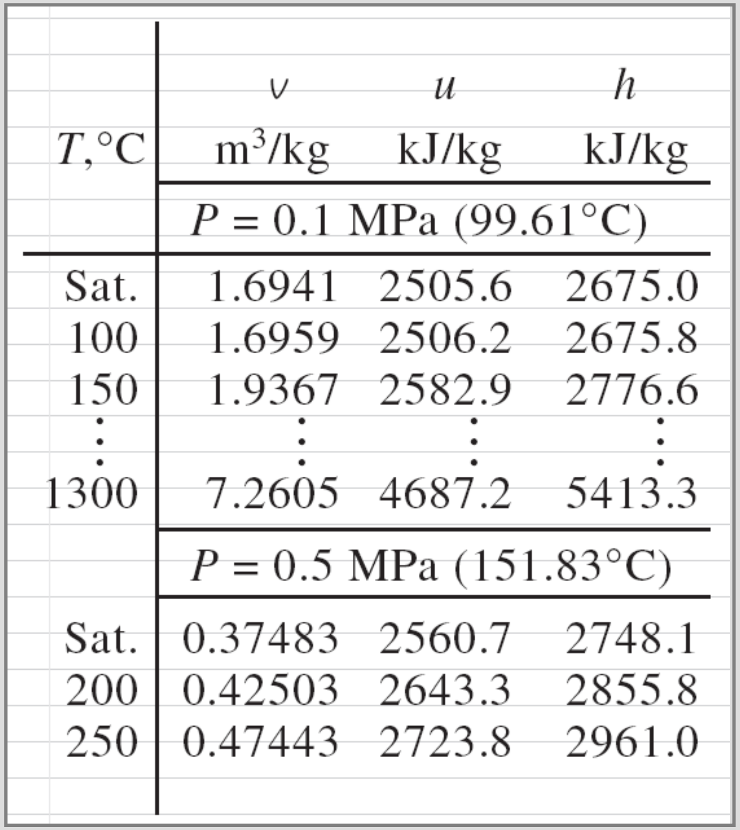




Superheated Vapor

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.

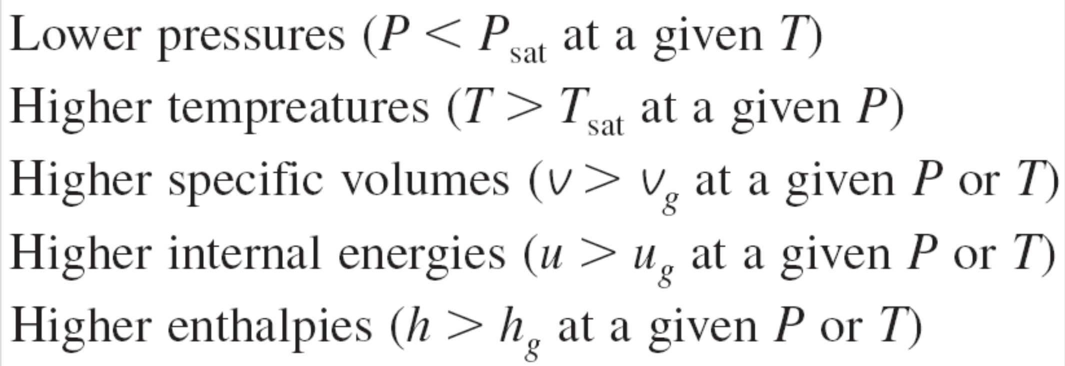
In this region, temperature and pressure are independent properties.



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

A partial listing of Table A–6.

Compared to saturated vapor, superheated vapor is characterized by



Lower pressures ($P < P_{sat}$ at a given T)

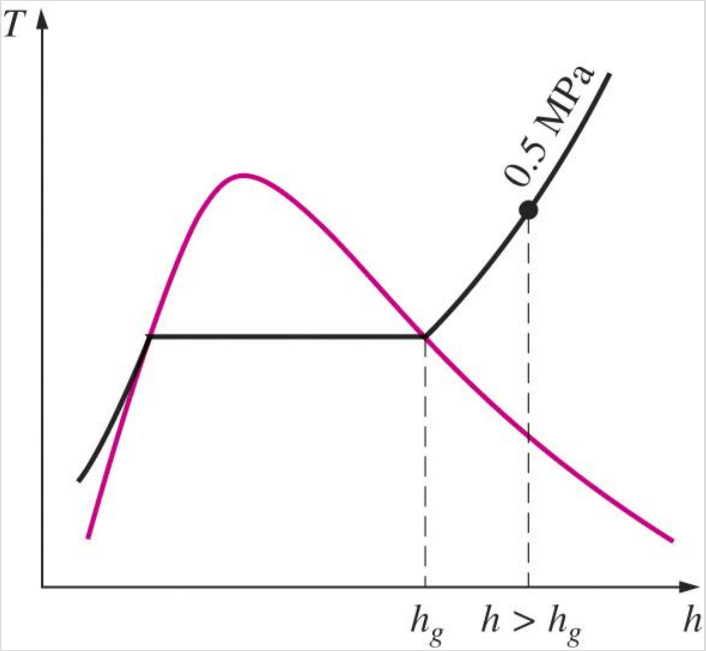
Higher tempreatures ($T > T_{sat}$ at a given P)

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)

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



Compressed Liquid

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

$y \cong y_{f\,@\,T}$ ***y*** → *v*, *u*, or *h*

A more accurate relation for *h*

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

Compressed liquid is characterized by

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

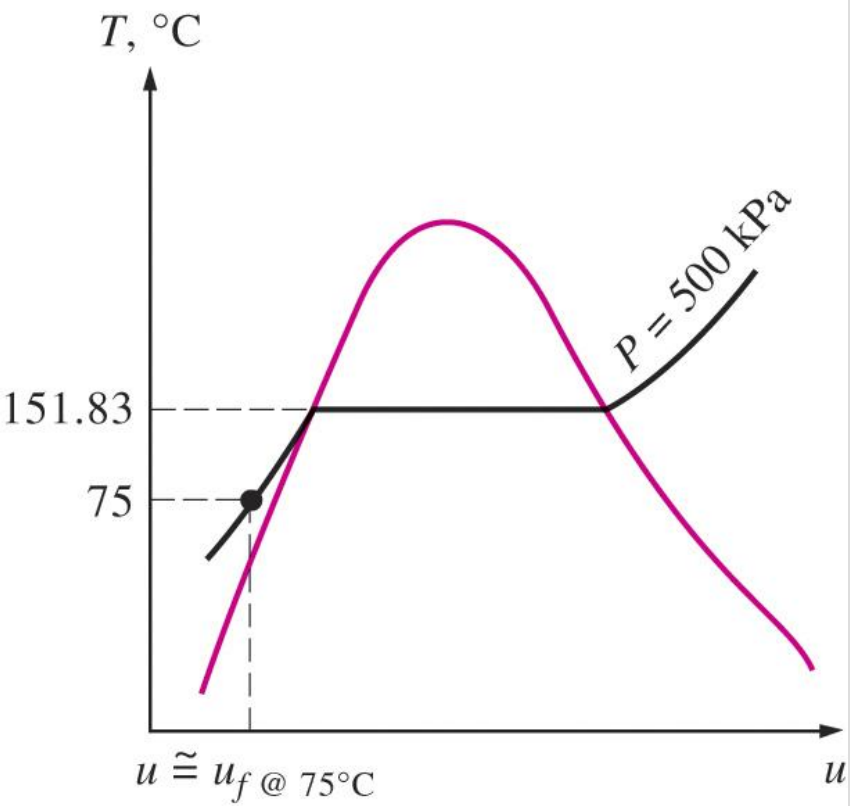
Given: P and T

$$v \cong v_{f\,@T}$$
$$u \cong u_{f\,@T}$$
$$h \cong h_{f\,@T}$$

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

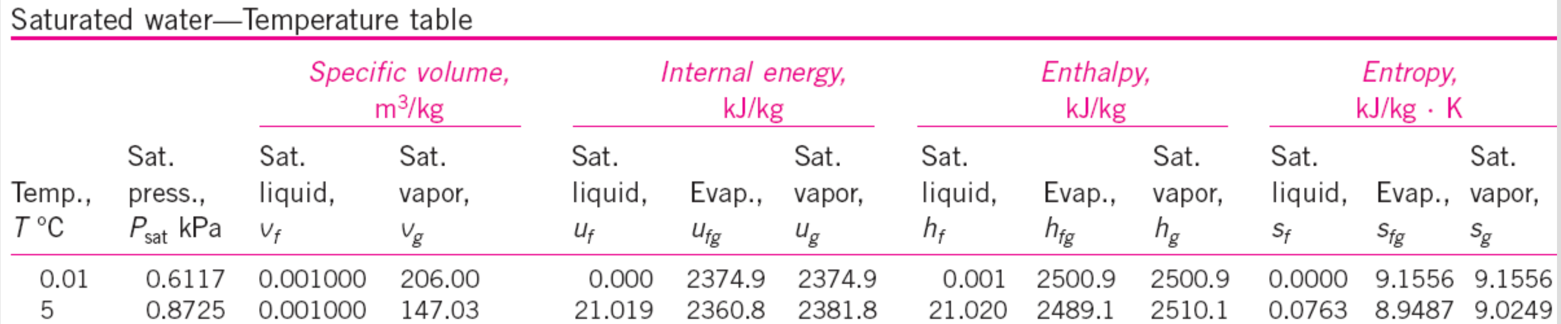
At a given *P* and *T*, a pure substance will exist as a compressed liquid if

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



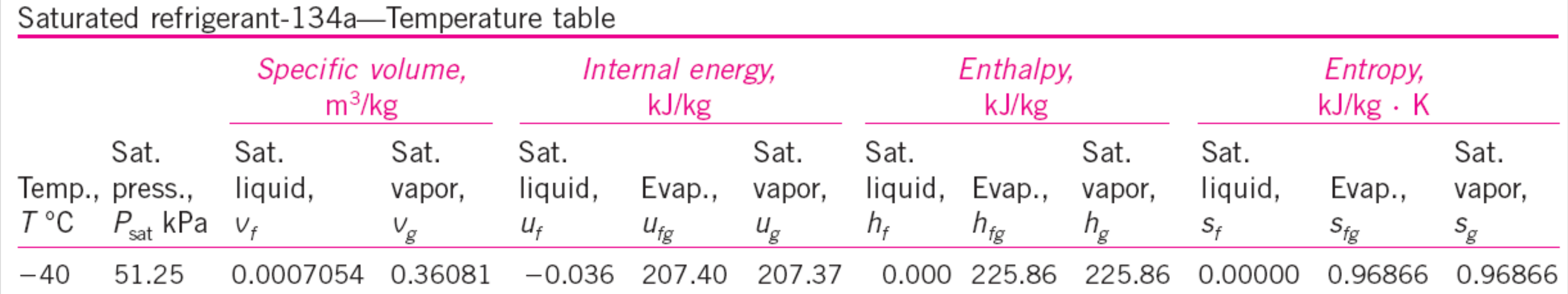
Reference State and Reference Values

- The values of *u*, *h*, and *s* cannot be measured directly, and they are calculated from measurable properties using the relations between properties.
- However, those relations give the *changes* in properties, not the values of properties at specified states.
- Therefore, we need to choose a convenient *reference state* and assign a value of *zero* for a convenient property or properties at that state.
- The referance state for water is 0.01°C and for R-134a is -40°C in tables.
- Some properties may have negative values as a result of the reference state chosen.
- Sometimes different tables list different values for some properties at the same state as a result of using a different reference state.
- However, In thermodynamics we are concerned with the *changes* in properties, and the reference state chosen is of no consequence in calculations.



Saturated water—Temperature table

		Specific volume, m^3/kg		*Internal energy,* kJ/kg			*Enthalpy,* kJ/kg			*Entropy,* kJ/kg · K		
Temp., T °C	Sat. press., P_{sat} kPa	Sat. liquid, v_f	Sat. vapor, v_g	Sat. liquid, u_f	Evap., u_{fg}	Sat. vapor, u_g	Sat. liquid, h_f	Evap., h_{fg}	Sat. vapor, h_g	Sat. liquid, s_f	Evap., s_{fg}	Sat. vapor, s_g
0.01	0.6117	0.001000	206.00	0.000	2374.9	2374.9	0.001	2500.9	2500.9	0.0000	9.1556	9.1556
5	0.8725	0.001000	147.03	21.019	2360.8	2381.8	21.020	2489.1	2510.1	0.0763	8.9487	9.0249



Saturated refrigerant-134a—Temperature table

		Specific volume, m^3/kg		*Internal energy,* kJ/kg			*Enthalpy,* kJ/kg			*Entropy,* kJ/kg · K		
Temp., T °C	Sat. press., P_{sat} kPa	Sat. liquid, v_f	Sat. vapor, v_g	Sat. liquid, u_f	Evap., u_{fg}	Sat. vapor, u_g	Sat. liquid, h_f	Evap., h_{fg}	Sat. vapor, h_g	Sat. liquid, s_f	Evap., s_{fg}	Sat. vapor, s_g
−40	51.25	0.0007054	0.36081	−0.036	207.40	207.37	0.000	225.86	225.86	0.00000	0.96866	0.96866

THE IDEAL-GAS EQUATION OF STATE

- **Equation of state**: Any equation that relates the pressure, temperature, and specific volume of a substance.
- The simplest : ideal-gas equation of state. This equation predicts the *P*-*v*-*T* behavior of a gas quite accurately within some properly selected region.

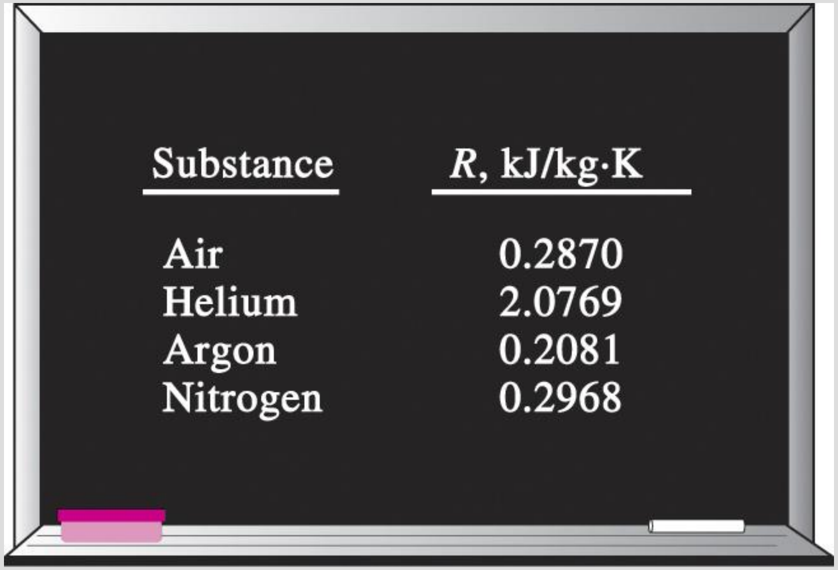
$$P = R\left(\frac{T}{v}\right) \qquad Pv = RT$$

Ideal gas equation of state

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

R: gas constant
M: molar mass (kg/kmol)
R_u: universal gas constant

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



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

Different substances have different gas constants.

Mass = Molar mass × Mole number

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

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

Ideal gas equation at two states for a fixed mass

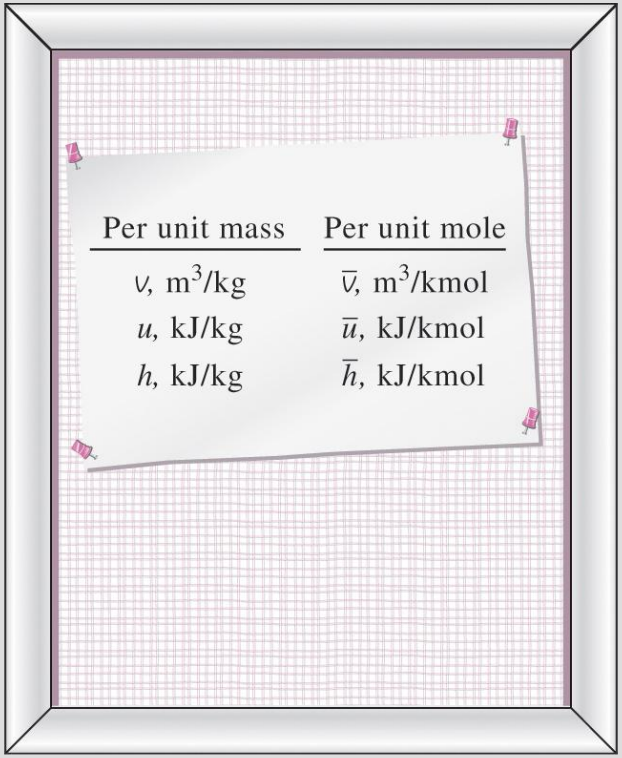
$$V = m\mathrm{v} \longrightarrow PV = mRT$$

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

$$V = N\bar{\mathrm{v}} \longrightarrow P\bar{\mathrm{v}} = R_uT$$

Various expressions of ideal gas equation

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



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

Properties per unit mole are denoted with a bar on the top.

The ideal-gas relation often is not applicable to real gases; thus, care should be exercised when using it.

When the Ideal gas equation is used

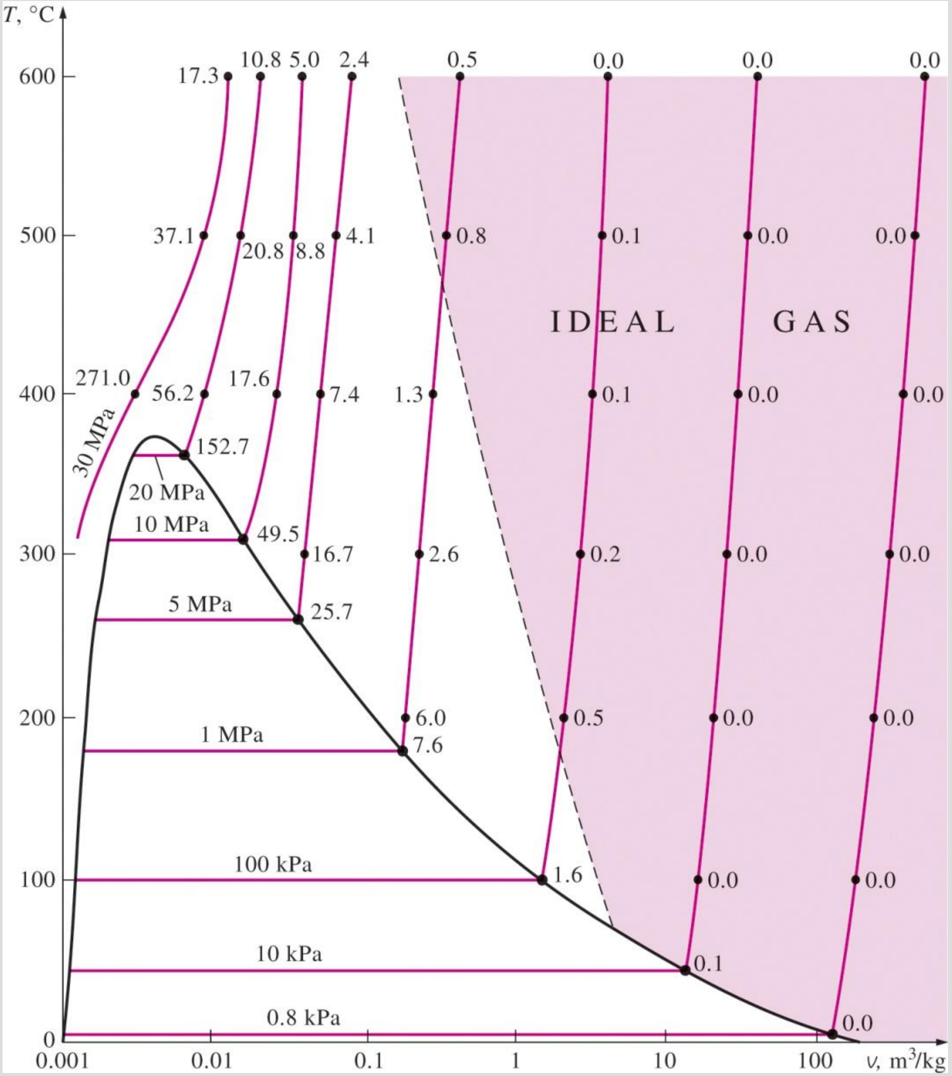
- The pressure is small compared to the critical pressure

$$P< P_{cr}$$

- The temperature is twice the critical temperature and pressure is less than 10 times of the critical pressure.

$$T=2T_{cr} \text{ and } P<10P_{cr}$$

Is Water Vapor an Ideal Gas?



- **YES**: at pressures below 10 kPa.
- **NO**: in actual application (higher pressure environment) such as Steam Power Plant

4-7 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.

Z bigger than 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).

$$Pv = ZRT$$

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

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

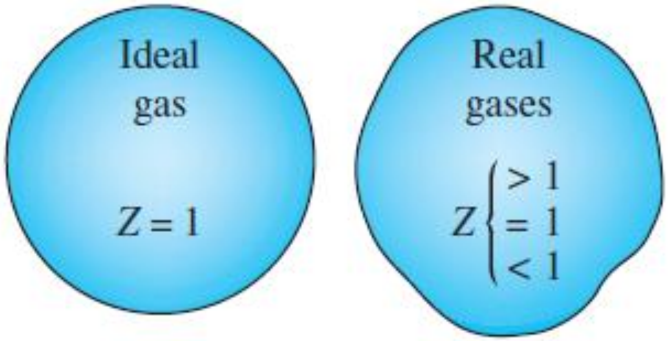


FIGURE 4–48

The compressibility factor is unity for ideal gases.

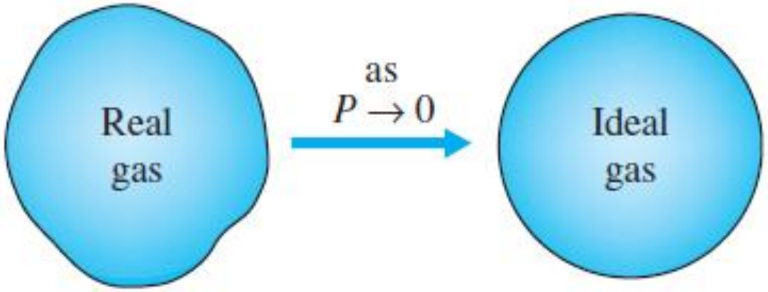


FIGURE 4–50

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

Summary

- Pure substance
- Phases of a pure substance
- Phase-change processes of pure substances
  - ✓ Compressed liquid, Saturated liquid, Saturated vapor, Superheated vapor
  - ✓ Saturation temperature and Saturation pressure
- Property diagrams for phase change processes
  - ✓ The *T-v* diagram, The *P-v* diagram, The *P-T* diagram, *The P-v-T* surface
- Property tables
  - ✓ Enthalpy
  - ✓ Saturated liquid, saturated vapor, Saturated liquid vapor mixture, Superheated vapor, compressed liquid
  - ✓ Reference state and reference values
- The ideal gas equation of state
  - ✓ Is water vapor an ideal gas?