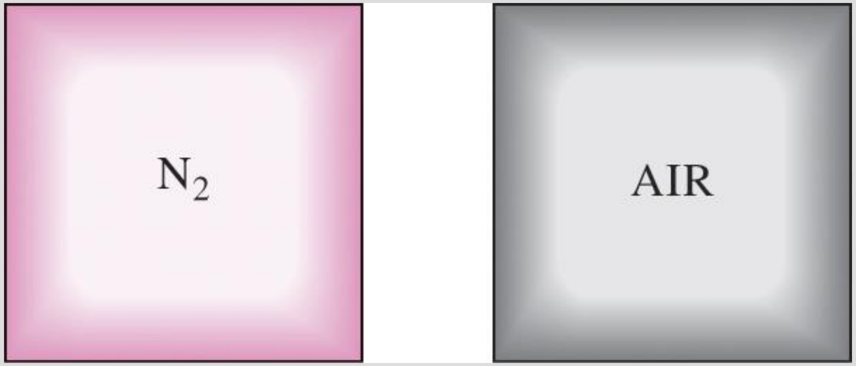
Chapter 3

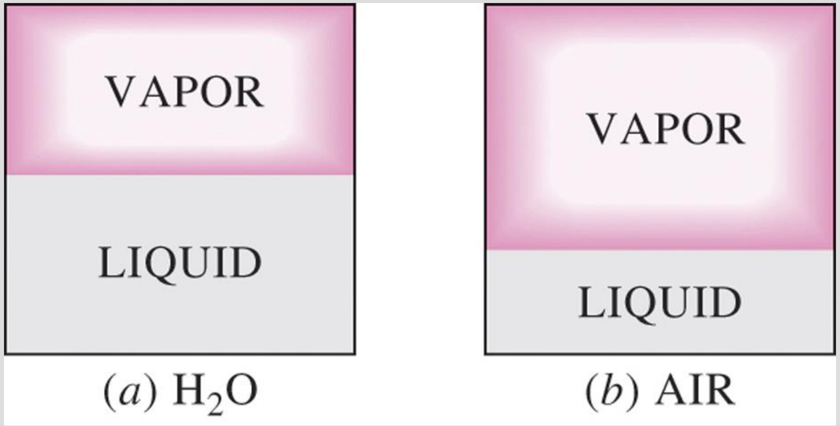
PROPERTIES OF PURE SUBSTANCES

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.



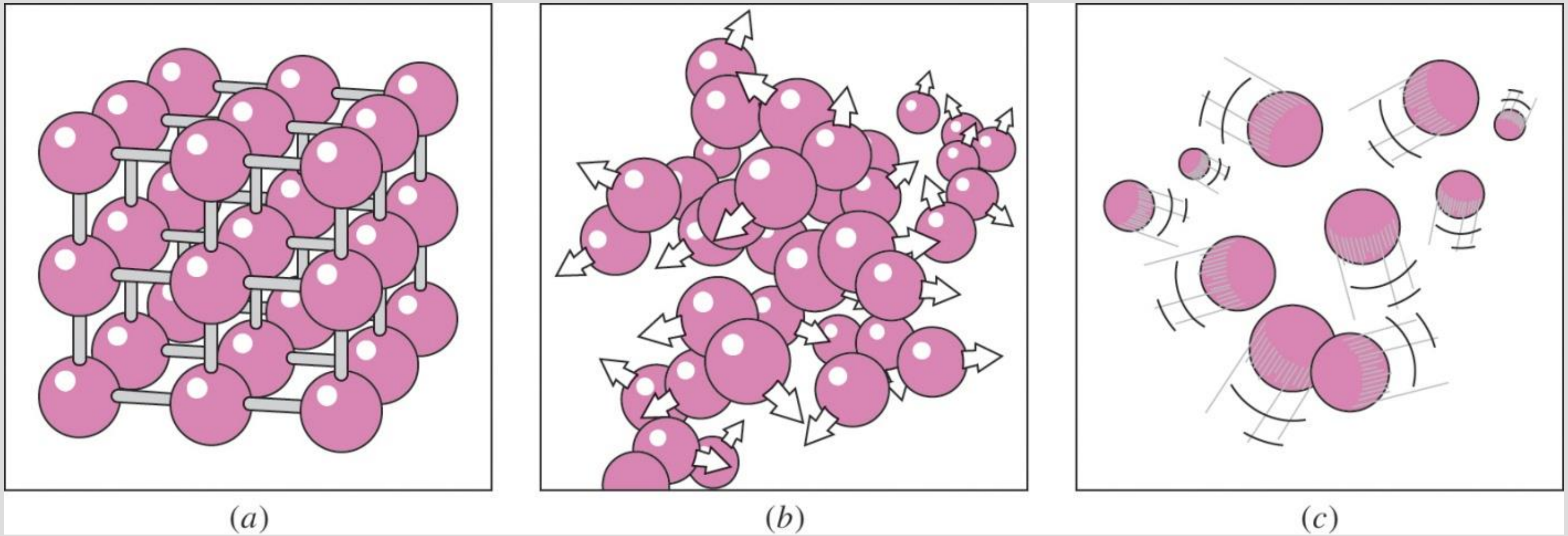
Nitrogen and gaseous air are pure substances.



(*a*) H_2O (*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

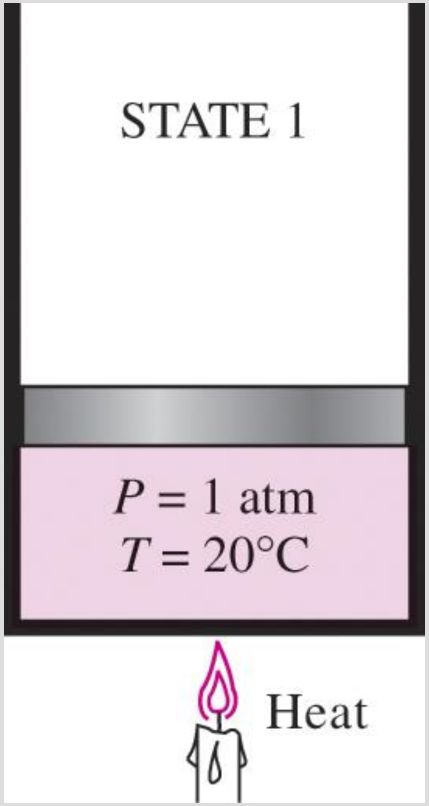


The arrangement of atoms in different phases: (*a*) molecules are at relatively fixed positions in a solid, (*b*) groups of molecules move about each other in the liquid phase, and (*c*) molecules move about at random in the gas phase.

PHASE-CHANGE PROCESSES OF PURE SUBSTANCES

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

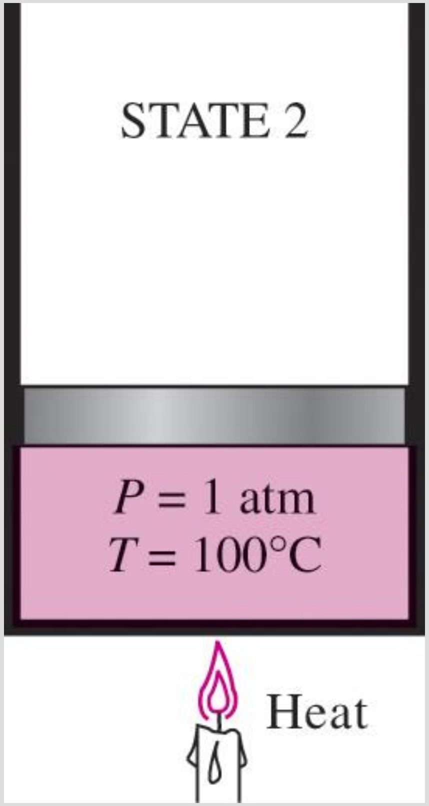
At 1 atm and 20°C, water exists in the liquid phase (***compressed liquid***).



PHASE-CHANGE PROCESSES OF PURE SUBSTANCES

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

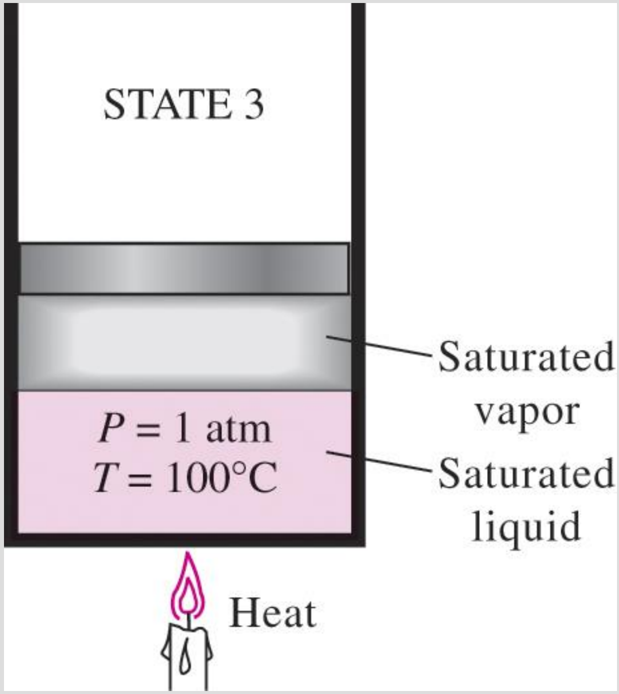
At 1 atm pressure and 100°C, water exists as a liquid that is ready to vaporize (***saturated liquid***).



PHASE-CHANGE PROCESSES OF PURE SUBSTANCES

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

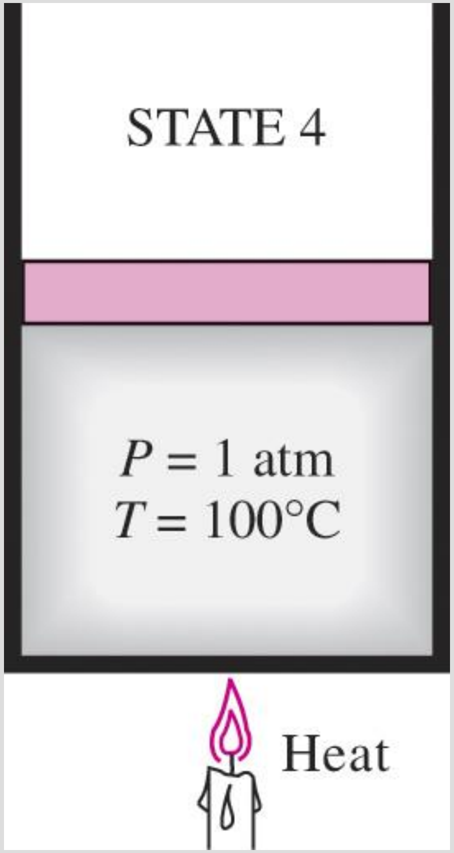
As more heat is transferred, part of the saturated liquid vaporizes (***saturated liquid–vapor mixture***).



PHASE-CHANGE PROCESSES OF PURE SUBSTANCES

Saturated vapor: A substance is at the end of vaporization.

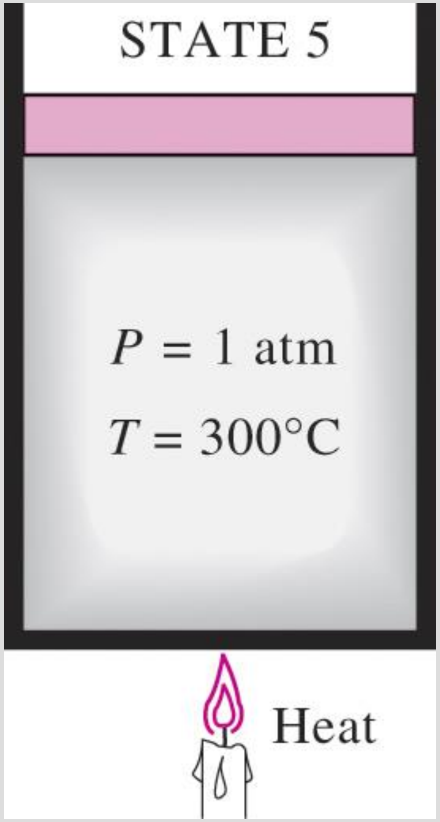
At 1 atm pressure, the temperature remains constant at 100°C until the last drop of liquid is vaporized (***saturated vapor***).

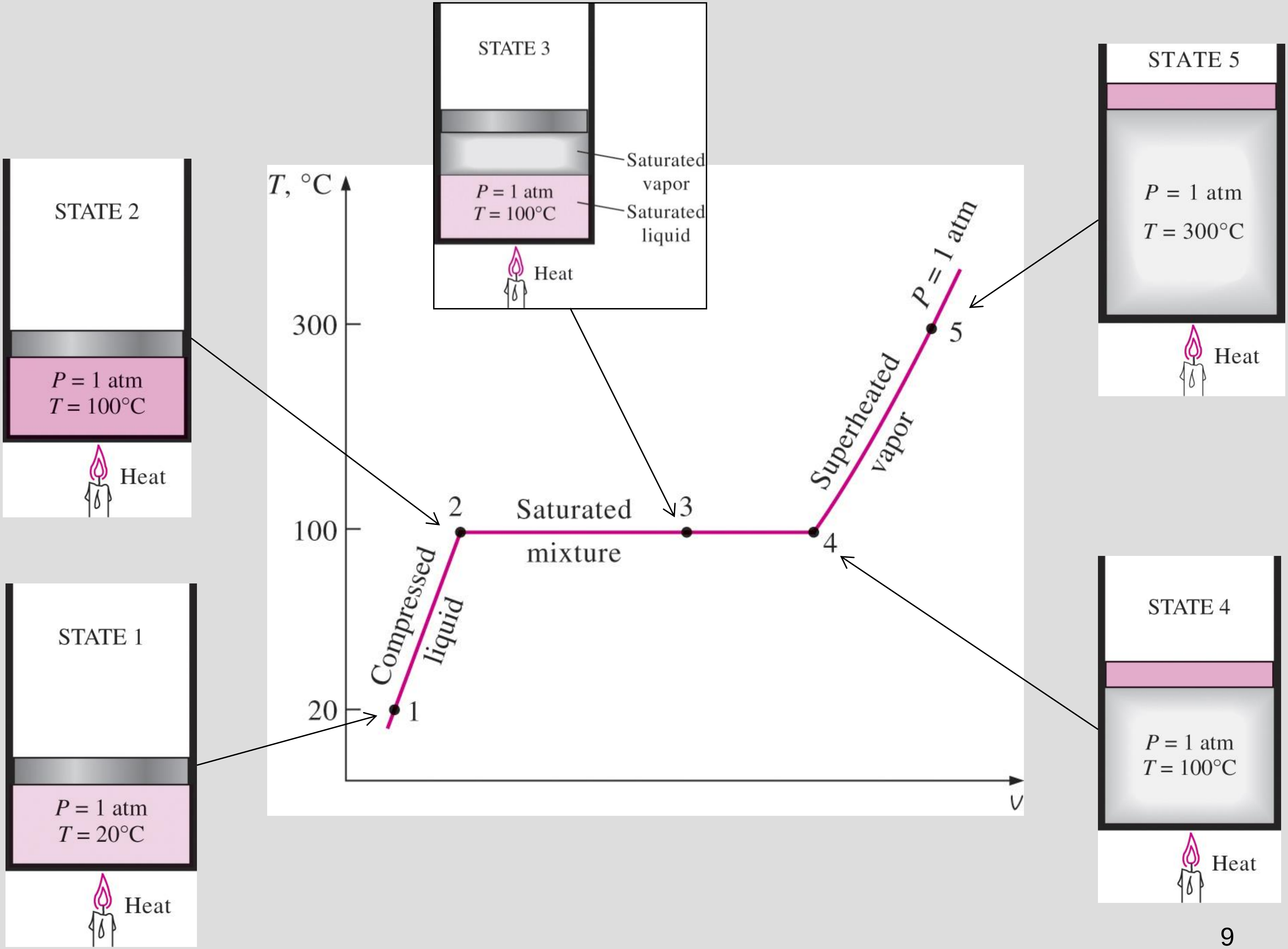


PHASE-CHANGE PROCESSES OF PURE SUBSTANCES

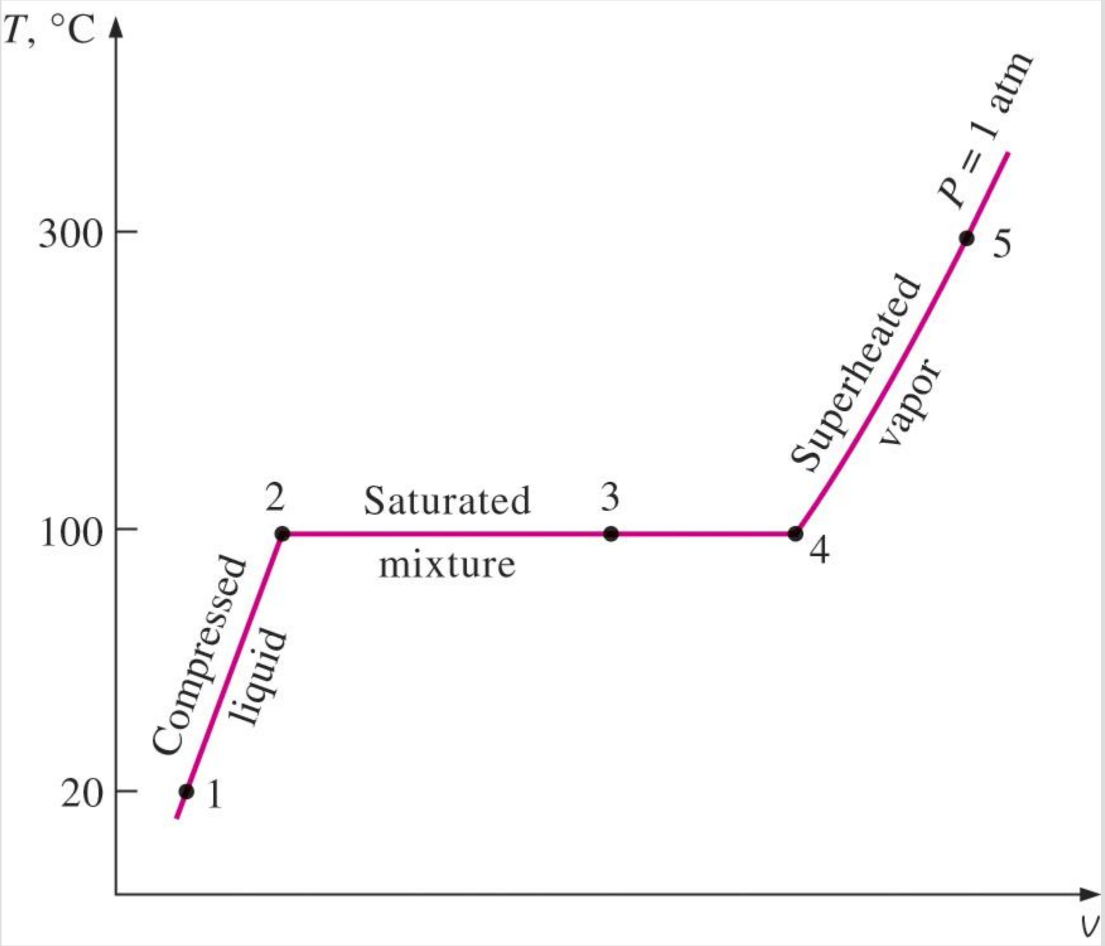
Superheated vapor: A vapor that is *not about to condense* (i.e., not a saturated vapor).

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



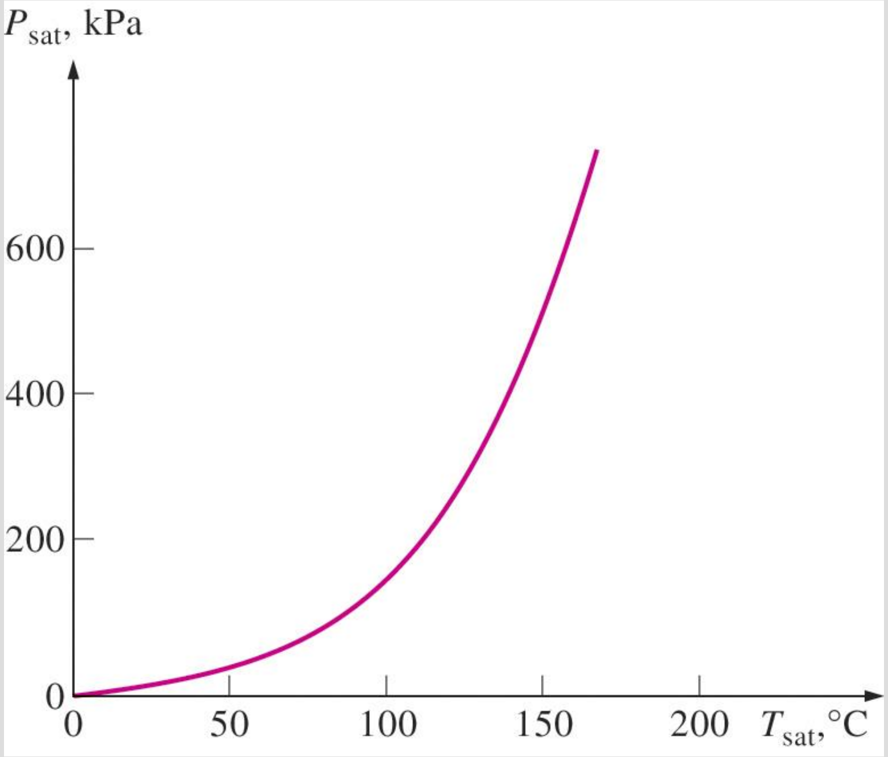

STATE 3
Saturated vapor
Saturated liquid
P = 1 atm
T = 100°C
Heat
STATE 5
P = 1 atm
T = 300°C
Heat
STATE 2
P = 1 atm
T = 100°C
Heat
T, °C
300
100
20
P = 1 atm
5
Superheated vapor
2
Saturated
3
mixture
4
Compressed liquid
1
v
STATE 4
P = 1 atm
T = 100°C
Heat
STATE 1
P = 1 atm
T = 20°C
Heat

- If the process is reversed by cooling the water, the water will go back to state 1 on the same path
- The water will release the same amount of heat it gained during the heating process.



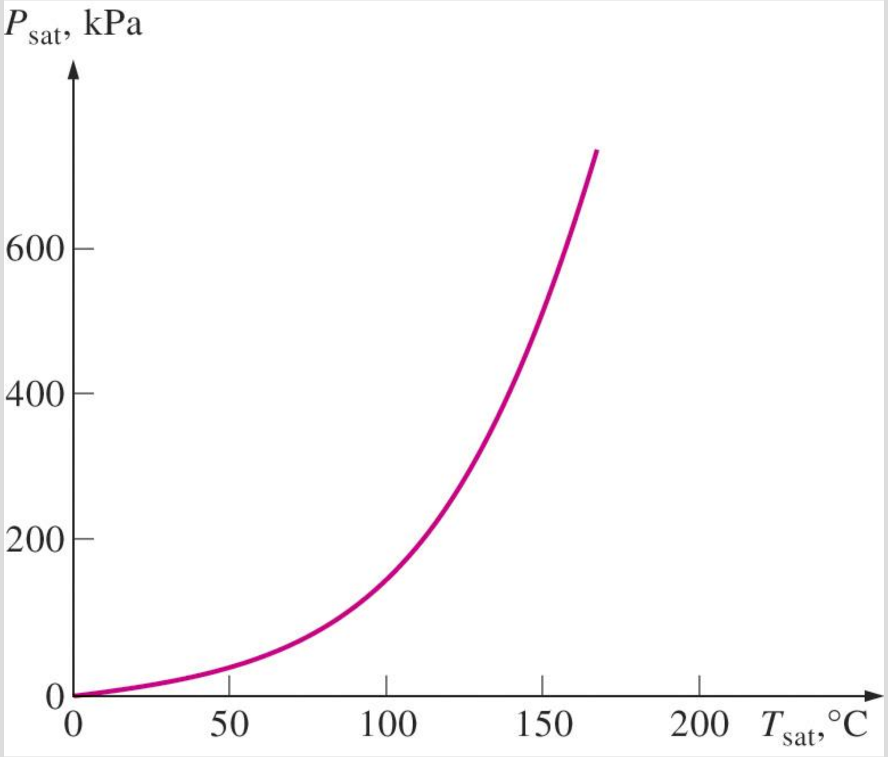
Boiling Temperature vs. Boiling Pressure

- 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 and Saturation 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.



Saturation Temperature and Saturation Pressure

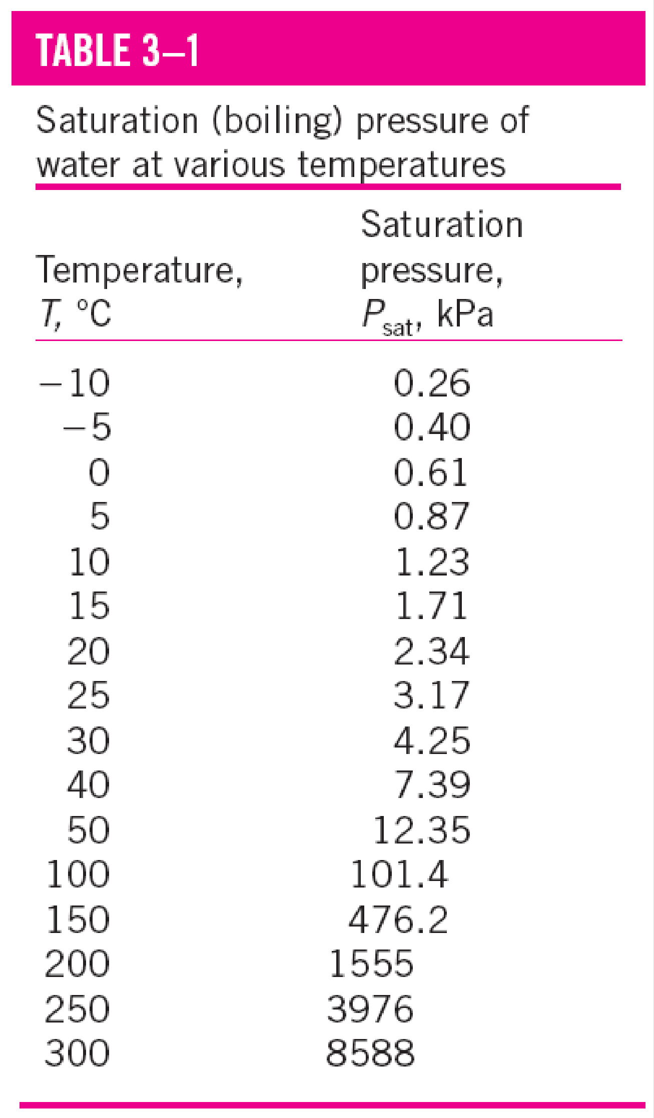


TABLE 3–1

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

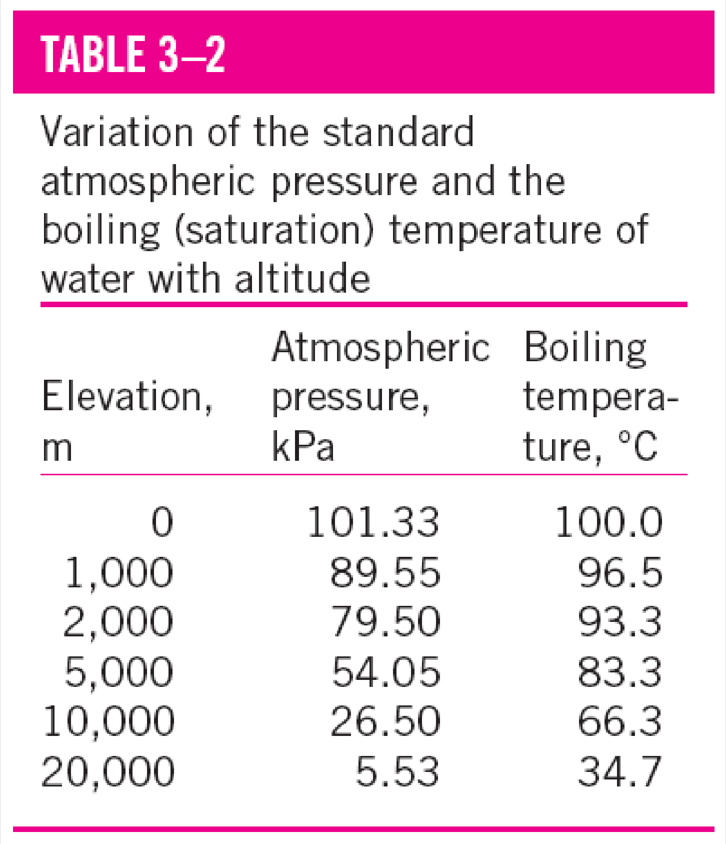


TABLE 3–2

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

Elevation, m	Atmospheric pressure, kPa	Boiling 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

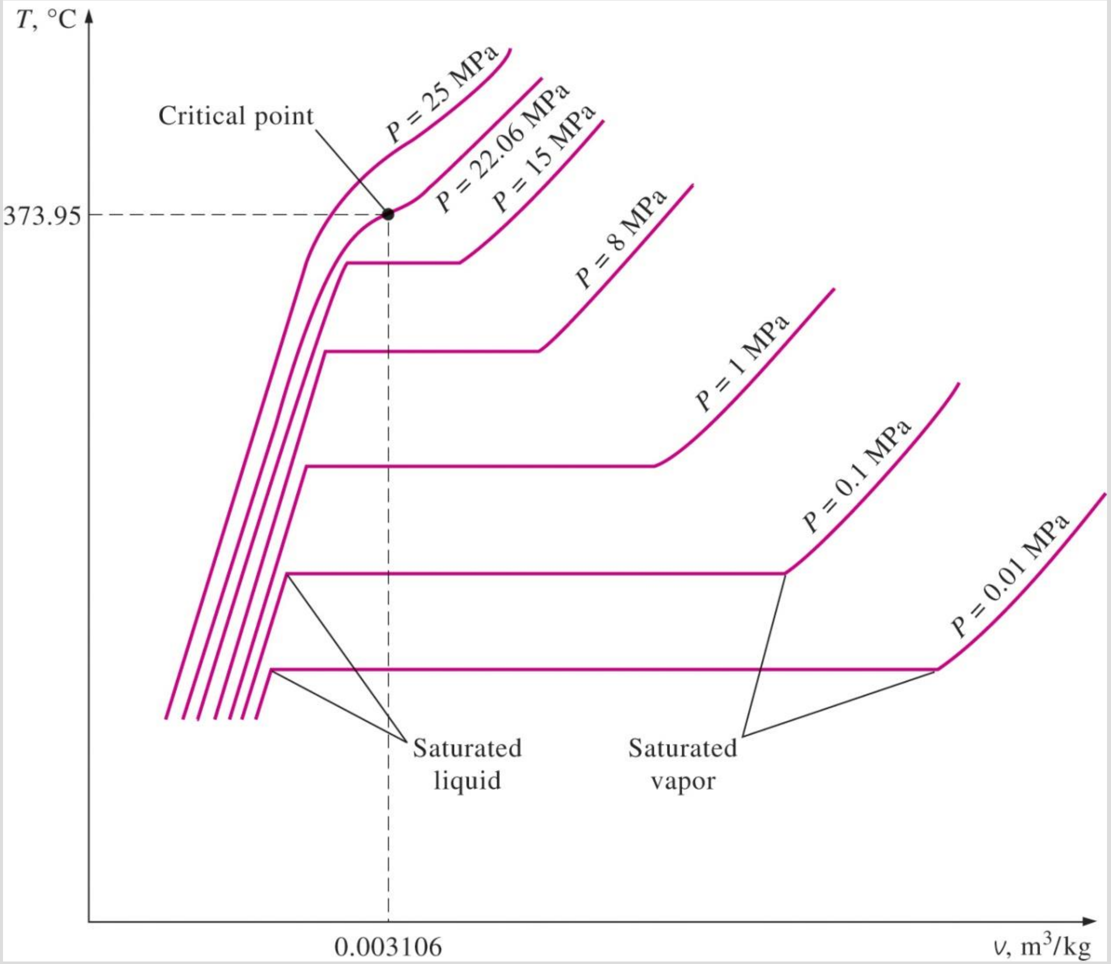
The atmospheric pressure, and thus the boiling temperature of water, decreases with elevation.

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.

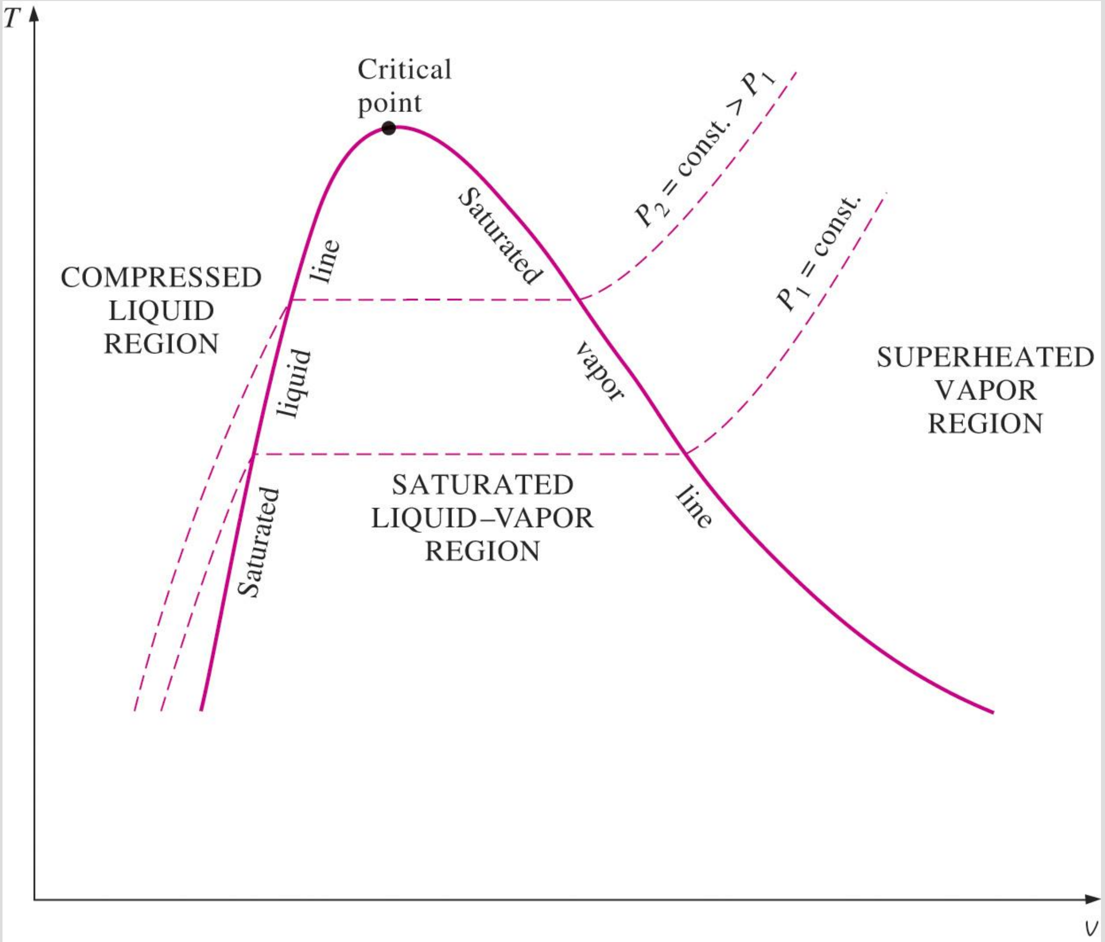
PROPERTY DIAGRAMS FOR PHASE-CHANGE PROCESSES

- 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.

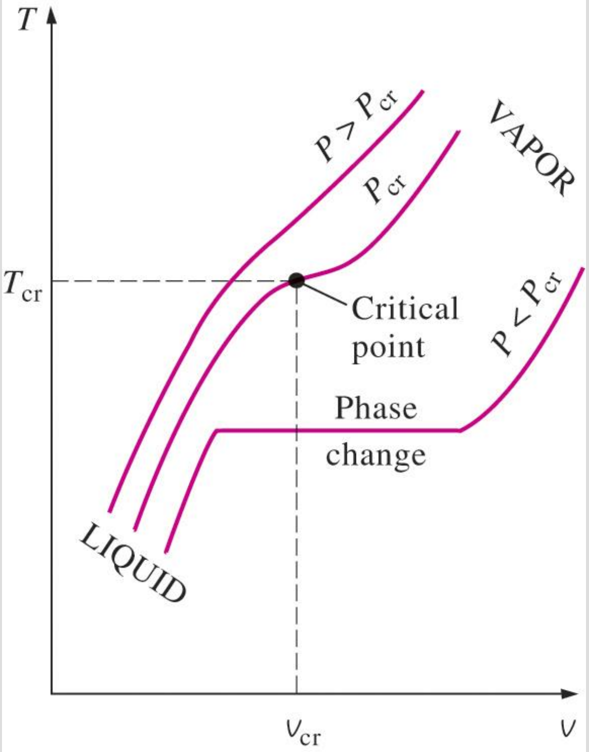


T-*v* diagram of constant-pressure phase-change processes of a pure substance at various pressures (numerical values are for water).

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

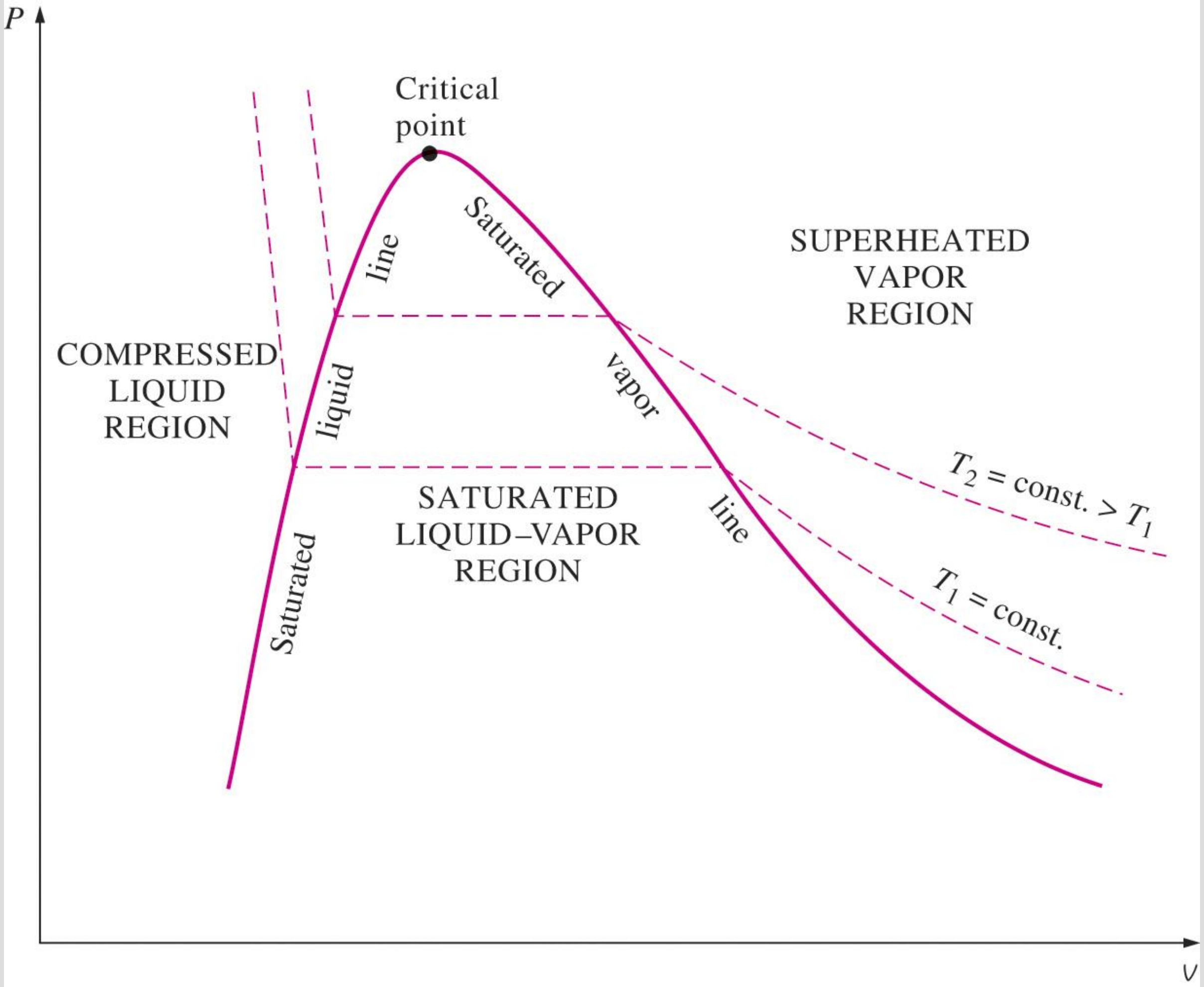


T-*v* diagram of a pure substance.

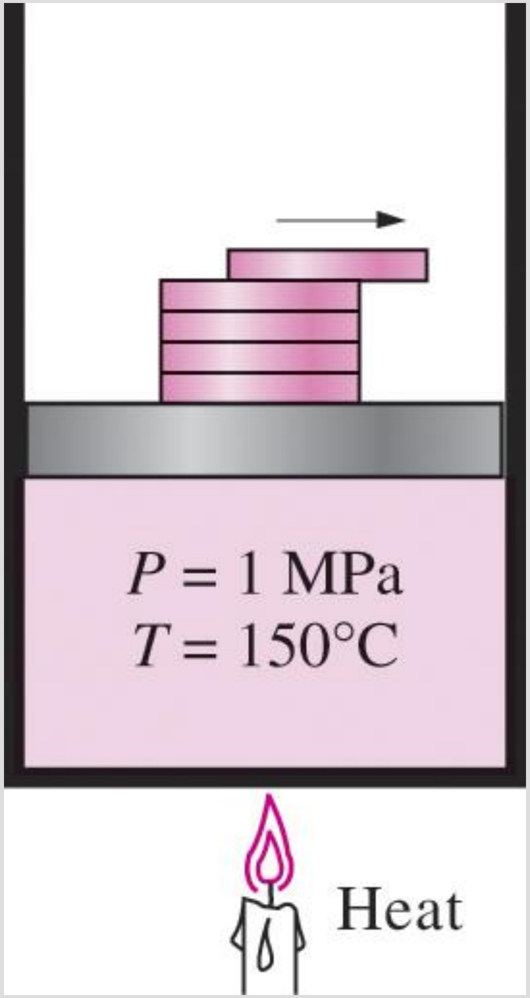


At supercritical pressures ($P > P_{cr}$), there is no distinct phase-change (boiling) process.

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



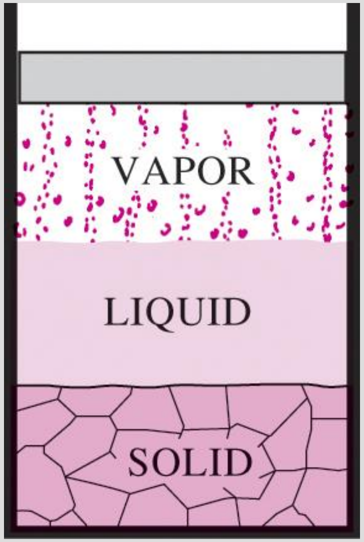
P-*v* diagram of a pure substance.



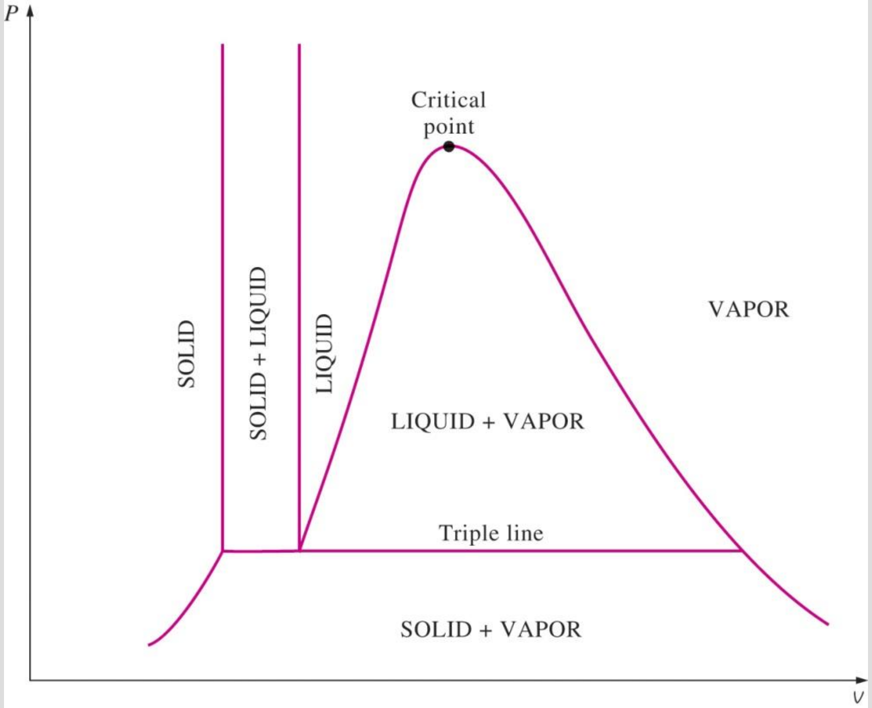
The pressure in a piston–cylinder device can be reduced by reducing the weight of the piston.

Extending the Diagrams to Include the Solid Phase

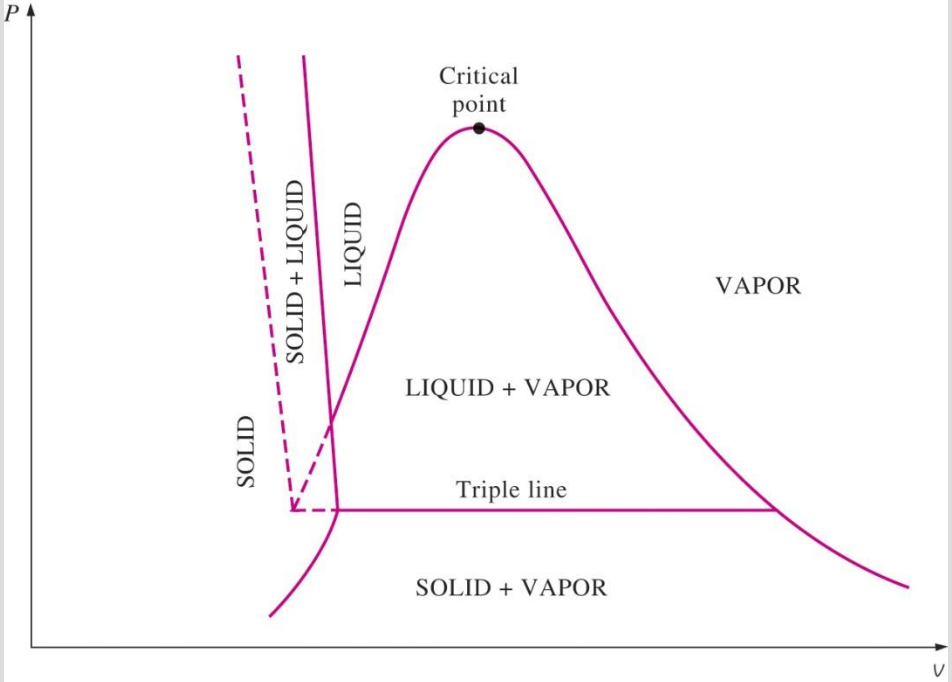
For water,
T_{tp} = 0.01°C
P_{tp} = 0.6117 kPa



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

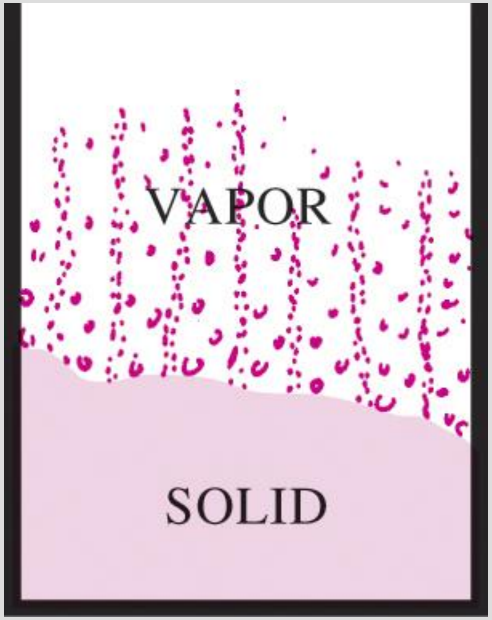


P-*v* diagram of a substance that contracts on freezing.



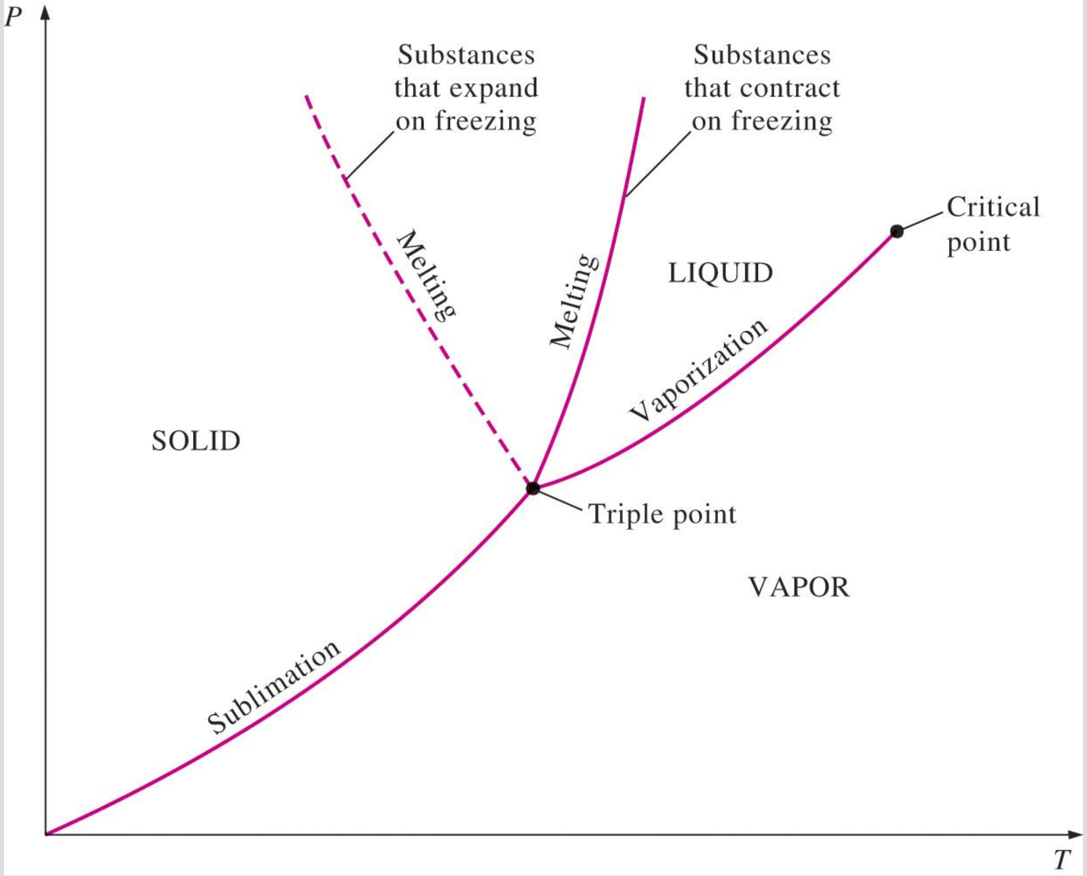
P-*v* diagram of a substance that expands on freezing (such as water).

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

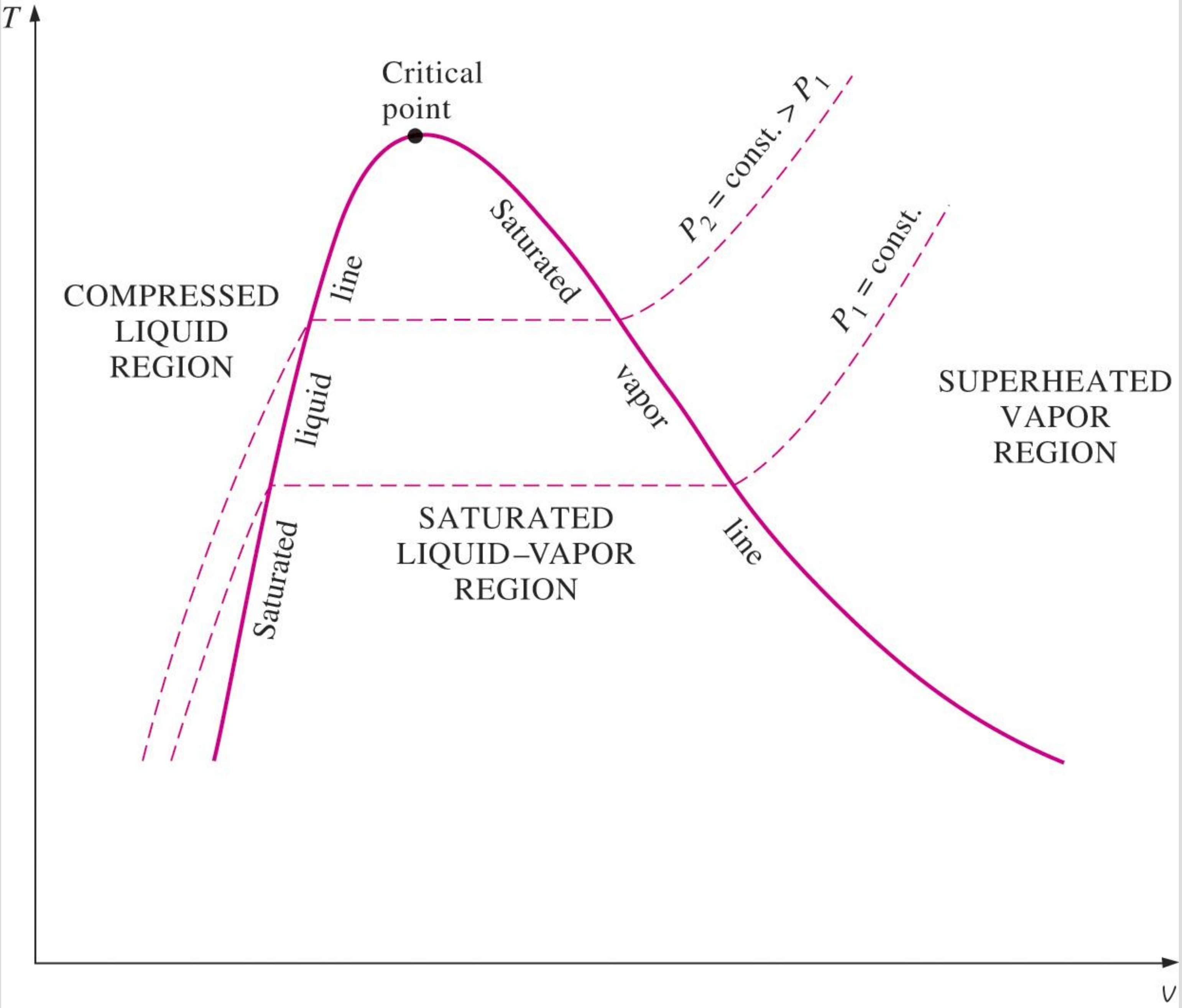


At low pressures (below the triple-point value), solids evaporate without melting first (*sublimation*).

Phase Diagram



P-T diagram of pure substances.


T
Critical point
P_2 = const. > P_1
P_1 = const.
COMPRESSED LIQUID REGION
Saturated liquid line
Saturated vapor line
SUPERHEATED VAPOR REGION
SATURATED LIQUID–VAPOR REGION
v

Why Determine Properties?

$$E_{\text{in}} - E_{\text{out}} = \underbrace{(Q_{\text{in}} - Q_{\text{out}})}_{\text{Heat Transfer}} + \underbrace{(W_{\text{in}} - W_{\text{out}})}_{\text{Work Transfer}} + \underbrace{(E_{\text{mass,in}} - E_{\text{mass,out}})}_{\text{Mass Transfer}} = \Delta E_{\text{system}}$$

$$\Delta E = \Delta U + \Delta \text{KE} + \Delta \text{PE}$$

$$\Delta U = m(u_2 - u_1)$$

$$\Delta \text{KE} = \tfrac{1}{2} m(V_2^2 - V_1^2)$$

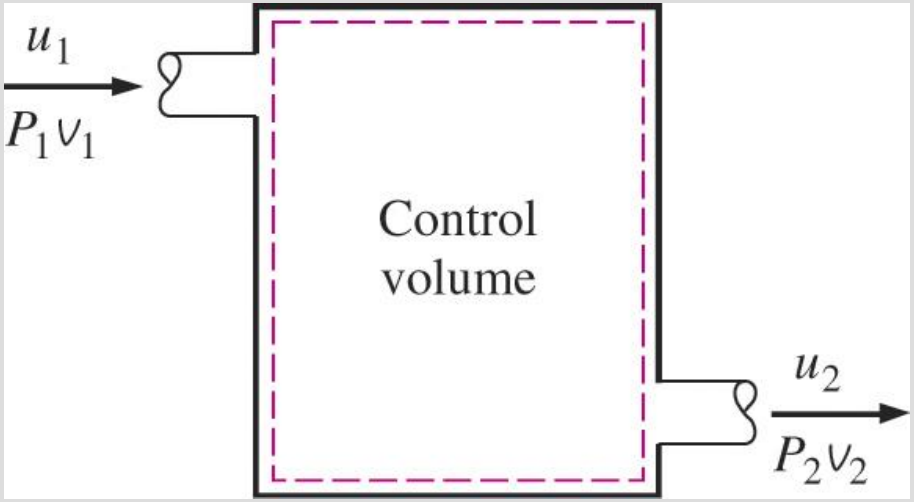
$$\Delta \text{PE} = mg(z_2 - z_1)$$

Enthalpy

- There is an important property called ***Enthalpy***
- Enthalpy is a combination property
- Enthalpy is frequently encountered in the analysis of control volumes

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

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

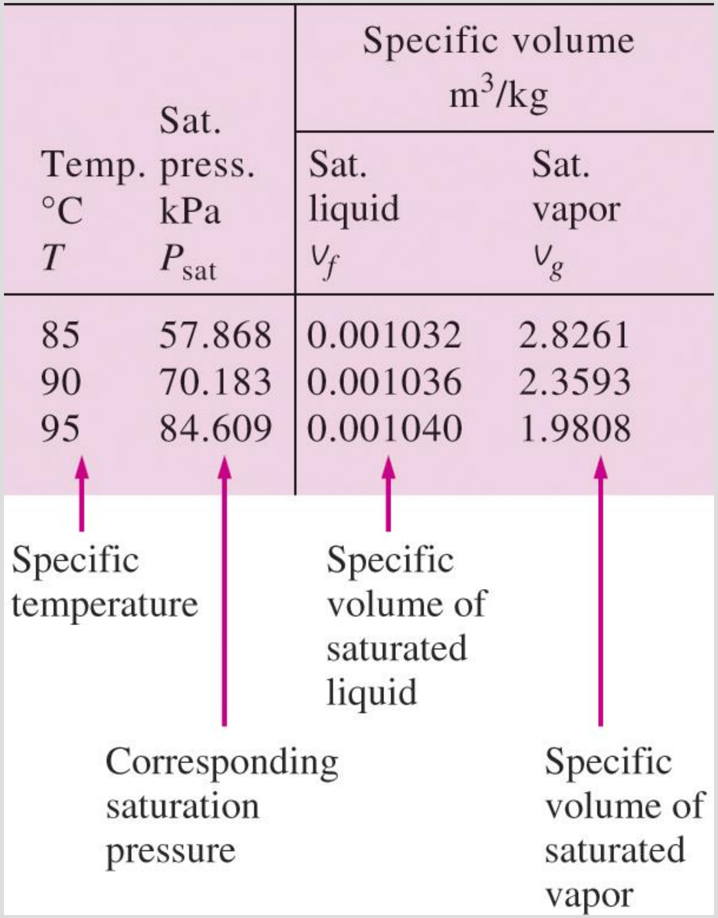


Property Tables

- For most substances, the relationships among thermodynamic properties are too complex to be expressed by simple equations.
- Properties are frequently presented in the form of tables.
- Some thermodynamic properties can be measured easily.
- Other properties are calculated by using the relations between them and measurable properties.

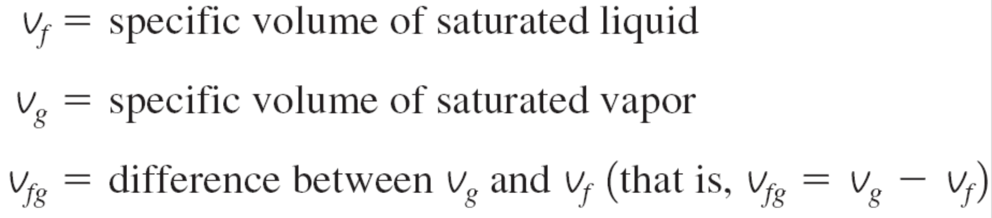
Saturated Liquid and Saturated Vapor States

Table A-4
Saturated Water
Temperature Table



Temp. °C T	Sat. press. kPa P_{sat}	Specific volume m³/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

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

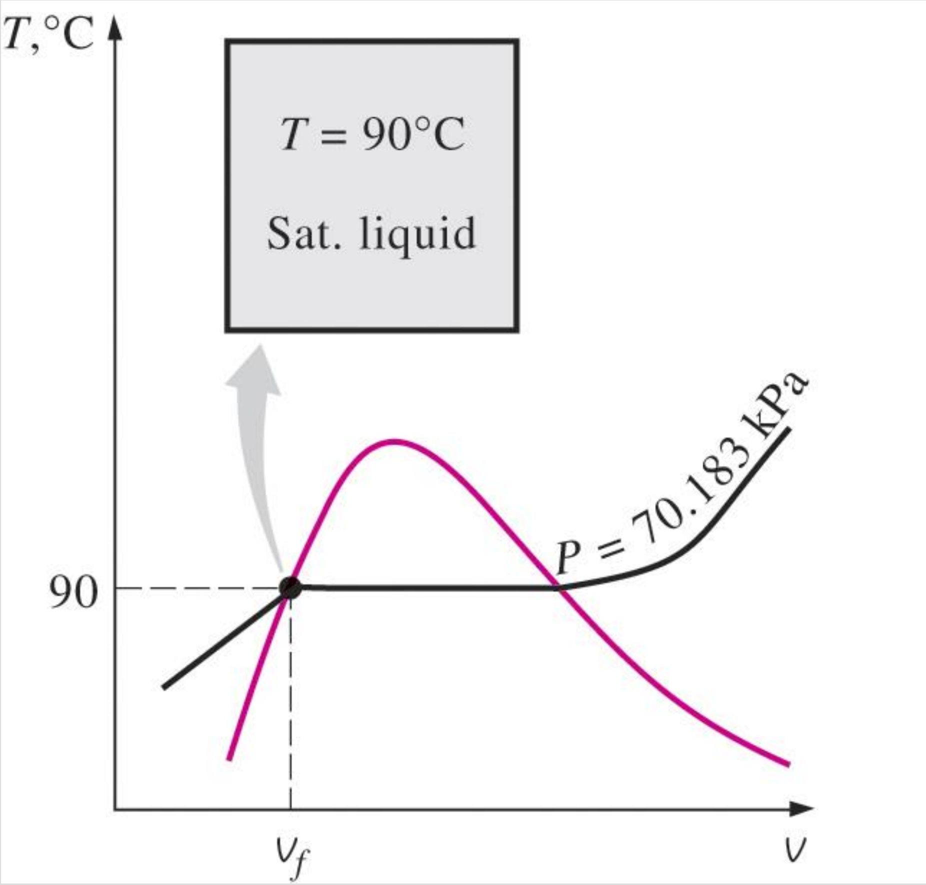


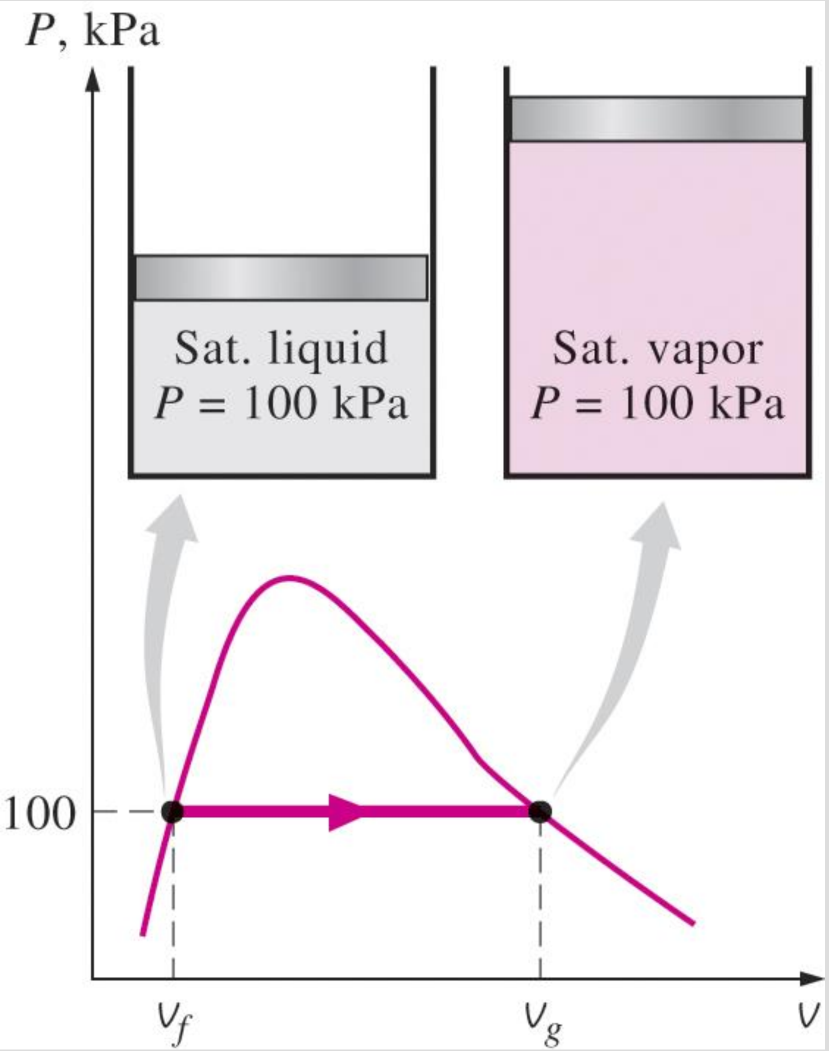
v_f = specific volume of saturated liquid
v_g = specific volume of saturated vapor
v_{fg} = difference between v_g and v_f (that is, $v_{fg} = v_g - v_f$)

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.

- Other properties (*u*, *h*, *s*) at the saturated liquid and saturated vapor state are found in the same manner.

Saturated Liquid and Saturated Vapor States

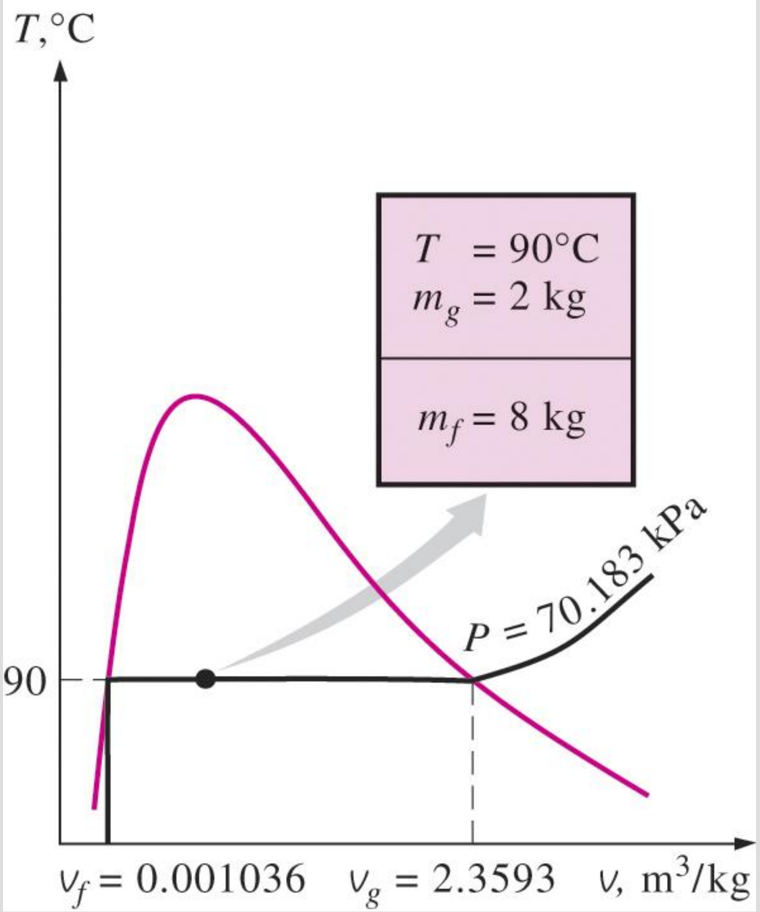


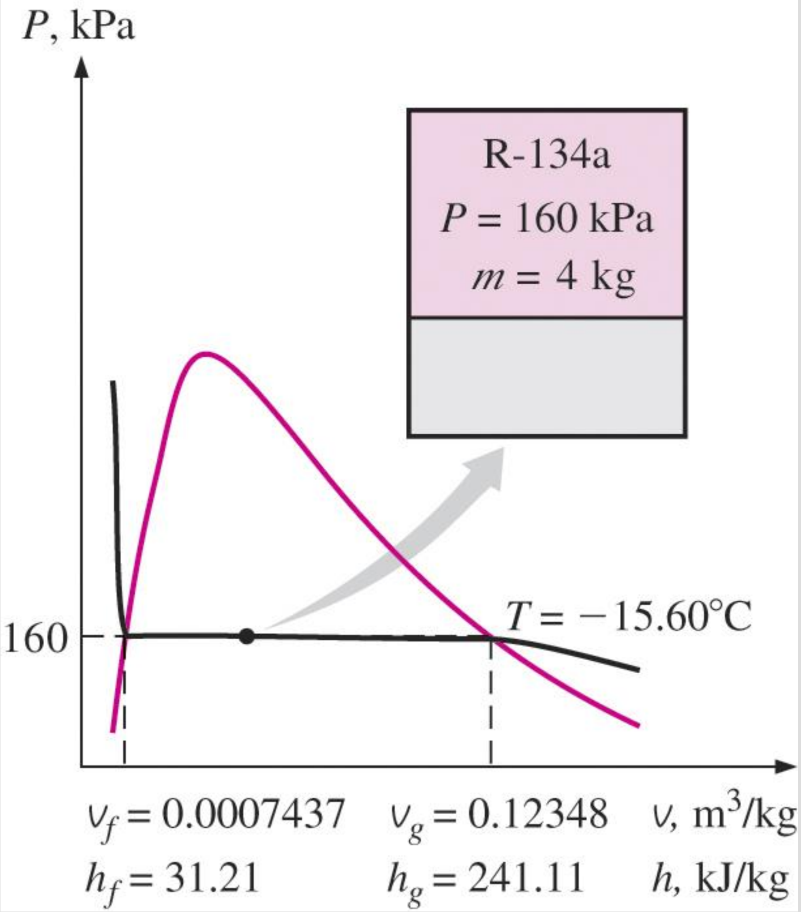


Saturated Liquid–Vapor Mixture

- During boiling, the temperature of a substance remains the same.
- This means that pressure and temperature are not independent during this period.
- Pressure and temperature cannot be used to specify the state in this case.
- Other properties are needed, e.g. v, u, or h
- How do we find v, u, or h?

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



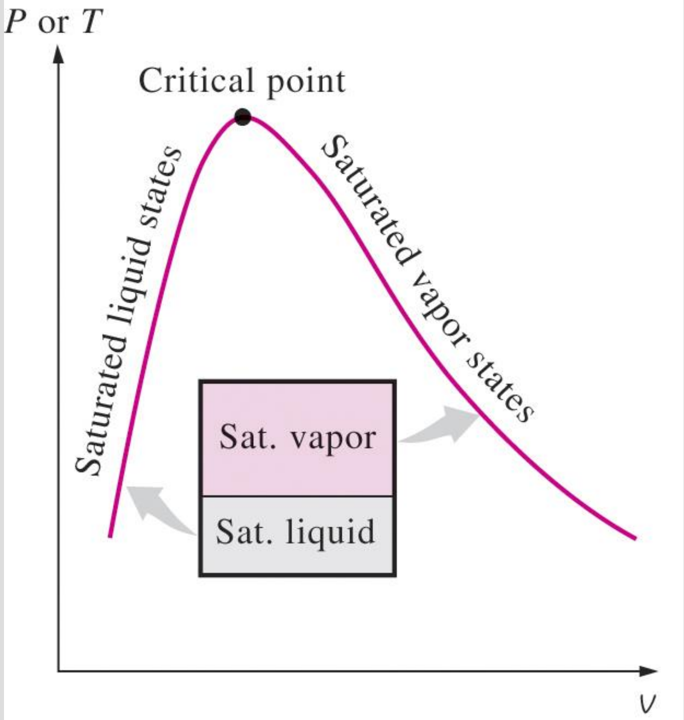


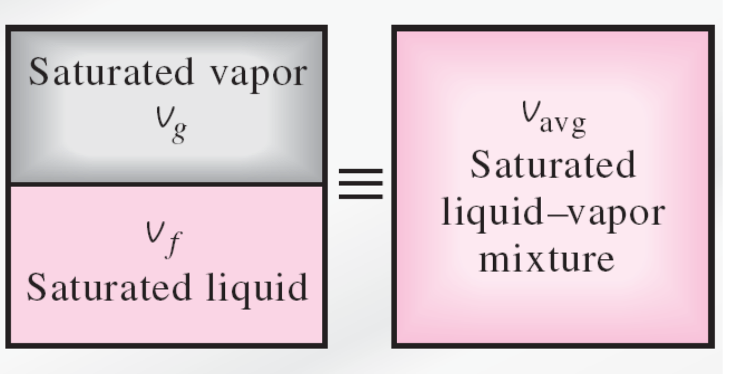
Saturated Liquid–Vapor Mixture

Important observation

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

- When an overall *v*, *u*, or *h* is found for the mixture, it is an average value.





Saturated Liquid–Vapor Mixture

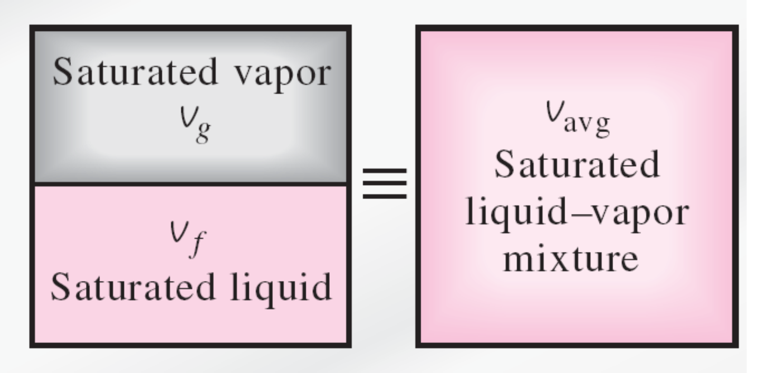
$$m_{\text{total}} = m_{\text{liquid}} + m_{\text{vapor}}$$

$$V = m_{\text{liquid}}\, v_f + m_{\text{vapor}}\, v_g$$

$$m_{\text{total}} v_{\text{avg}} = m_{\text{liquid}}\, v_f + m_{\text{vapor}}\, v_g$$

$$m_{\text{total}}\ \ v_{\text{avg}} = \left(m_{\text{total}} - m_{\text{vapor}}\right) v_f + m_{\text{vapor}}\, v_g$$

$$v_{avg} = \left(1 - \frac{m_{\text{vapor}}}{m_{\text{total}}}\right) v_f + \frac{m_{\text{vapor}}}{m_{\text{total}}}\ v_g$$



Saturated Liquid–Vapor Mixture

$$v_{avg} = \left(1 - \frac{m_{\text{vapor}}}{m_{\text{total}}}\right) v_f + \frac{m_{\text{vapor}}}{m_{\text{total}}} \, v_g$$

- The term $\frac{m_{\text{vapor}}}{m_{\text{total}}}$ is called ***quality*** and is denoted by ***x***

  $0 \leq x \leq 1$
- When $x = 0$ → saturated liquid
- When $x = 1$ → saturated vapor

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

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

Saturated Liquid–Vapor Mixture

- The same approach can be used to find other properties:

$$u_{avg} = u_f + x\,u_{fg}$$

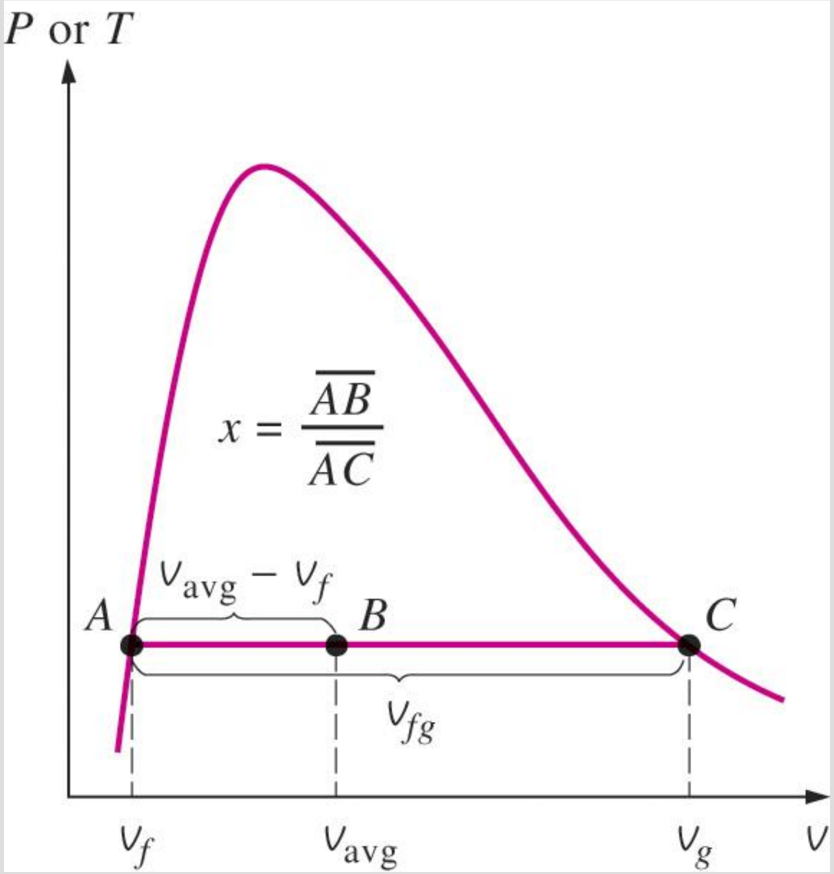
$$h_{avg} = h_f + x\,h_{fg}$$

- If v_{avg}, u_{avg}, or h_{avg} is given, x can be deduced:

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

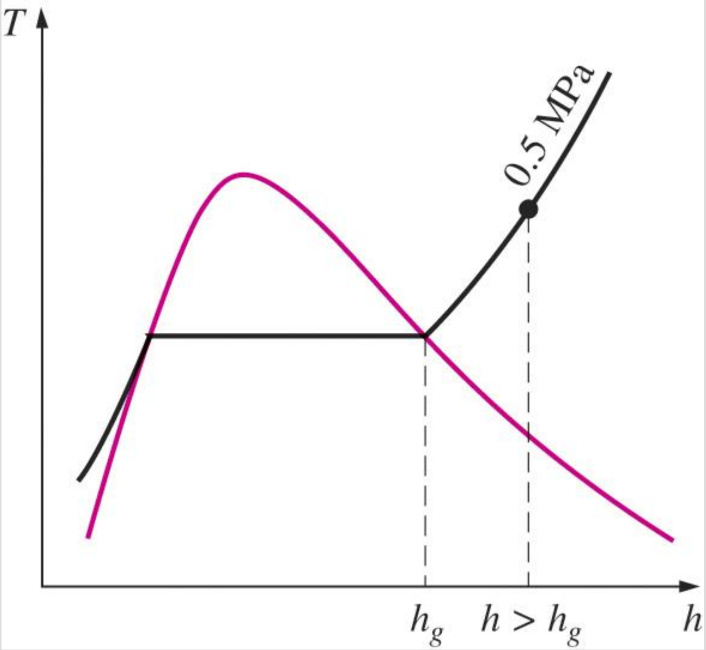
$$x = \frac{u_{\text{avg}} - u_f}{u_{fg}}$$

$$h \qquad - h$$



Superheated Vapor

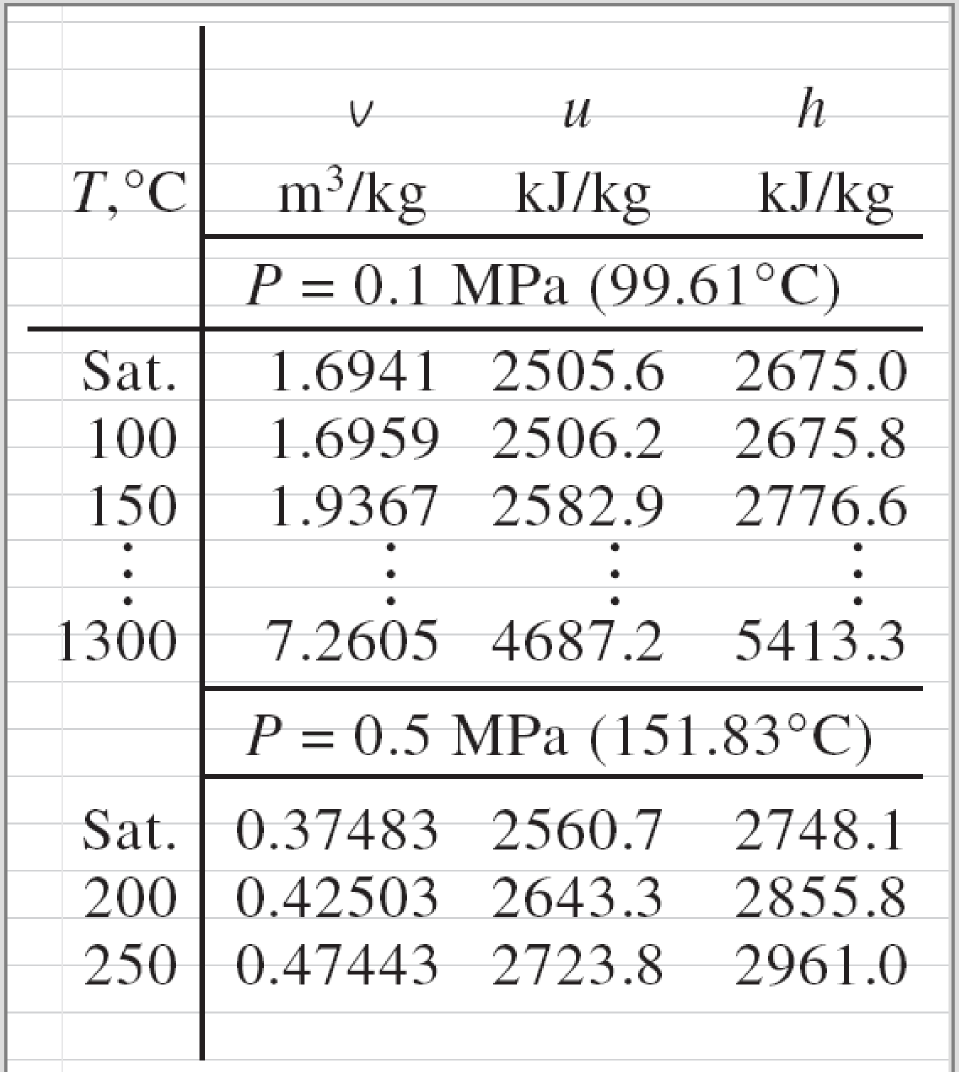
- In the region to the right of the saturated vapor line, a substance exists as superheated vapor.
- In this region, temperature and pressure are independent properties.



- The superheated region is characterized by:
  - **Higher temperatures ($T > T_{sat}$ 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)**

Superheated Vapor

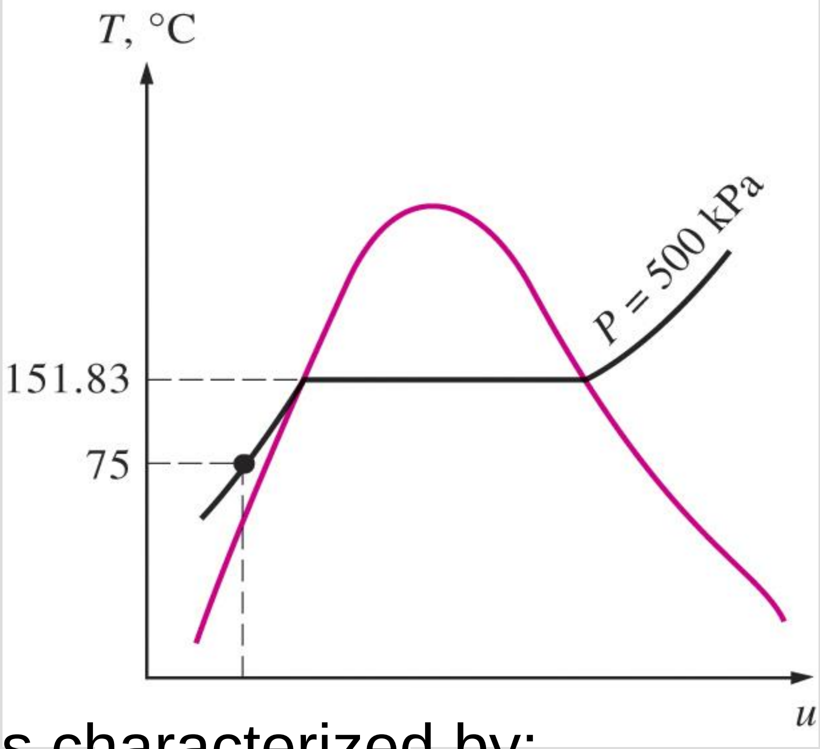
Table A-6
Superheated water



T,°C	v m^3/kg	u kJ/kg	h 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

Compressed Liquid

- In the region to the left of the saturated liquid line, a substance exists as compressed liquid.
- In this region, temperature and pressure are independent properties.



- The compressed liquid region is characterized by:
  - **Lower temperatures ($T < T_{sat}$ 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)**

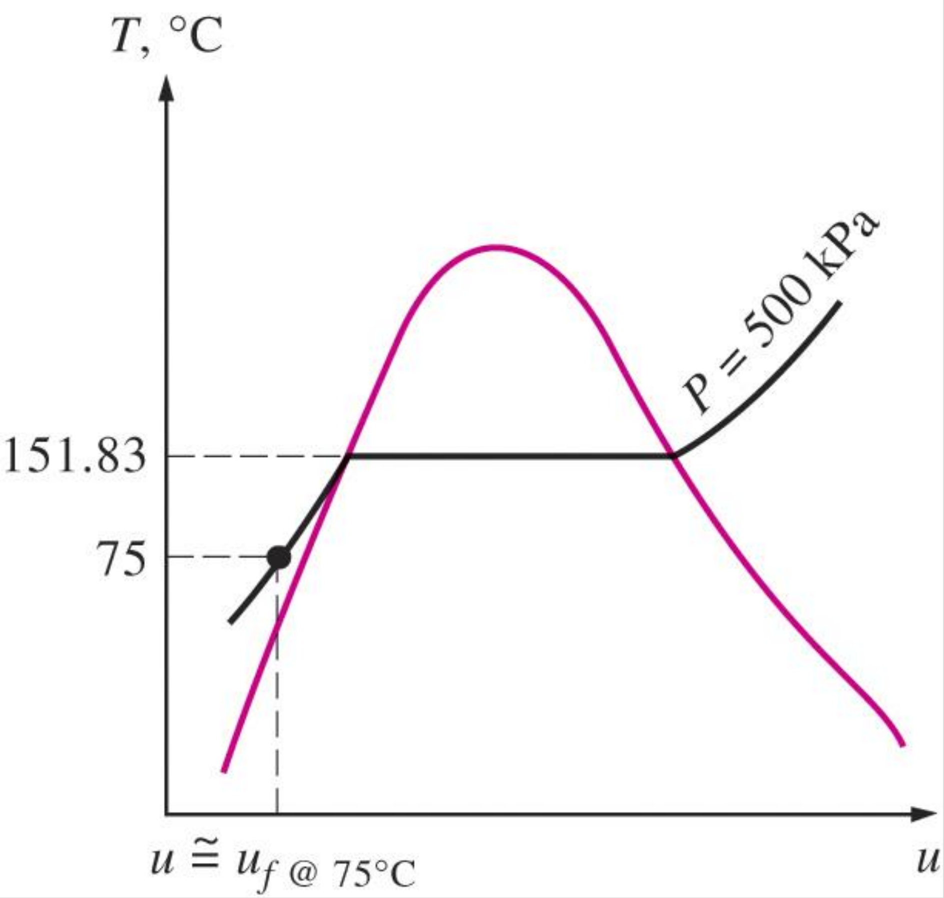
Compressed Liquid

- There is a table for the compressed liquid region.
- Data is very limited.
- A good approximation is given by:

$v \approx v_f$ at given T

$u \approx u_f$ at given T

$h \approx h_f$ at given T



Property Tables of Other Substances

- There are property tables for substances other than water.
- For example, tables for refrigerant 134a (R-134a) are listed in a number of textbooks.
- R-134a is a common refrigerant in many commercial air conditioners.

Identification of Phase

If P and T are given

- Find T_{sat} corresponding to P
- If $T > T_{sat}$: superheated vapor
- If $T < T_{sat}$: compressed liquid
- If $T = T_{sat}$: saturated (but additional information is needed)

Identification of Phase

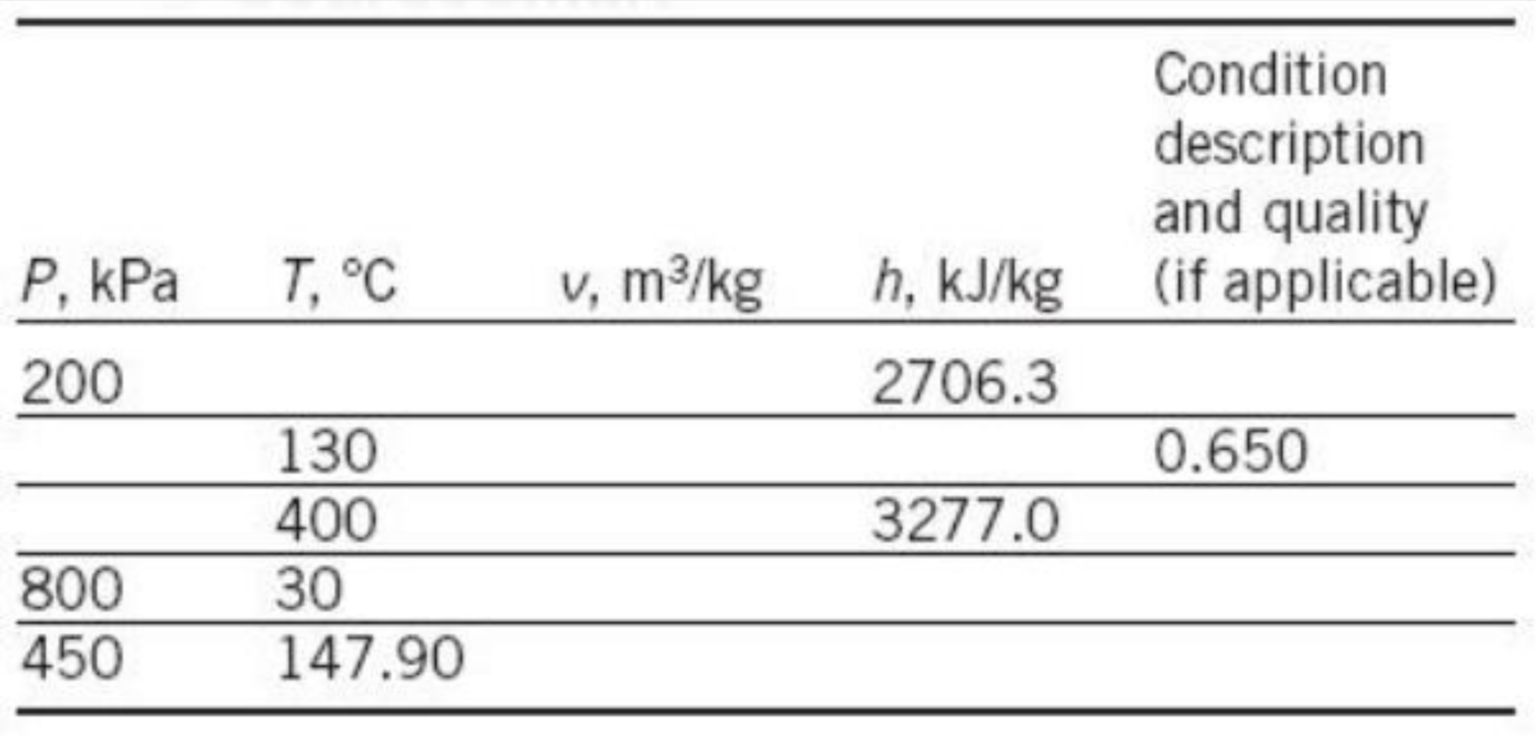
If (P or T) and v are given

- Find v_f and v_g corresponding to P or T
- If $v > v_g$: superheated vapor
- If $v < v_f$: compressed liquid
- If $v_f < v < v_g$: saturated liquid vapor mixture

The same procedure applies if u or h is given (instead of v)

Example

- Fill the missing information for water.



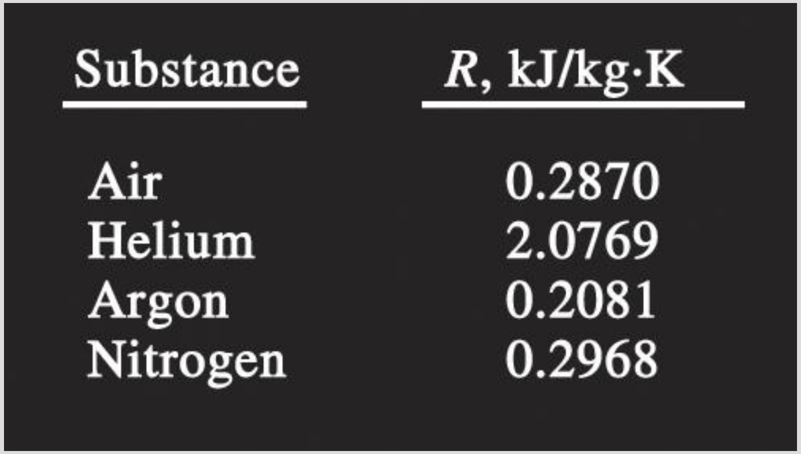
P, kPa	T, °C	v, m^3/kg	h, kJ/kg	Condition description and quality (if applicable)
200			2706.3	
	130			0.650
	400		3277.0	
800	30			
450	147.90			

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.



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

THE GAS CONSTANT

$$Pv = RT$$

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

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

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

OTHER EXPRESSIONS OF THE IDEAL-GAS EQUATION OF STATE

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

Mass = Molar mass × Mole number

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

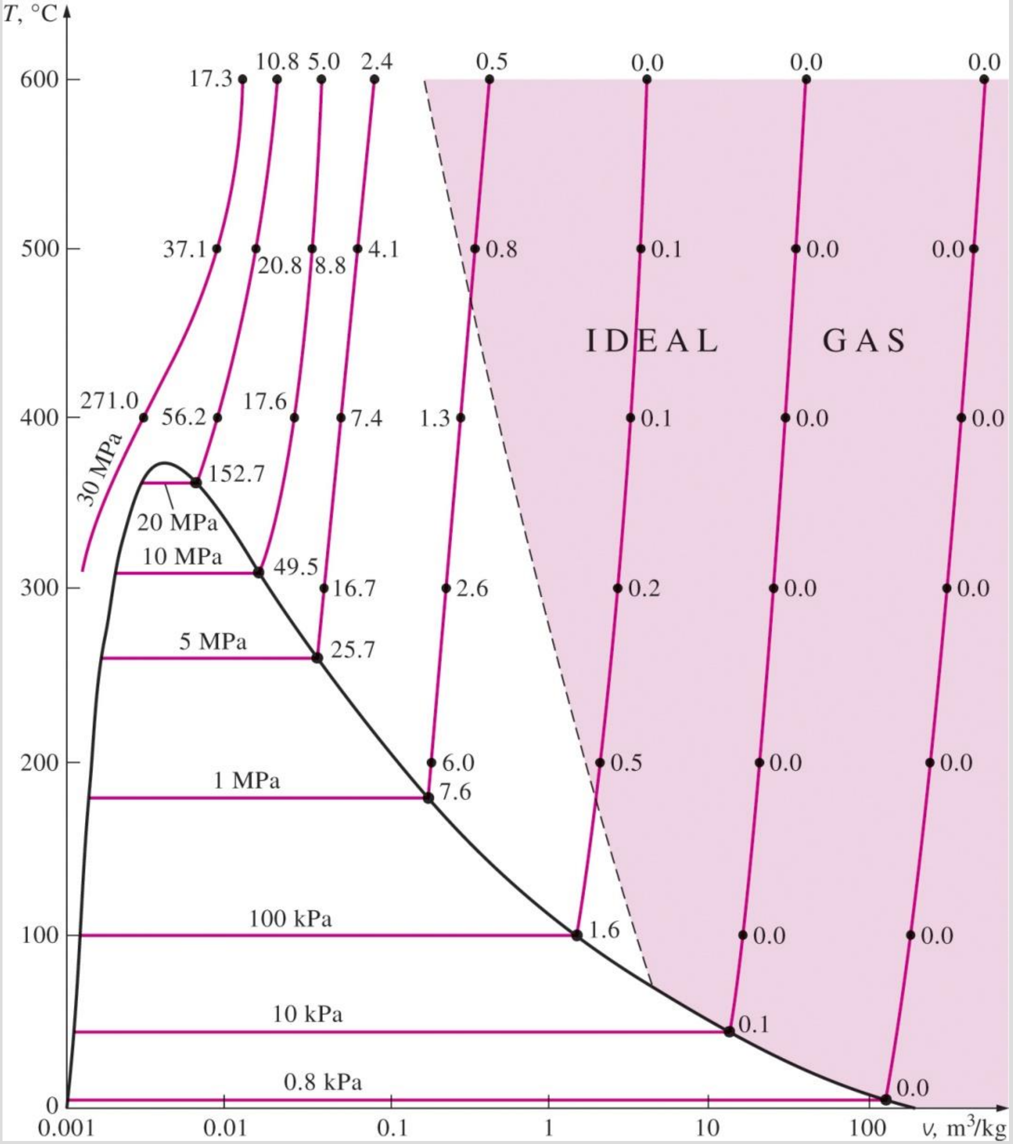
$$mR = (MN)R = NR_u \longrightarrow \boxed{PV = NR_uT}$$

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.



Percentage of error ($[|v_{table} - v_{ideal}|/v_{table}] \times 100$)

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.

$$Pv = ZRT$$

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

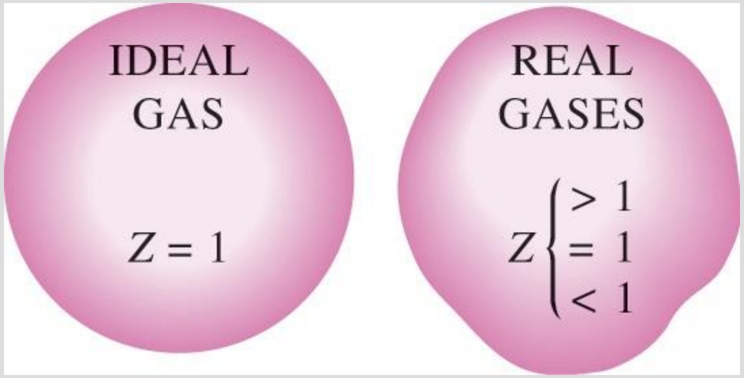
$$Z = \frac{v_{\text{actual}}}{v_{\text{ideal}}}$$

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

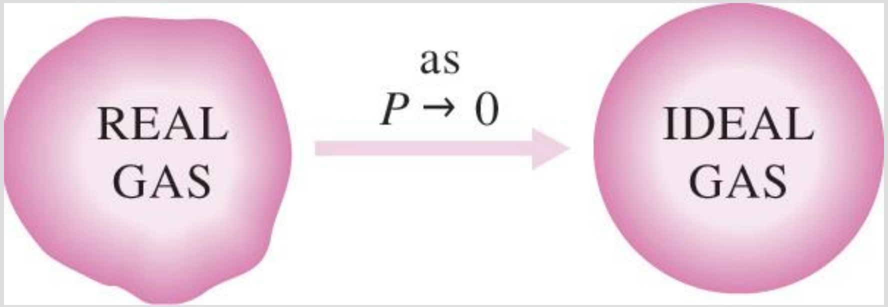
Gases behave as an ideal gas at low densities (i.e., low pressure, high temperature).

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

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

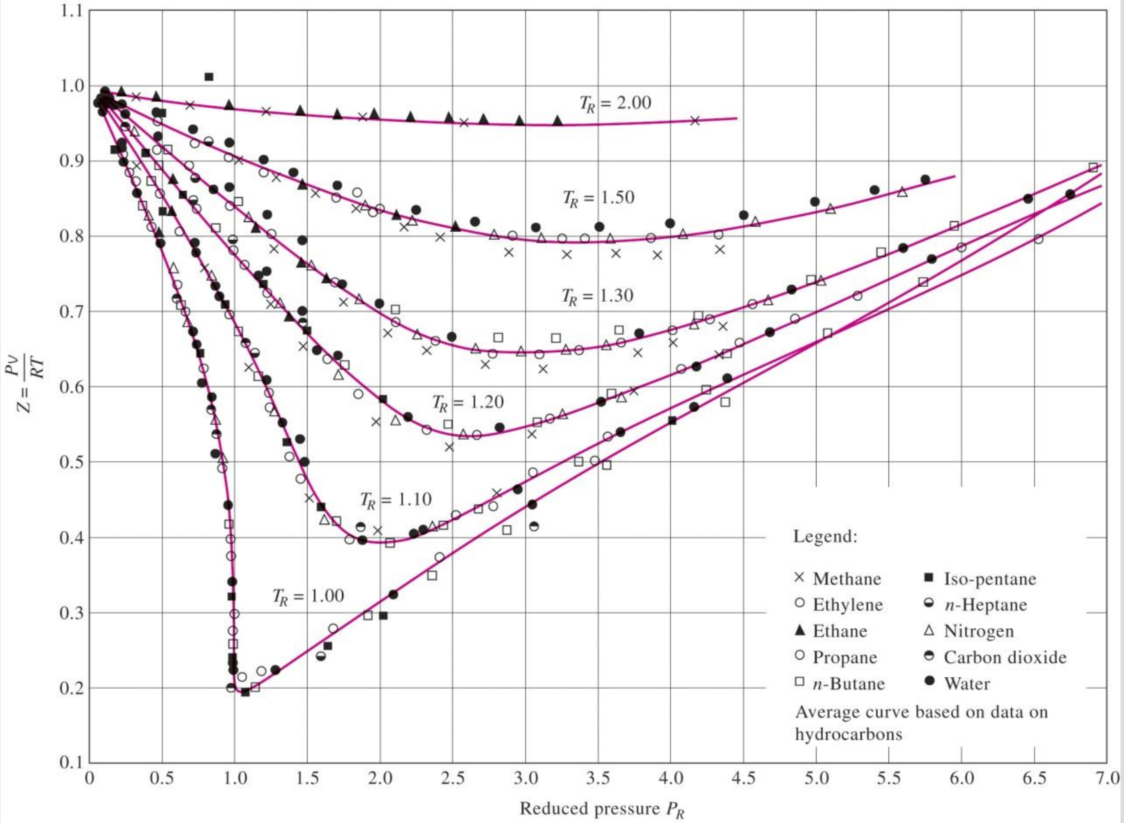
Reduced temperature

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

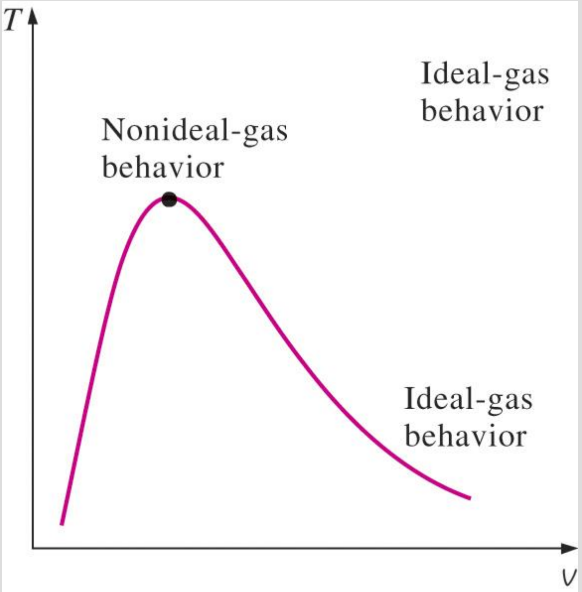
Pseudo-reduced specific volume

$$\left.\begin{array}{l} P_R = \dfrac{P}{P_{cr}} \\ \\ v_R = \dfrac{v}{RT_{cr}/P_{cr}} \end{array}\right\} \begin{array}{l} Z = \ldots \\ \text{(Fig. A–15)} \end{array}$$

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
Berthelet
Redlich-Kwang
Beattie-Bridgeman
Benedict-Webb-Rubin
Strobridge
Virial

Van der Waals Equation of State

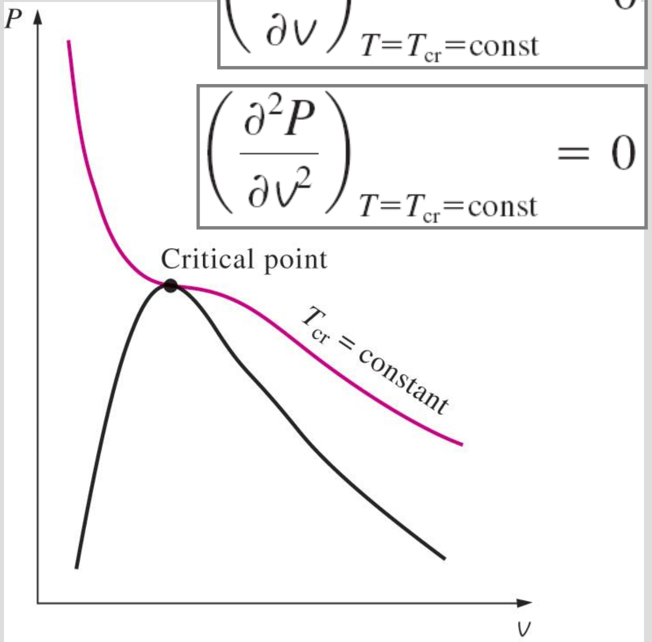
$$\left(P + \frac{a}{v^2}\right)(v - b) = RT$$

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

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

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

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



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

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

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

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

Benedict-Webb-Rubin Equation of State

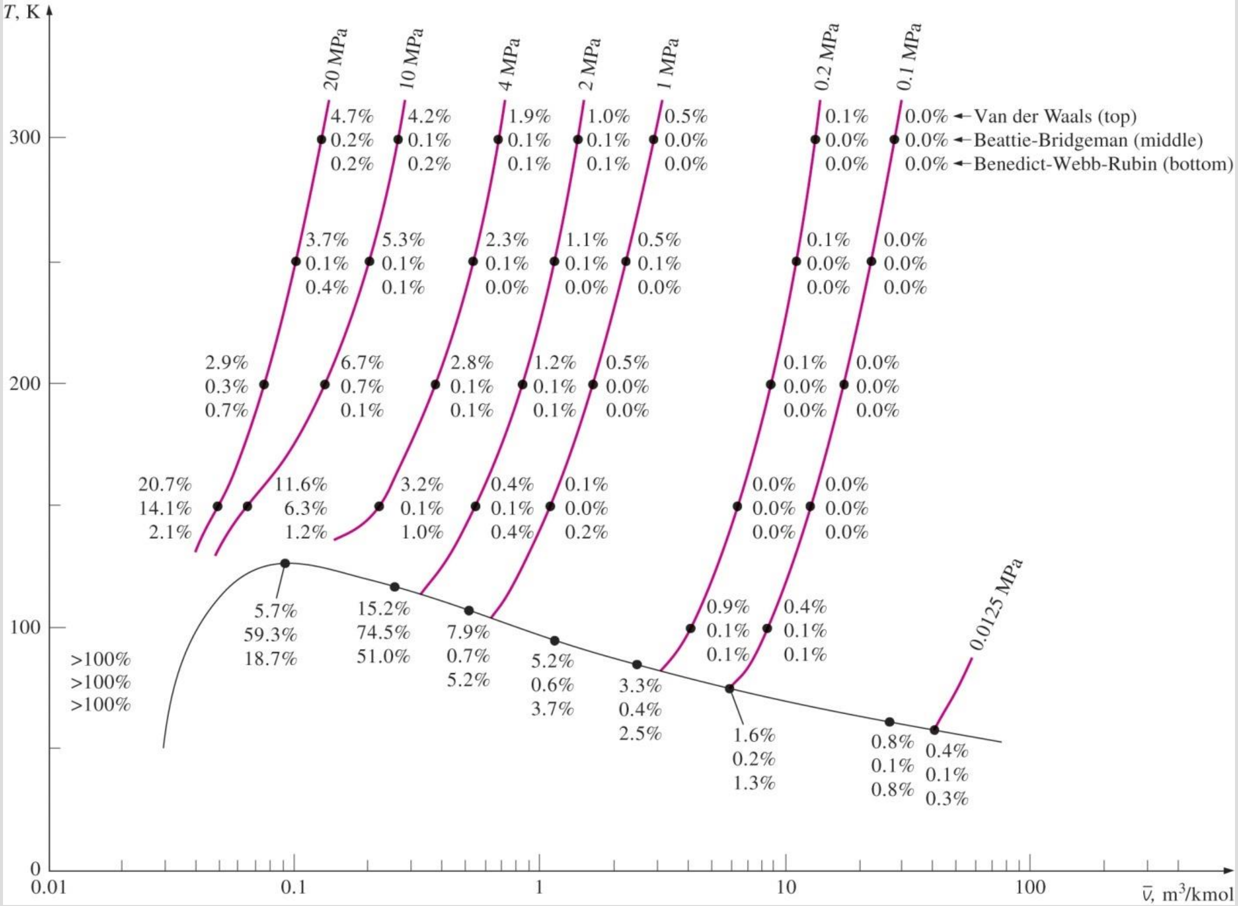
$$P = \frac{R_u T}{\overline{v}} + \left(B_0 R_u T - A_0 - \frac{C_0}{T^2}\right)\frac{1}{\overline{v}^2} + \frac{bR_u T - a}{\overline{v}^3} + \frac{a\alpha}{\overline{v}^6} + \frac{c}{\overline{v}^3 T^2}\left(1 + \frac{\gamma}{\overline{v}^2}\right)e^{-\gamma/\overline{v}^2}$$

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

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

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



Percentage of error involved in various equations of state for nitrogen
(% error = $[(|v_{\text{table}} - v_{\text{equation}}|)/v_{\text{table}}] \times 100$).

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.