

Properties of Pure Substances

A Pure Substance

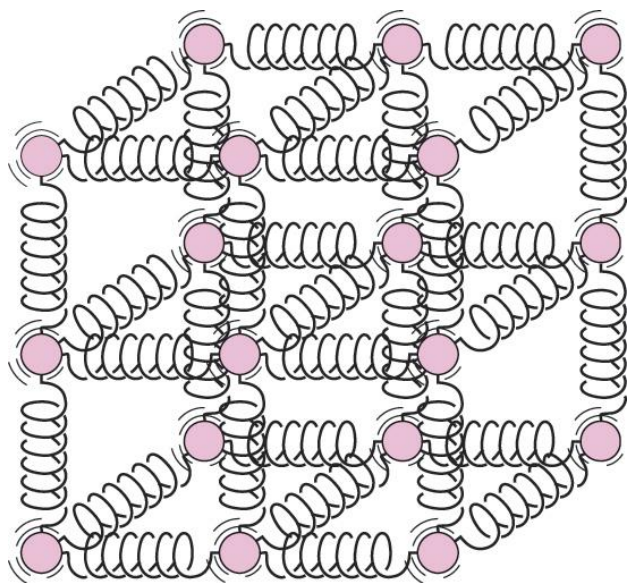
Is a substance that is chemically homogenous and fixed in chemical composition.(e.g. water, nitrogen, air & etc.)

→mixture of oil and water is not a pure substance.

→a mixture of two or more phases of a pure substance is still a pure substance.

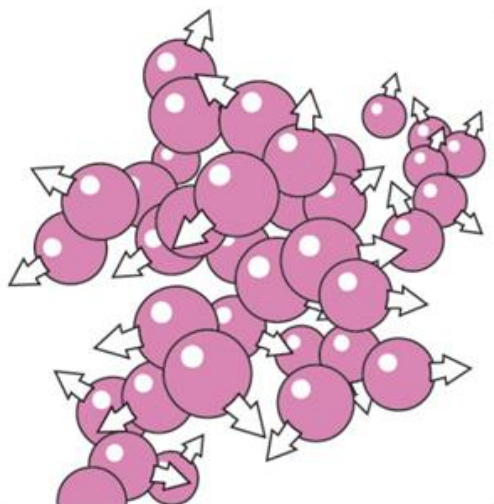
Phase of a Pure Substance

The phase of a substance is the homogeneous, chemical, and physical of aggregation of its molecules.

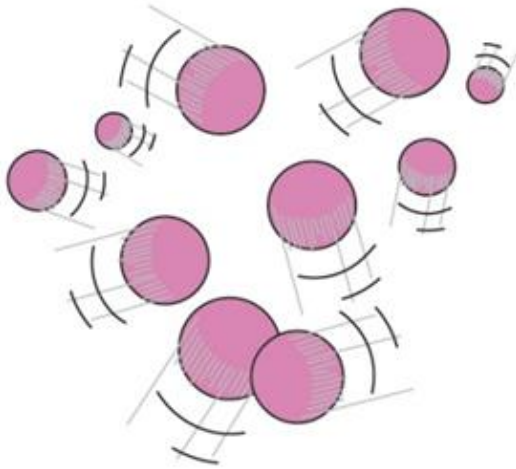


The molecules in a solid are kept at their positions by the large spring like inter-molecular forces.

At high temperature, molecules overcome the inter molecules forces and break away.



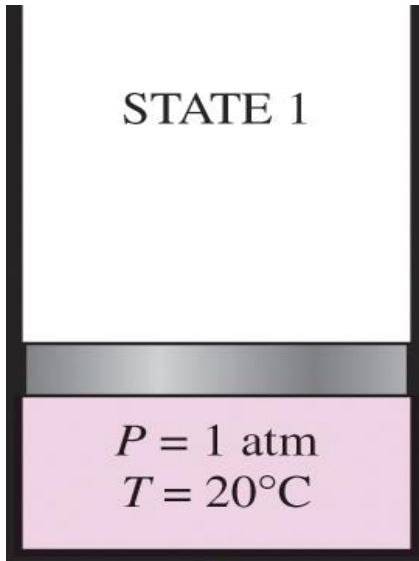
In the liquid phase the molecules are no longer at fixed positions, and chunks of the molecules float about each other.



In the gas phase the molecules are far apart from each other, irregular and move about at random colliding with each other. Molecules are higher energy level than they are in liquid or solid phases.

Phase Change of Pure Substances

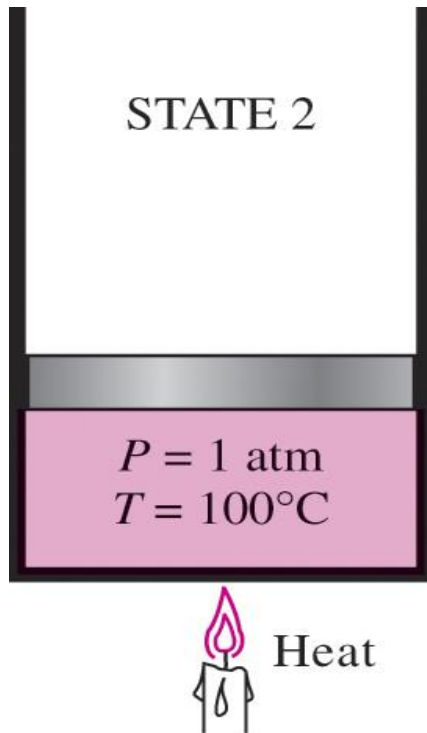
Attention will be focused on liquid and vapor phases in this section. All substances exhibit general behavior. Water will be used in the following example.



compressed liquid or subcooled liquid

At 1 atm and 20°C , water exists in the liquid phase(i.e. not about to vaporize).

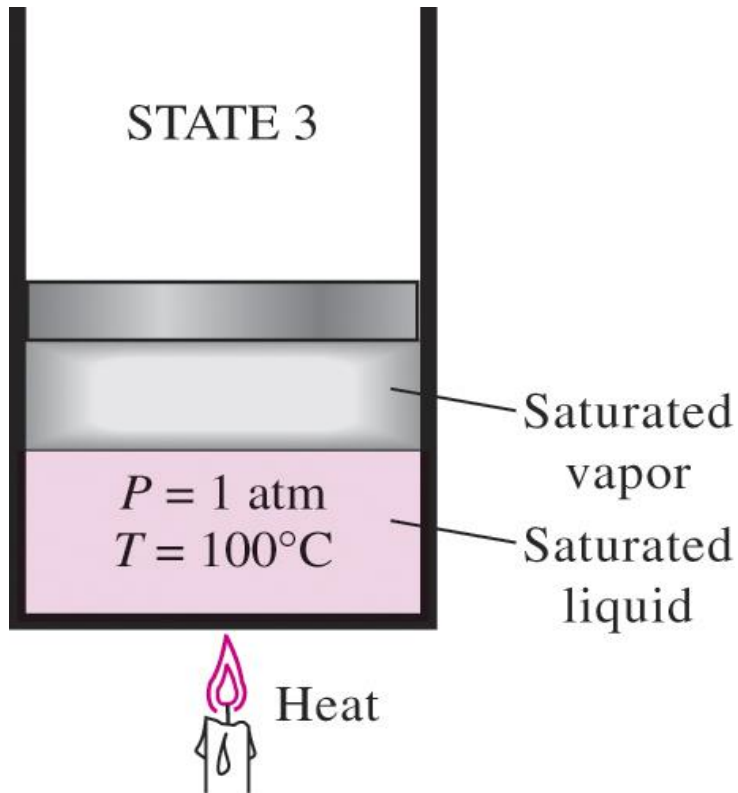
As heat added the temperature increases and water expands.(i.e. v increases)



Saturated liquid

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

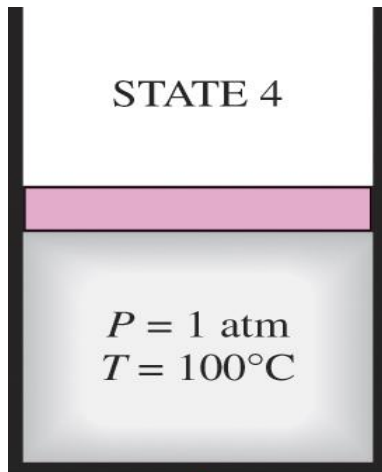
Any addition of heat will cause the phase change.



Saturated liquid–vapor mixture

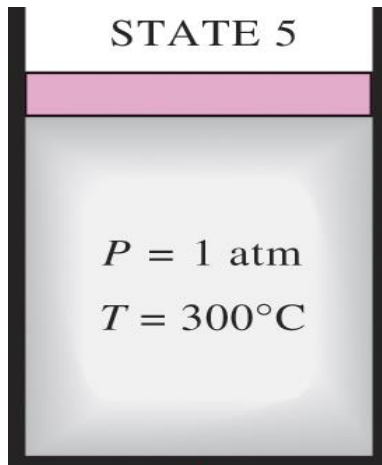
The state at which the liquid and vapor phases coexist in equilibrium.

Once boiling starts, the temperature will not rise until the liquid completely vaporizes.



Saturated vapor

A vapor that is *about to condense*.

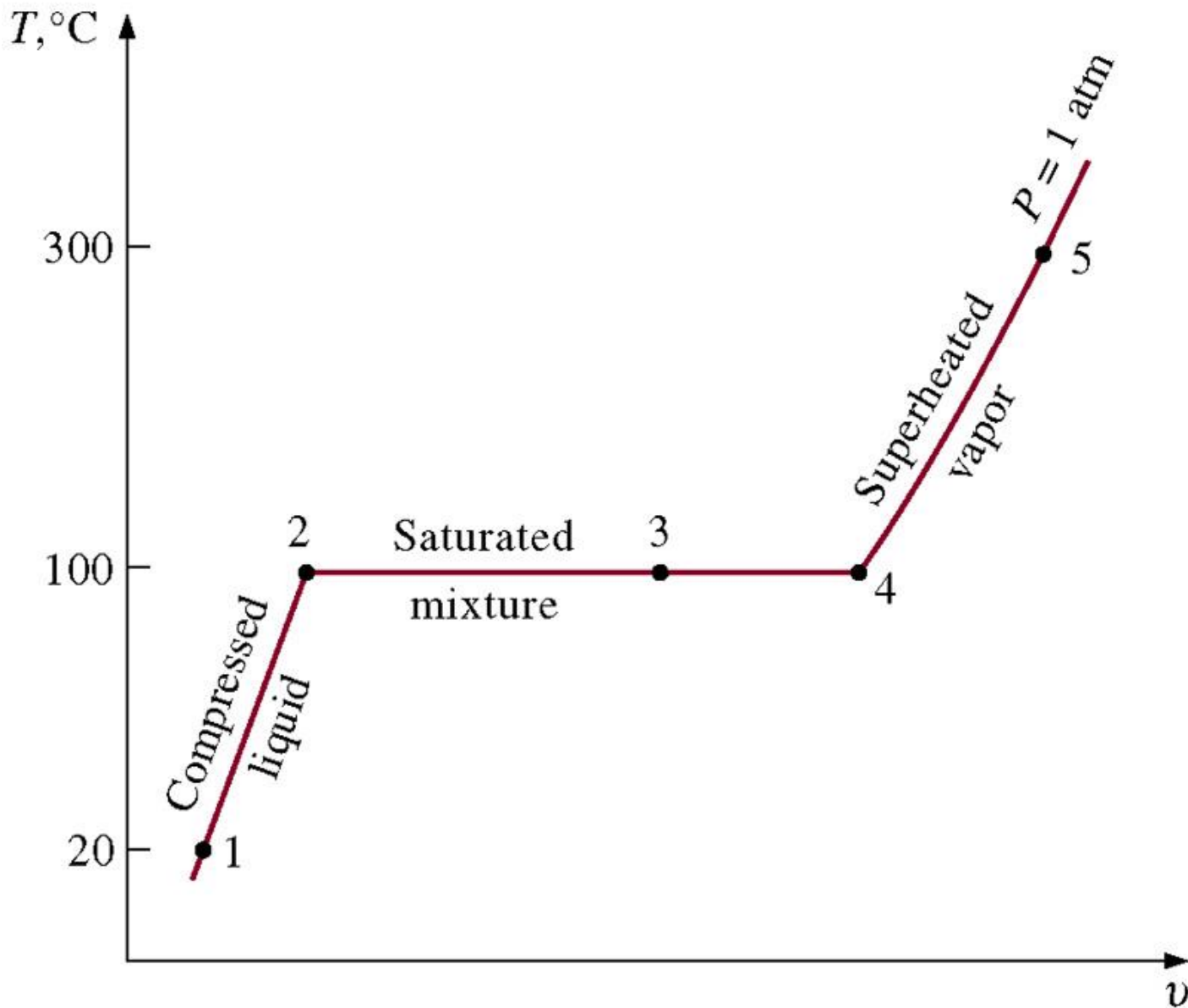


Superheated vapor

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

FIGURE 2-1

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



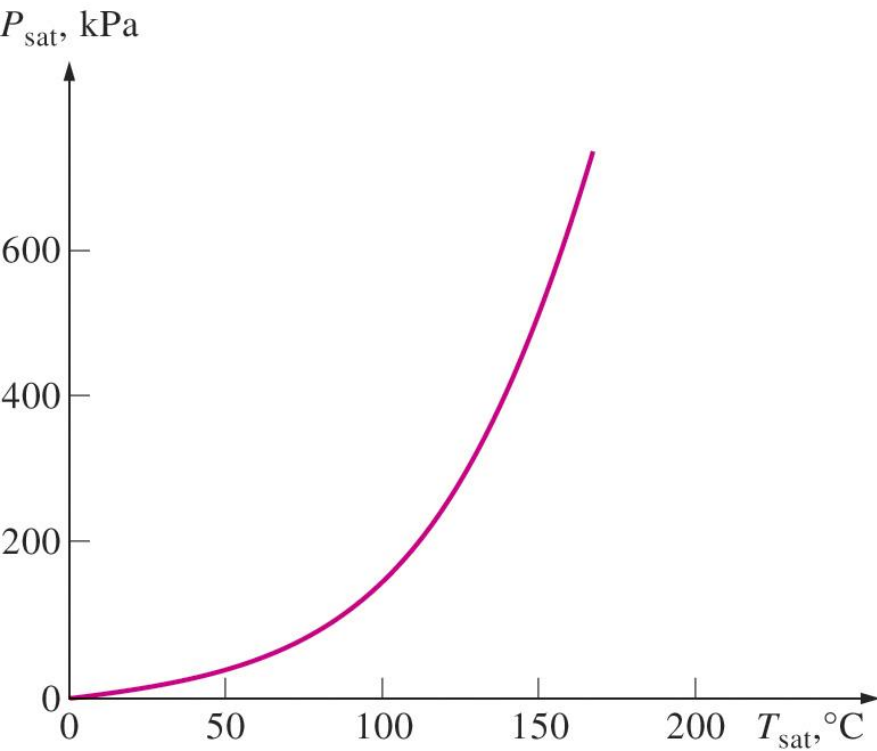


FIGURE 2-2 Liquid-vapor saturation curve

Holding the pressure constant at 1 atm, boiling takes place at 100°C. By changing the pressure we can change the boiling temperature of water.

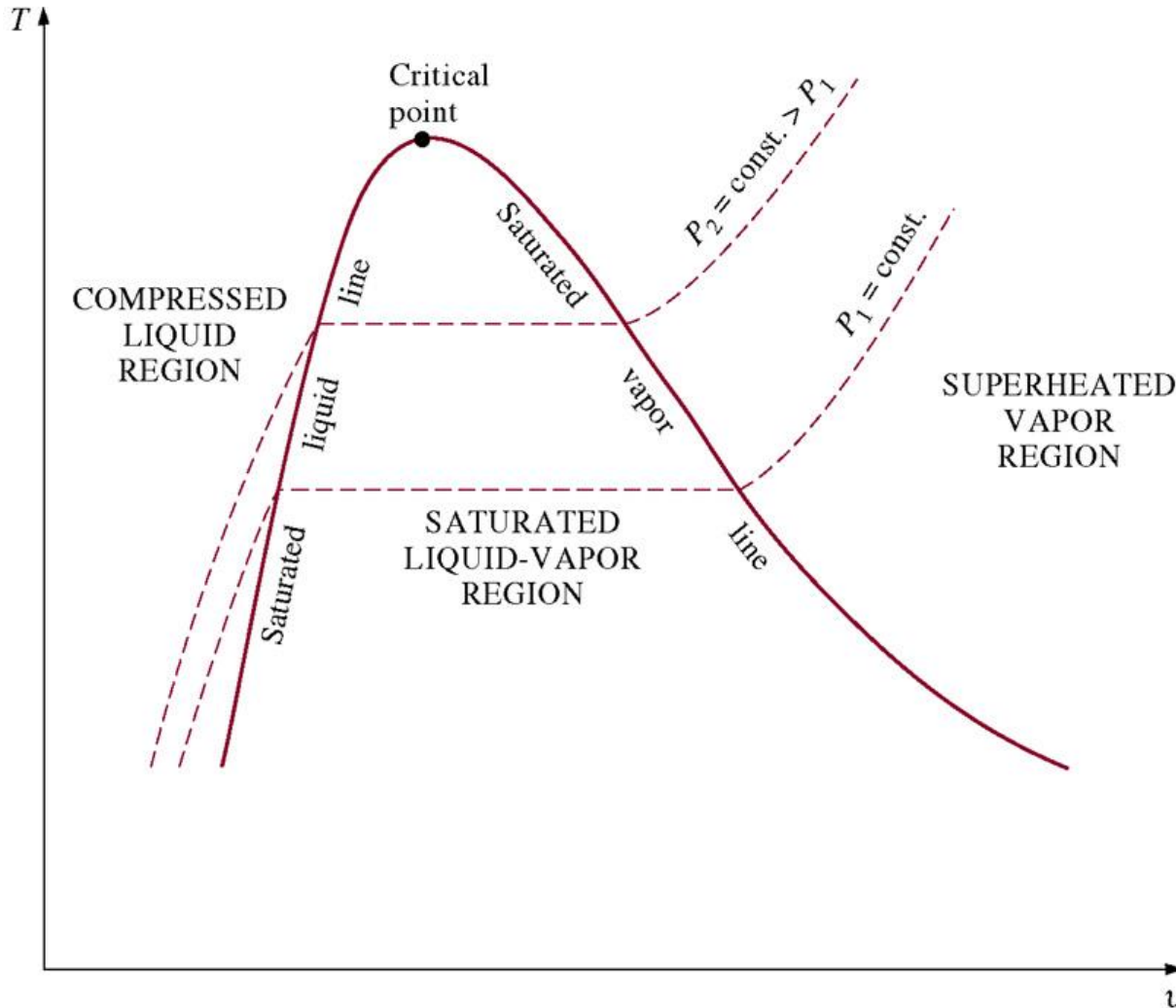
Saturation temperature T_{sat}

The temperature at which a pure substance starts boiling.

Saturation pressure P_{sat}

The pressure at which a pure substance starts boiling.

Property Diagrams for phase-Change Processes



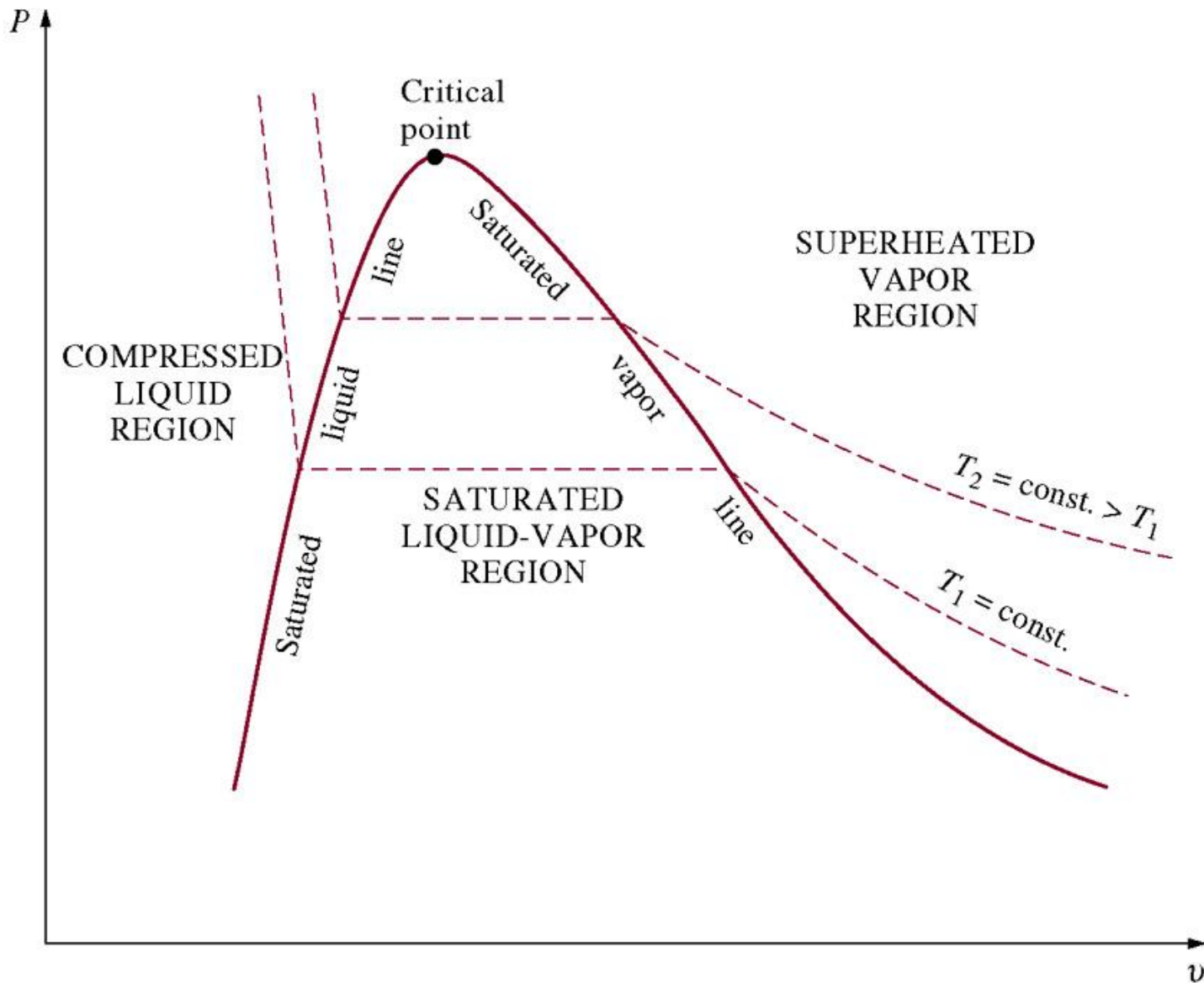
Critical point

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

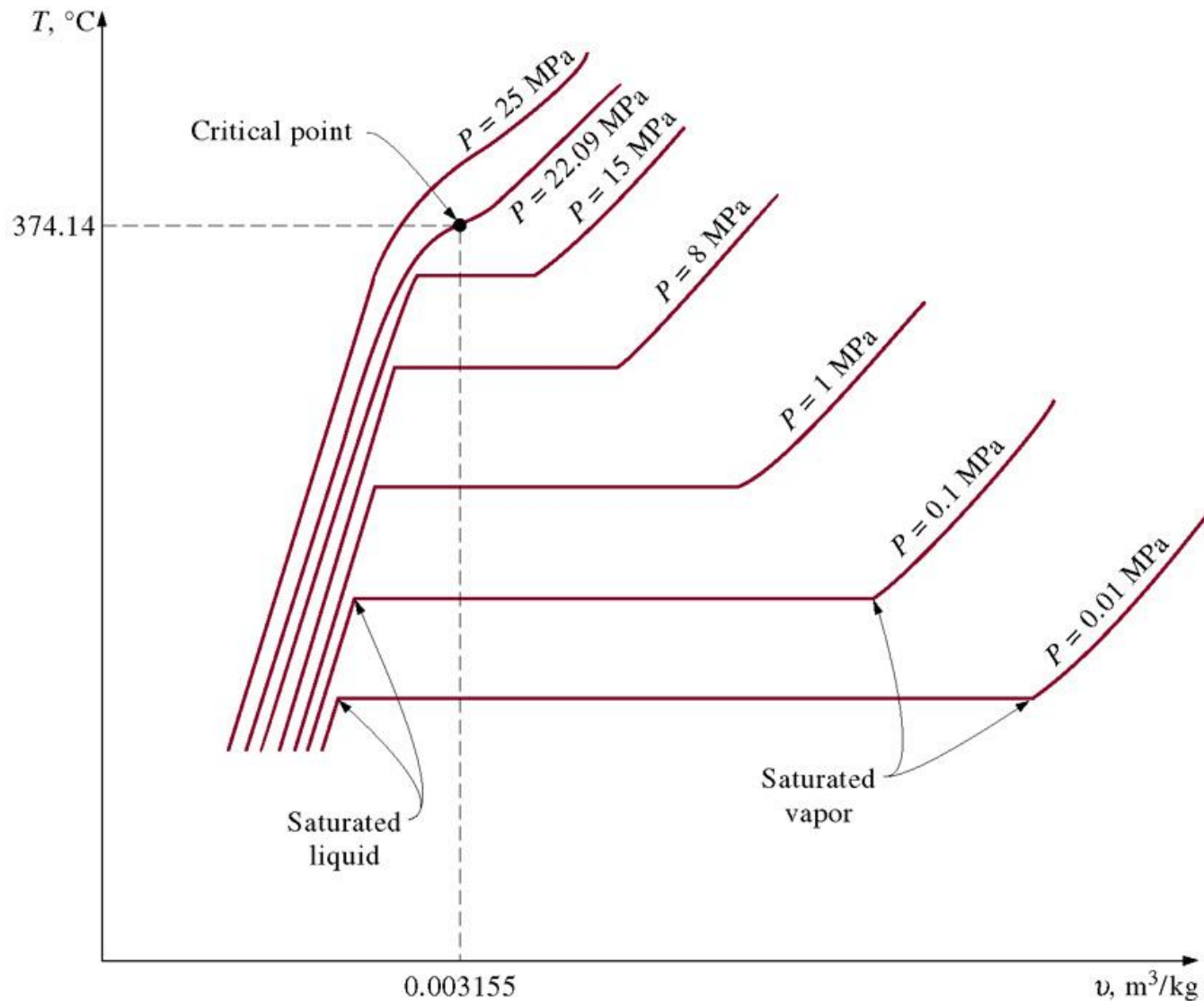
T_c is the maximum temperature at which liquid and vapor phases can co-exist in equilibrium.

FIGURE 2-3 T-V Diagram of a Pure Substance

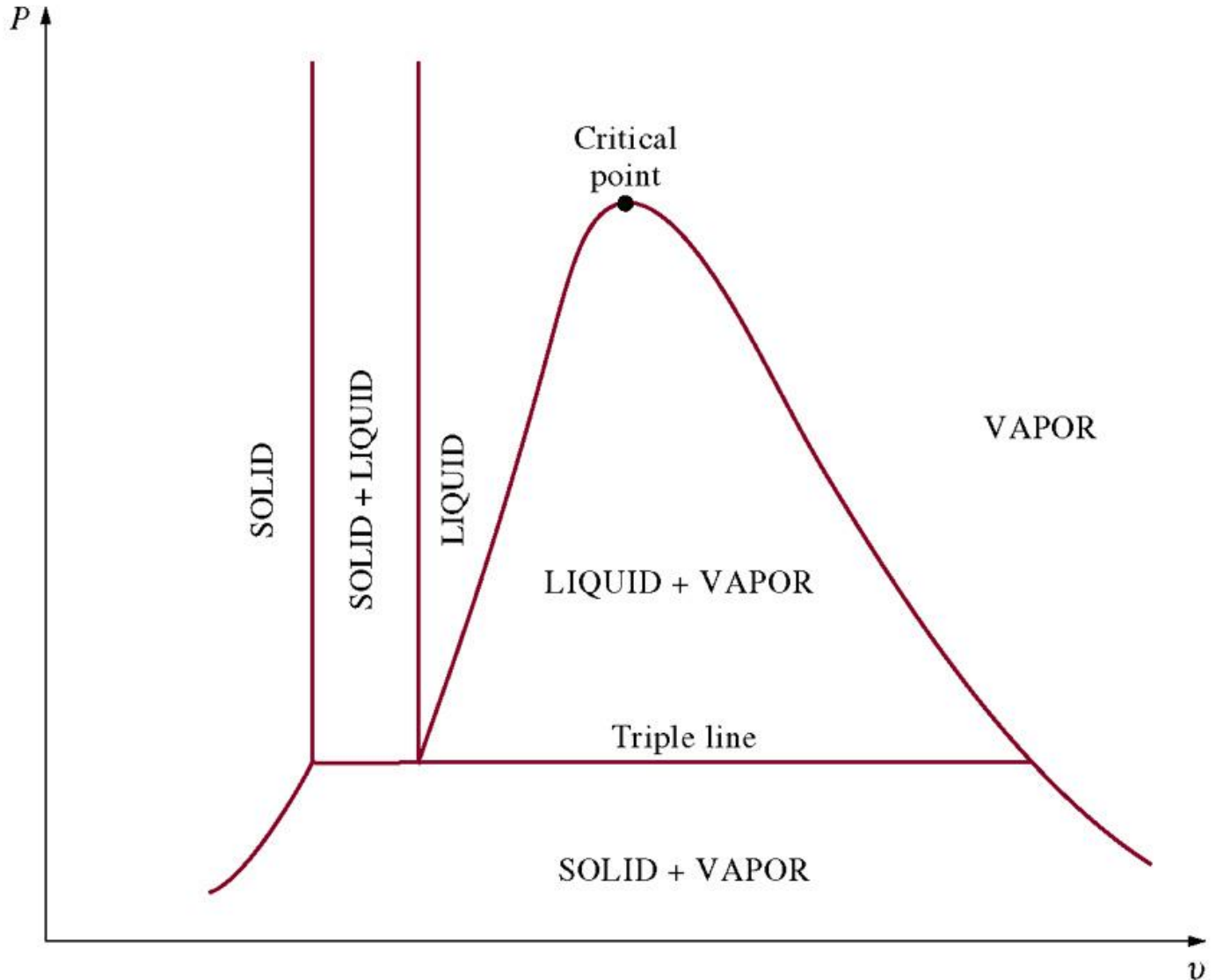
***P-v* diagram
of a pure
substance.**



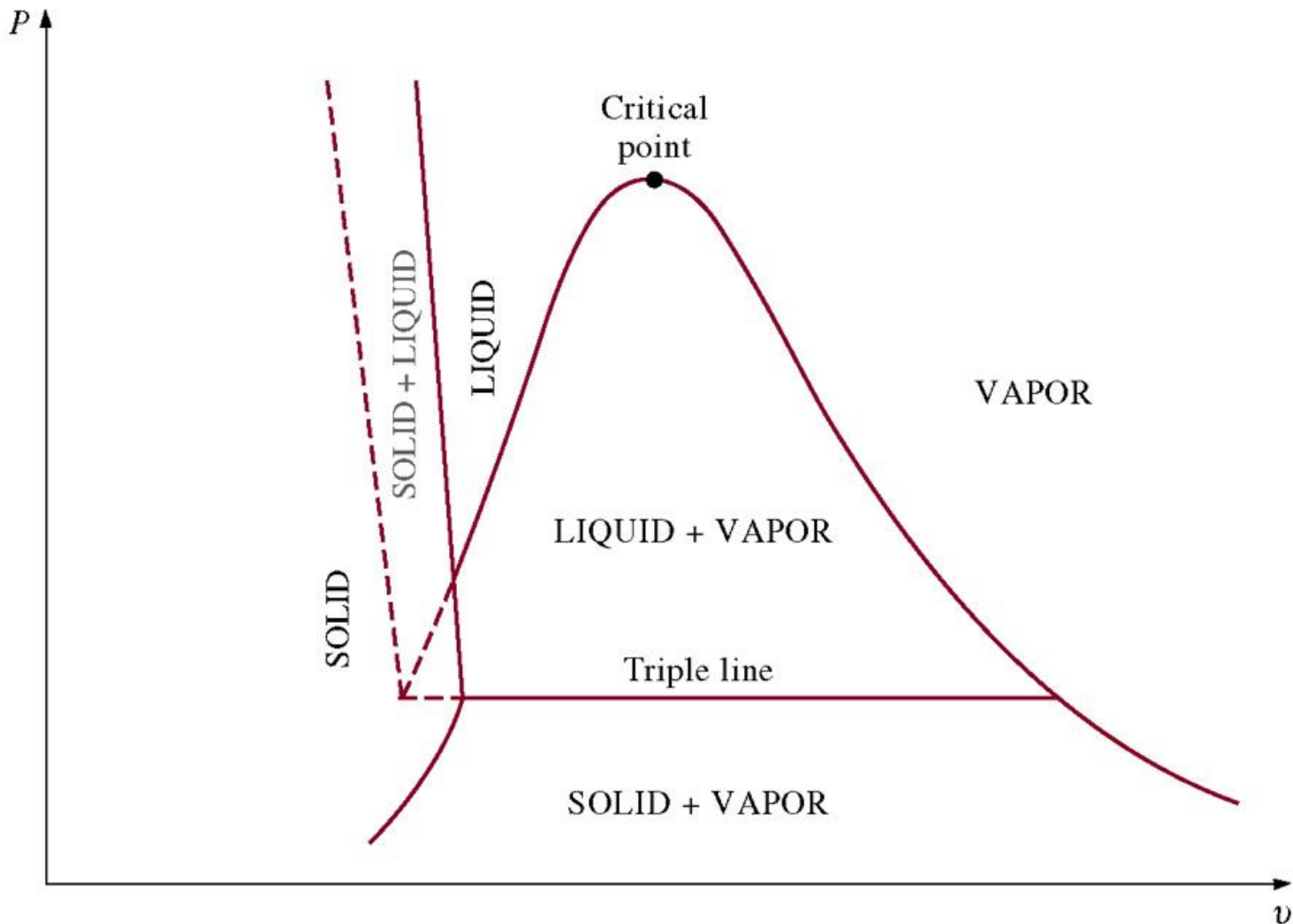
***T-v* diagram of constant-pressure phase-change processes of a pure substance at various pressures (numerical values are for water).**



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



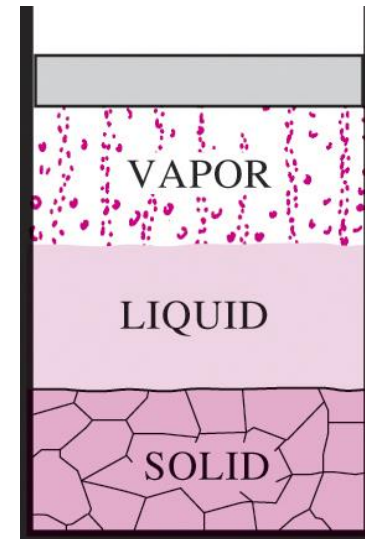
P-v diagram
of a
substance
that expands
on freezing
(such as
water).



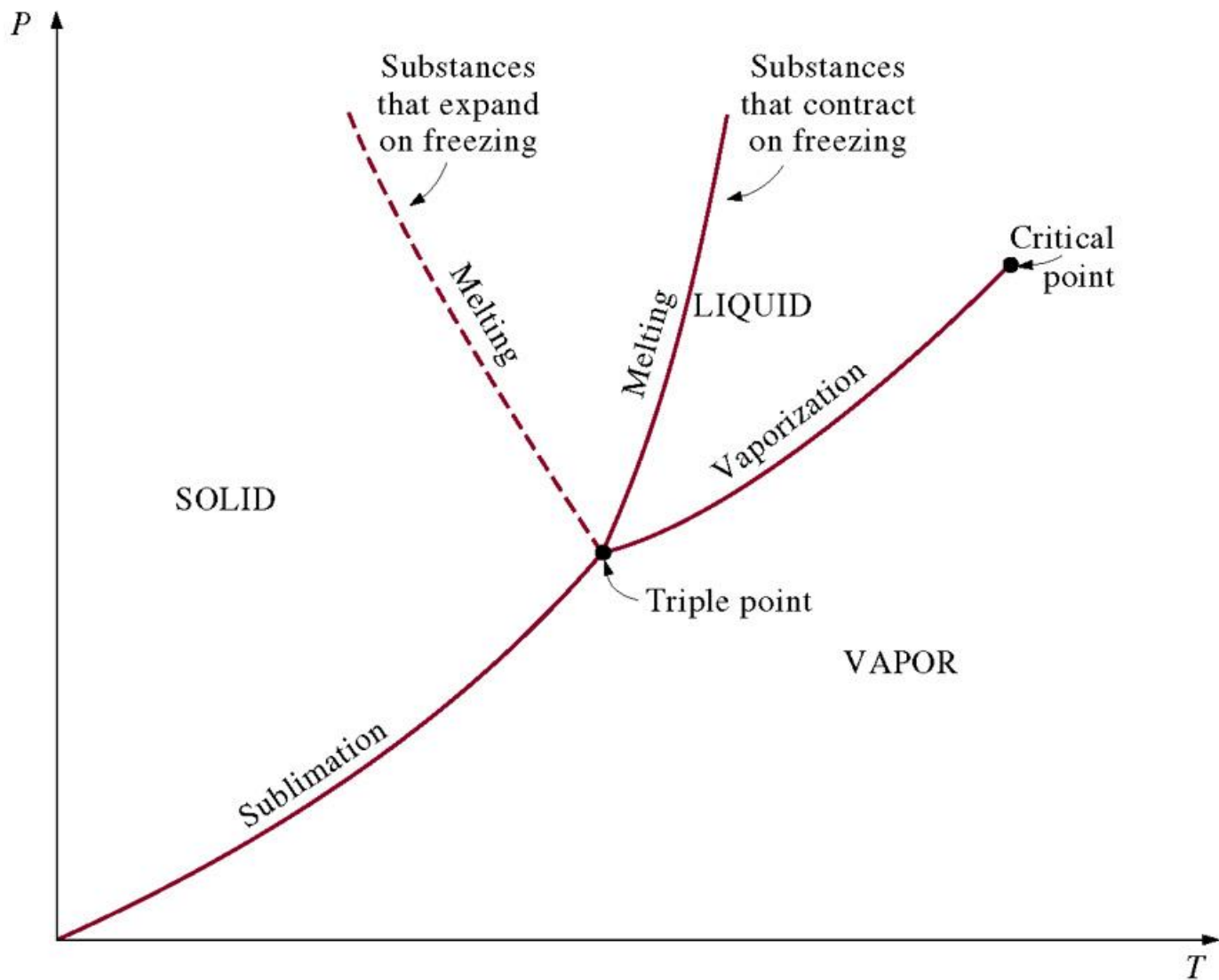
When all three phases of a substance co-exist in equilibrium under some conditions, it is called triple phase.

On P-v or T-v diagrams \longrightarrow Triple line

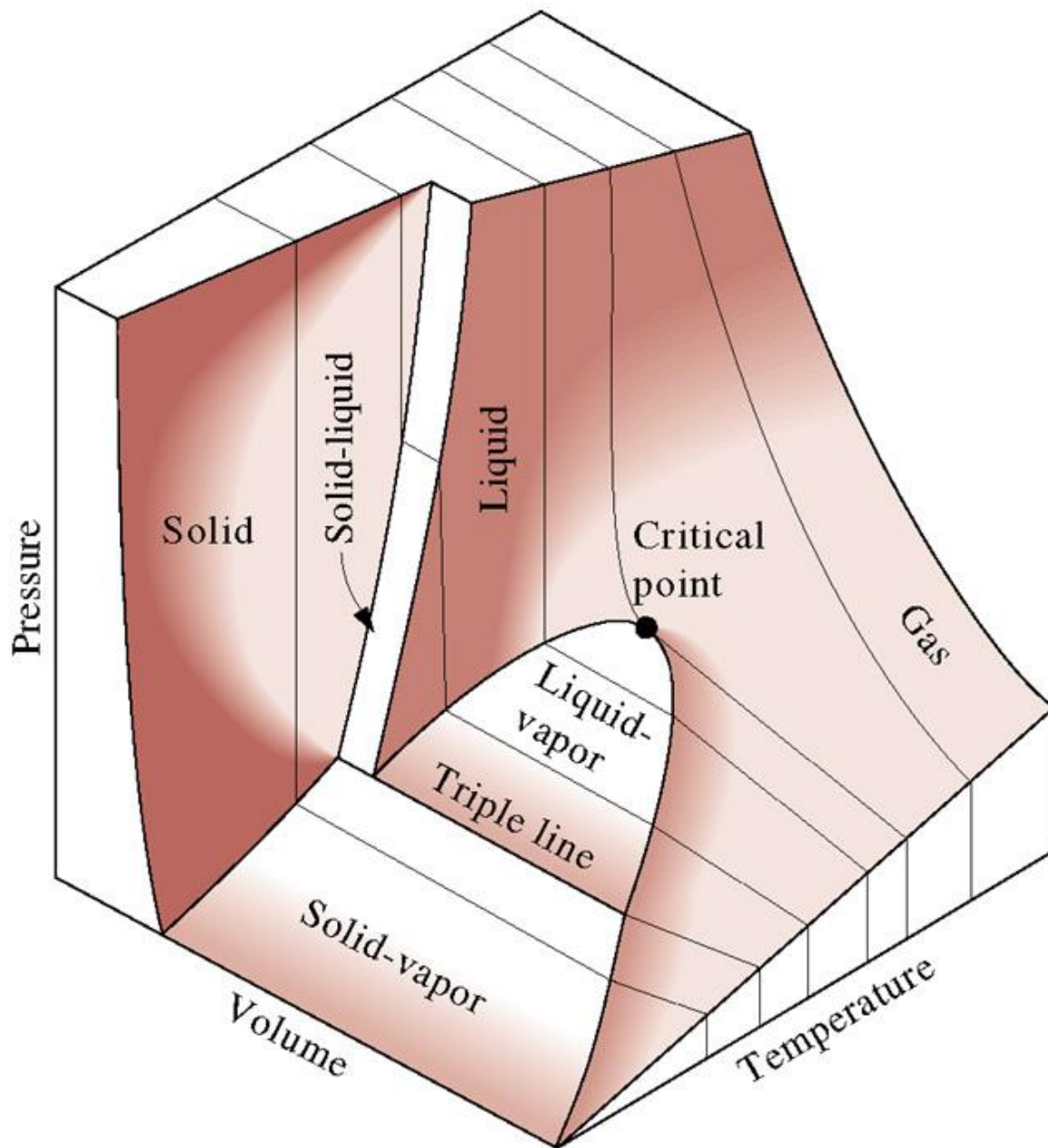
On P-T or T-v diagrams \longrightarrow Triple point



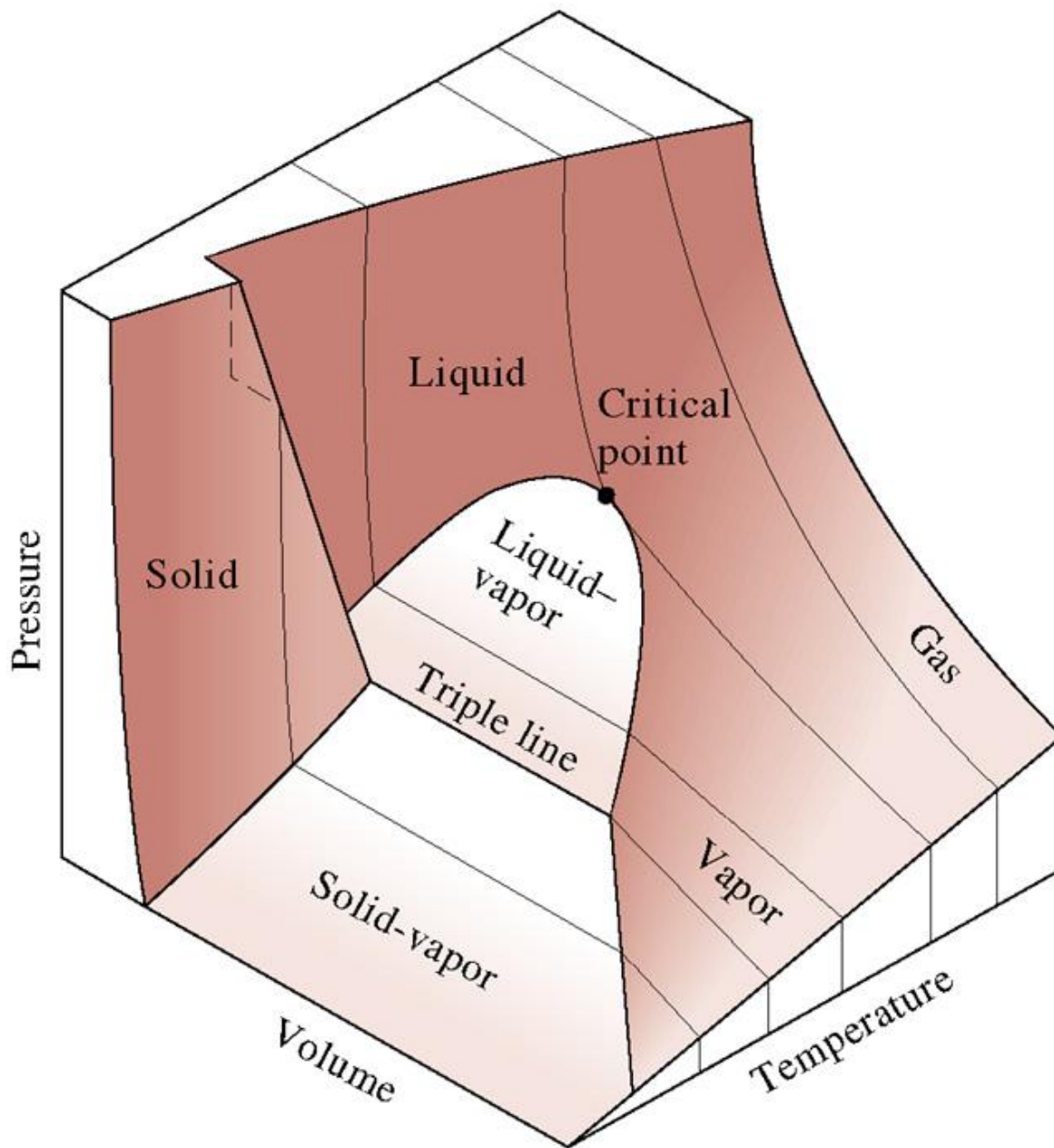
***P-T* diagram
of pure
substances.**



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



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



PROPERTY TABLES

$$\text{Enthalpy} \rightarrow H = U + PV \quad (\text{kJ}) \quad \text{or} \quad h = u + Pv \quad (\text{kJ/kg})$$

$$\text{If } u \text{ is not listed} \rightarrow u = h - Pv$$

Saturated Liquid and Saturated Vapor States

(Tables A4 and A5 in Çengel)

Subscripts

f – saturated liquid

g – saturated vapor

fg – the difference between saturated vapor and saturated liquid

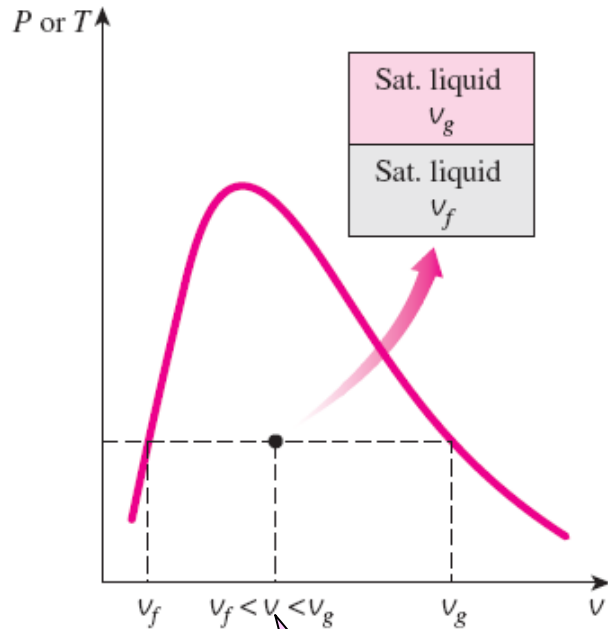
For example:

v_f = specific volume of saturated liquid

v_g = specific volume of saturated vapor

$$v_{fg} = v_g - v_f$$

**A partial list
of Table A-4.**



v-value of
sat. liq.+vap
mixture

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

Specific temperature

Specific volume of saturated liquid

Corresponding saturation pressure

Specific volume of saturated vapor

A partial list of Table A–5.

			Enthalpy kJ/kg		
Press. P kPa	Sat temp. T_{sat} °C	Sat. liquid h_f	Evap. h_{fg}	Sat. Vapor h_g
20	60.06		251.42	2357.5	2608.9
25	64.94		271.96	2345.5	2617.5
30	69.09		289.27	2335.3	2624.6
40	75.86		317.62	2318.4	2636.1
50	81.32		340.54	2304.7	2645.2
75	91.76		384.44	2278.0	2662.4

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.

Saturated Liquid–Vapor Mixture

In order to know the properties of the liquid and vapor phase in the mixture a new property is defined:

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.

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

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

$$V = V_f + V_g$$

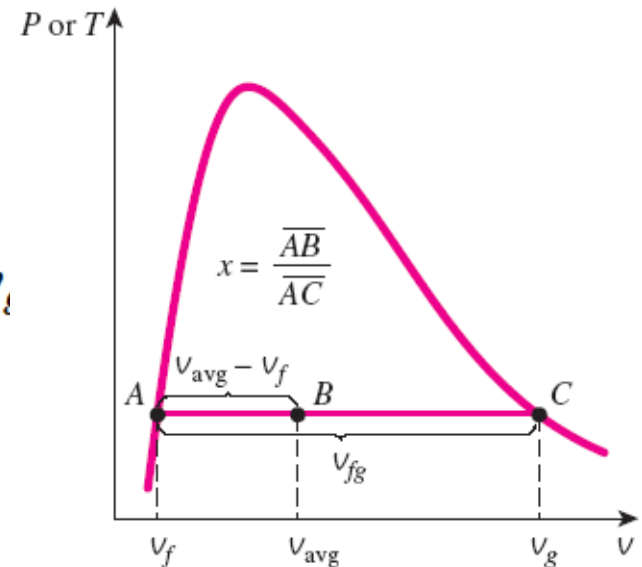
$$V = mv \rightarrow m_t v_{av} = m_f v_f + m_g v_g$$

$$m_f = m_t - m_g \rightarrow m_t v_{av} = (m_t - m_g) v_f + m_g v_g$$

$$\div m_t \rightarrow v_{av} = (1 - x)v_f + xv_g$$

or $v_{av} = v_f + xv_{fg}$

$$x = \frac{v_{av} - v_f}{v_{fg}}$$



Similar equations can be derived for u or h : $u_{\text{avg}} = u_f + xu_{fg}$ (kJ/kg)

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

Example 5 kg of steam at 200kPa occupied a volume of 2.60 m^3 .
Determine temperature and quality.

$$v_{\text{av}} \rightarrow v = \frac{\text{volume}}{\text{mass}} = \frac{2.60}{5} = 0.52 \text{ m}^3/\text{kg}$$

Compare this with the values given in Table A-5

Note : $T_{\text{sat}} = 120.23 \text{ }^\circ\text{C}$ at 200 kPa (=0.200 Mpa)

$$v_f = 0.001061 \quad \text{and} \quad v_g = 0.8857$$

$$x = \frac{v_{\text{av}} - v_f}{v_{fg}} = \frac{v - v_f}{v_g - v_f} = \frac{0.52 - 0.001061}{0.8857 - 0.001061} = 0.587$$

A partial listing
of Table A–6.

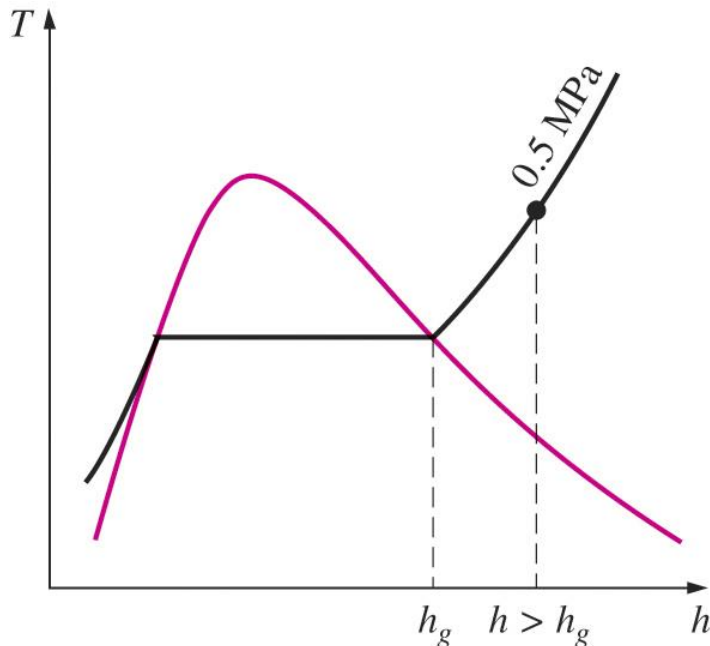
	v	u	h
$T, ^\circ\text{C}$	m^3/kg	kJ/kg	kJ/kg
$P = 0.1 \text{ MPa} (99.61^\circ\text{C})$			
Sat.	1.6941	2505.6	2675.0
100	1.6959	2506.2	2675.8
150	1.9367	2582.9	2776.6
\vdots	\vdots	\vdots	\vdots
1300	7.2605	4687.2	5413.3
$P = 0.5 \text{ MPa} (151.83^\circ\text{C})$			
Sat.	0.37483	2560.7	2748.1
200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

Superheated Vapor (Table A-6)

characterized by

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

Example



at 0.5 MPa $\rightarrow h_g = 2748.7 \text{ kJ/kg}$

$T_{sat} = 151.86 \text{ }^\circ\text{C}$

However at the same pressure,
if $T = 200 \text{ }^\circ\text{C} \rightarrow h = 2855.4 \text{ kJ/kg}$

$\rightarrow h > h_g$

Compressed Liquid

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)

In the absence of data a compressed liquid is approximated as a saturated liquid at the given temperature.

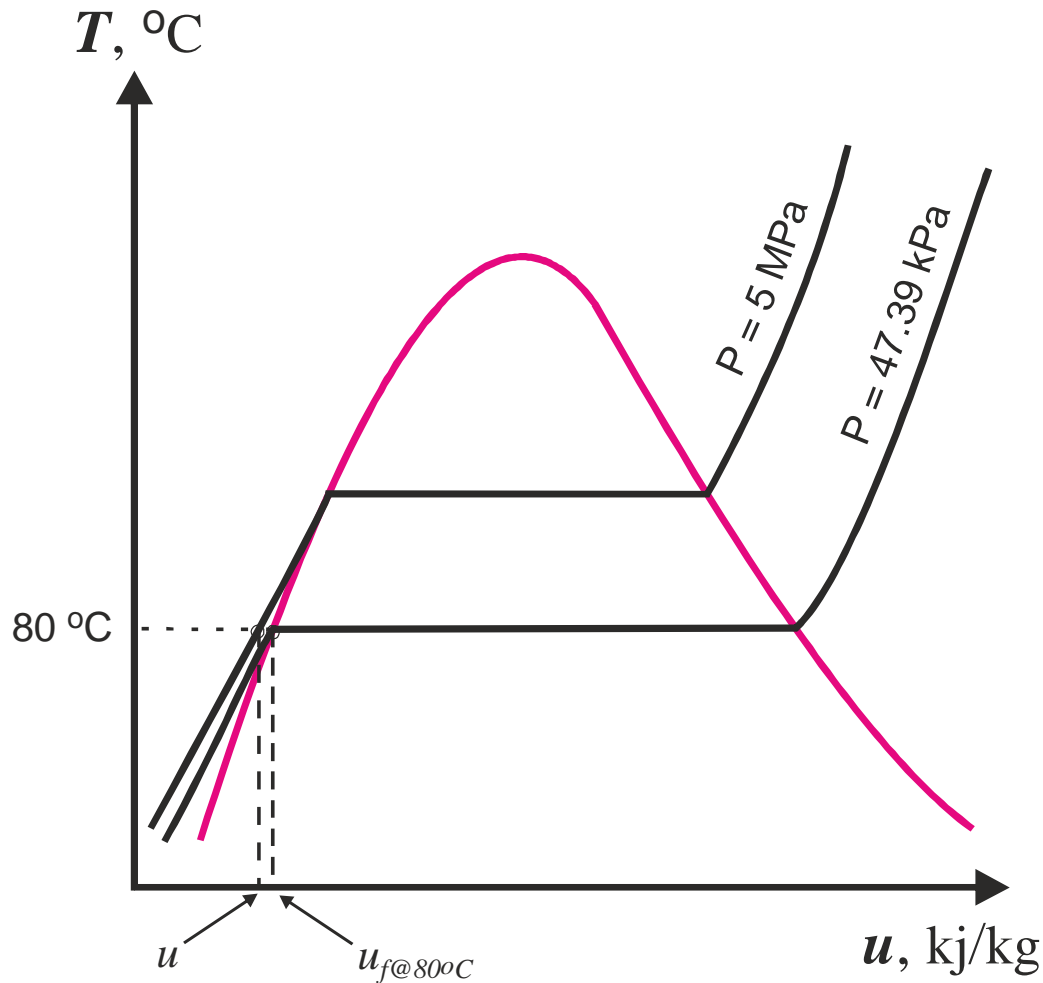
Given: P and T

$$v \cong v_f @ T$$

$$u \cong u_f @ T$$

$$h \cong h_f @ T$$

Example



at 80 °C $P_{sat} = 47.39 \text{ kPa}$

If our pressure is 5 MPa then we have compressed liquid.

For compressed liquid table(A-7):

$$\left. \begin{array}{l} P = 5 \text{ MPa} \\ T = 80^\circ\text{C} \end{array} \right\} u = 333.72 \text{ kJ/kg}$$

From the saturation table(A-4):

$$u_f = 334.86 \text{ kJ/kg}$$

If we make $u \cong u_{f@80^\circ\text{C}}$,the error is:

$$\frac{334.86 - 333.72}{333.72} = 0.0034(0.34\%)$$

Example

State	1	2	3	4	5
P, kPa	200	300	2000	476.1	5000
$T, ^\circ\text{C}$	120.23	133.56	300	150	100
$x, \%$	80	I	M	92	M
$v, \text{m}^3/\text{kg}$	0.709	I	0.125	0.361	0.00104

state 1 (table A - 5) $\rightarrow T = T_{sat@200\text{kPa}} = 120.23^\circ\text{C}$

$$v = v_f + xv_{fg}$$

$$= 0.001061 + 0.8(0.8857 - 0.001061) = 0.709$$

state 2 \rightarrow at 300 kPa $T_{sat} = 133.55^\circ\text{C}$

$x = \text{indeterminate} = I$

$v = \text{indeterminate} = I$

} either saturated liquid
or saturated vapor
or saturated liquid-vapor mixture

state 3 → at 2000 kPa $T_{sat} = 212.42^\circ\text{C}$

∴ Superheated (Table A – 6)

x=meaning less=M

$$v=012547 \text{ m}^3/\text{kg}$$

state 4 → at 150°C $P_{sat} = 0.4758\text{MPa}$ $v_f = 0.001091$ $v_g = 0.3928 \text{ m}^3/\text{kg}$

$$x = \frac{v - v_f}{v_g - v_f} = \frac{0.361 - 0.001091}{0.3928 - 0.001091} = 0.919 \text{ (or 92\%)}$$

state 5 → at 5000kPa $T_{sat} = 263.99^\circ\text{C}$ Compressed liquid → x=meaningless=M

Table (A – 7) at 5MPa and 100°C $v = 0.001041 \text{ m}^3/\text{kg}$

The Ideal Gas Equation of State

Equation of State: any equation that relates the pressure, temperature, and specific of a substance.

Ideal-gas equation of state \longrightarrow $P = R \left(\frac{T}{v} \right)$ or $Pv = RT$

Absolute pressure \longleftarrow P R \longleftarrow **Gas constant** T \longleftarrow **Absolute temperature**

v \longleftarrow **Specific volume**

Ideal gas \longrightarrow is a gas which obeys the above relation. The gas constant R is different for each gas.

$$R = \frac{R_u}{M} \text{ kJ/kg.K}$$

R_u = universal gas constant
M = molar mass (molecules weight)

$$R_u = 8.314 \text{ kJ/(kmol.K)} \quad \text{or} \quad 1.986 \text{ Btu/(lbmol.R)} \quad (\text{same for all substances})$$

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

\downarrow ↘
 Mass of system Mole number

Ideal Gas Equation in different forms:

$$V = m\bar{v} \longrightarrow PV = mRT \quad \begin{matrix} \text{State 1} \\ \rightarrow P_1V_1 = mRT_1 \end{matrix} \quad \begin{matrix} \text{State 2} \\ P_2V_2 = mRT_2 \end{matrix}$$

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

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

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

\downarrow
 Molar specific volume

Example

Determine the density and specific volume of air at room temperature.

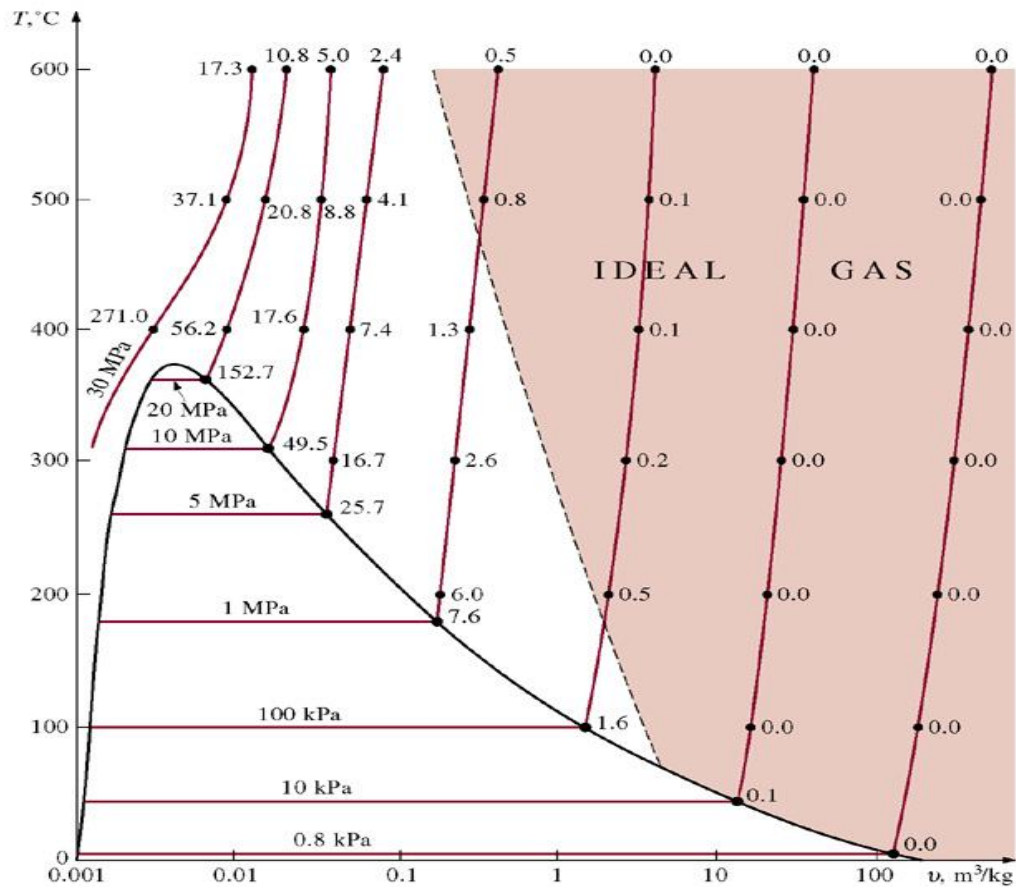
Room temperature = 20°C
273+20 = 293 K

$$\rightarrow PV = m RT \quad P \mathbf{1}/\rho = RT$$

$$\rho = \frac{P}{RT} = \frac{101(kPa)}{0.287 \left(\frac{kJ}{kg} \right) 293(K)} = 1.2 \text{ kg}/m^3$$

$$v = \frac{1}{\rho} = 0.83 \text{ m}^3/kg$$

FIGURE 2-14
Percentage of error
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

Gases deviate from ideal-gas behavior significantly at state near saturation region and the critical point.

Hence a correction is introduced:

$$\longrightarrow \text{compressibility factor} = Z = \frac{Pv}{RT} \quad (\text{for ideal gases } Z=1)$$

Z is an indication of deviation from ideal gas behavior.

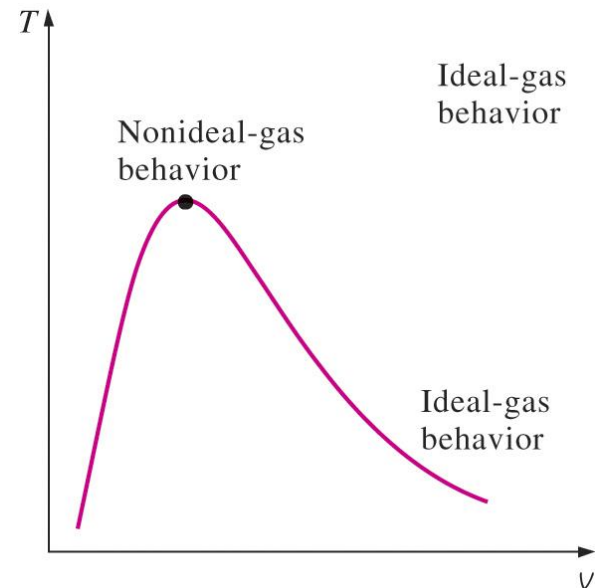
Gases behave differently at a given temperature and pressure.

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

Reduced Pressure

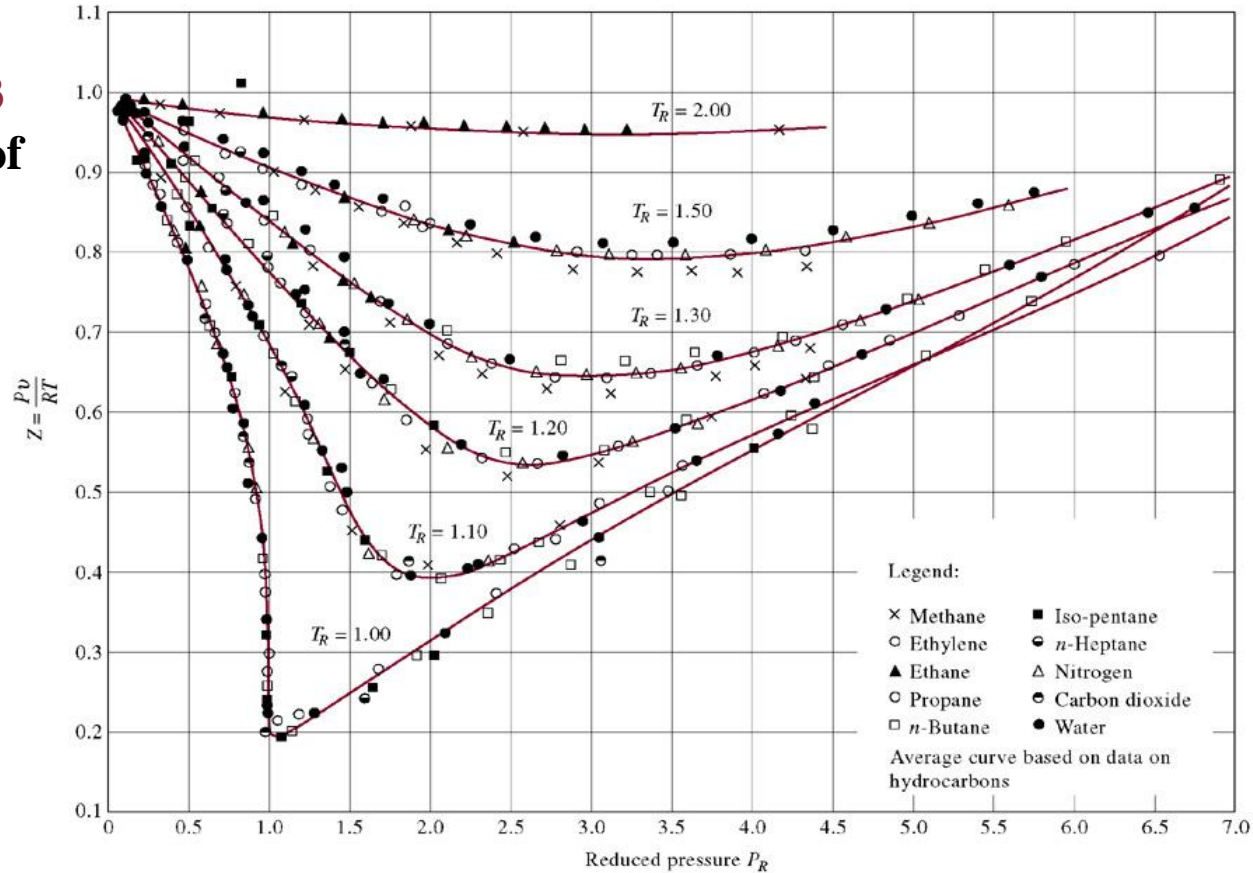
$$T_R = \frac{T}{T_{cr}}$$

Reduced Temperature



The Z – factor is approximately the same for all gases at the same reduced temperature and pressure.

FIGURE 2-13
Comparison of Z factors for various gases.



- 1) $P_R \ll 1$, gases behave as an ideal gas regardless of T .
- 2) $T_R > 2$, ideal gas assumed regardless of P (except $P_R \gg 1$)
- 3) The deviation from ideal-gas is greatest around critical point (i.e. $T_R = 1, P_R = 1$)

Example

Determine the specific volume of R-134-a at 1 MPa and 50°C.

————→ if ideal gas equation used

$$\rightarrow v = \frac{RT}{P} = \frac{0.08149 \times 323}{1000} = 0.02632 \text{ m}^3/\text{kg}$$

Z can be determined:

$$P_R = \frac{P}{P_{cr}} = \frac{1 \text{ MPa}}{4.067 \text{ MPa}} = 0.245$$

$$T_R = \frac{T}{T_{cr}} = \frac{323 \text{ K}}{374.3 \text{ K}} = 0.862$$

$$\left. \begin{array}{l} P_R = 0.245 \\ T_R = 0.862 \end{array} \right\} Z = 0.835 \rightarrow v = Zv_{ideal}$$
$$v = 0.835 \times 0.02632$$
$$= 0.02197 \text{ m}^3/\text{kg}$$

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.

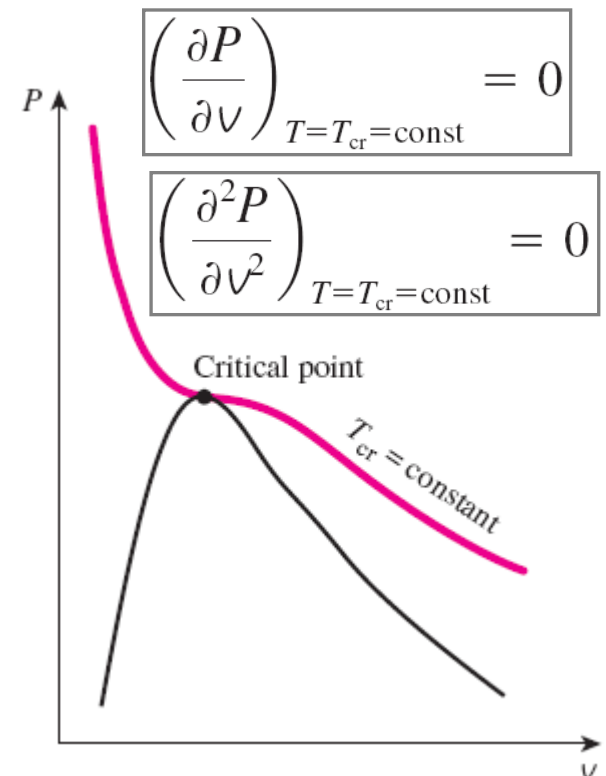
Van der Waals Equation of State

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

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

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

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

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

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

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

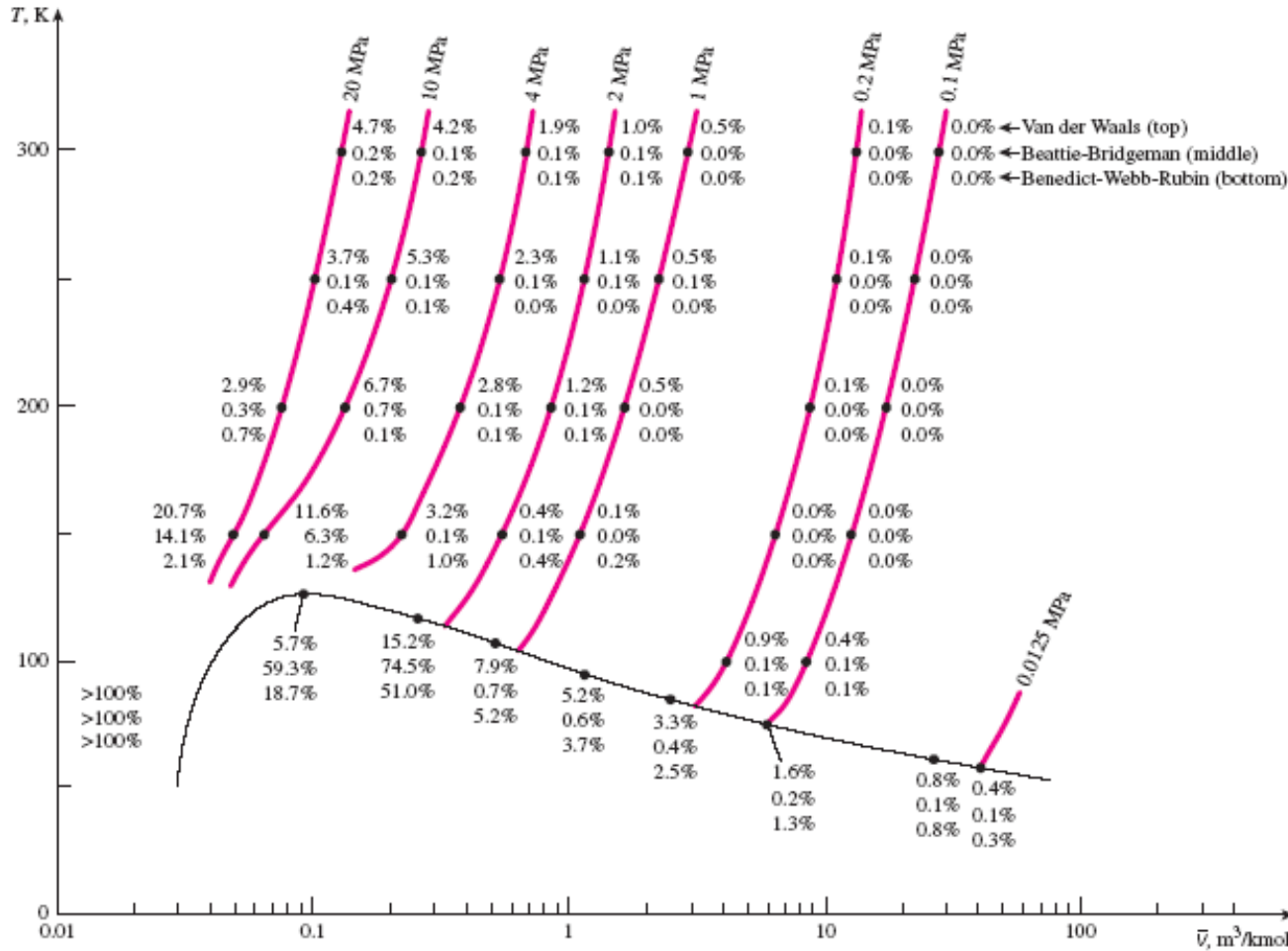
$$P = \frac{R_u T}{\bar{v}} + \left(B_0 R_u T - A_0 - \frac{C_0}{T^2} \right) \frac{1}{\bar{v}^2} + \frac{b R_u T - a}{\bar{v}^3} + \frac{a\alpha}{\bar{v}^6} + \frac{c}{\bar{v}^3 T^2} \left(1 + \frac{\gamma}{\bar{v}^2} \right) e^{-\gamma/\bar{v}^2}$$

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 $\rho \leq 0.8\rho_{cr}$.

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

Strobridge: 16 constants.
 More suitable for computer calculations.

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

Percentage of error involved in various equations of state for nitrogen

$$(\% \text{ error} = [(|v_{\text{table}} - v_{\text{equation}}|)/v_{\text{table}}] \times 100).$$

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