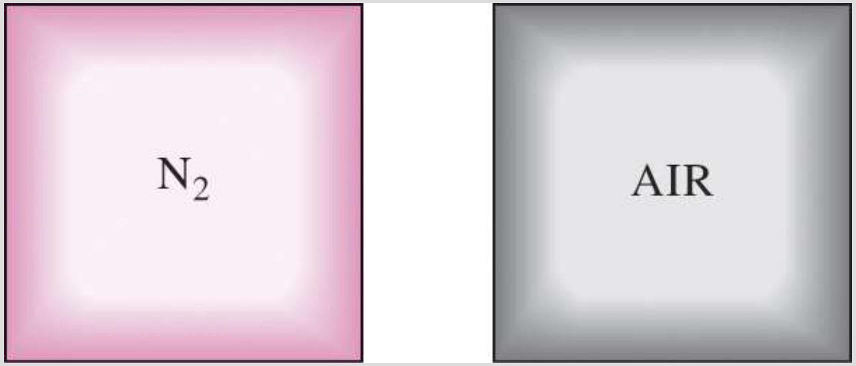
Chapter 3

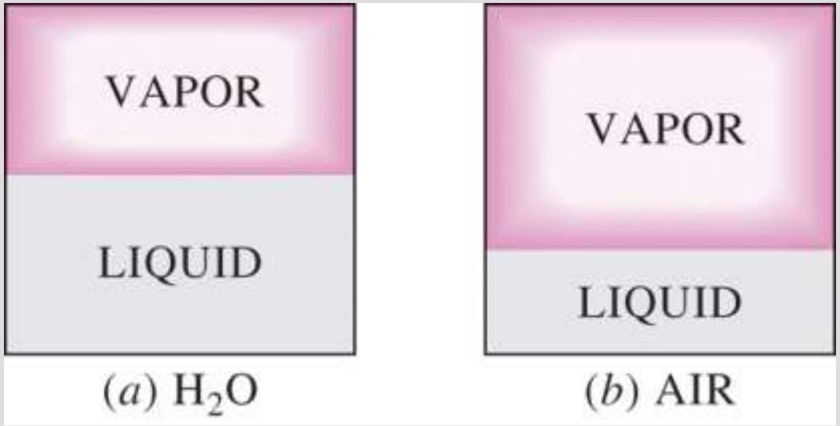
PROPERTIES OF PURE SUBSTANCES

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.

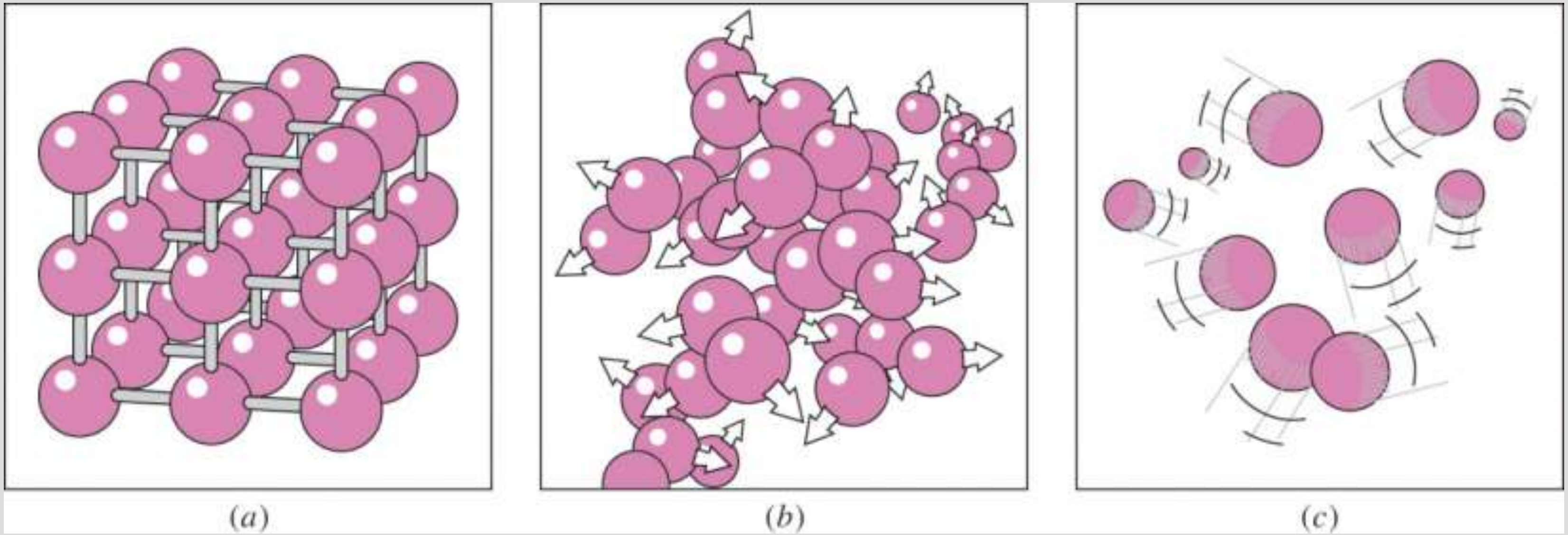
Phases of a Pure Substance

The arrangement of atoms in different phases:

(a) Solid Phase: molecules are at relatively fixed positions

(b) Liquid Phase: groups of molecules move about each other

(c) Gas Phase: molecules move about at random

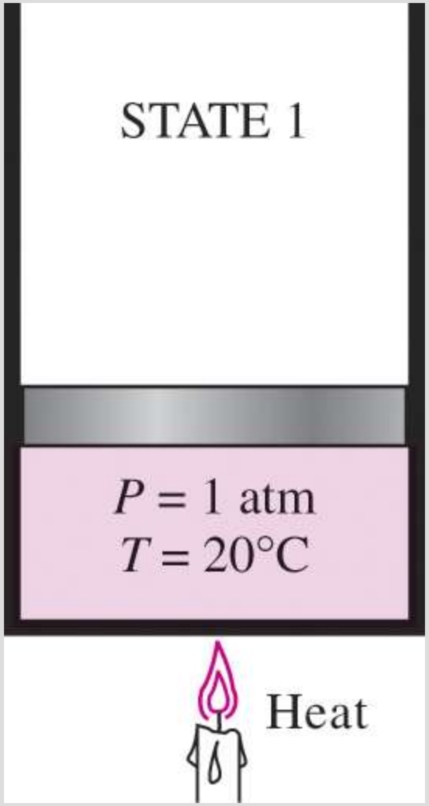


Phase Change of A Pure Substance

Compressed liquid (subcooled liquid)

A substance that is ***not** about to vaporize.*

At 1 atm and 20°C, water exists in the liquid phase.

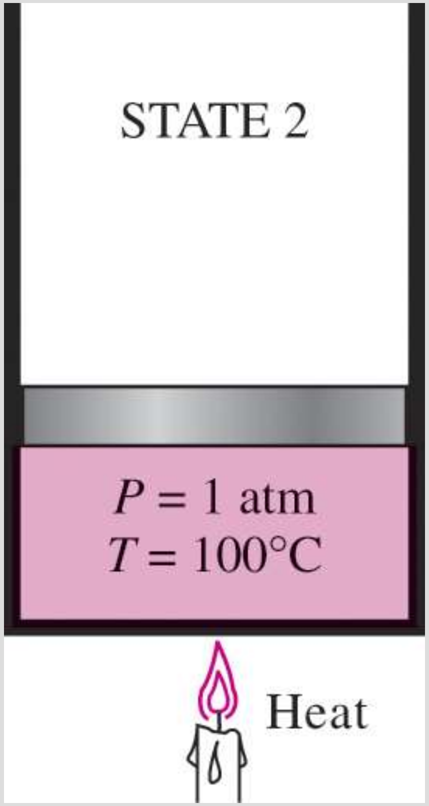


Phase Change of A Pure Substance

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.

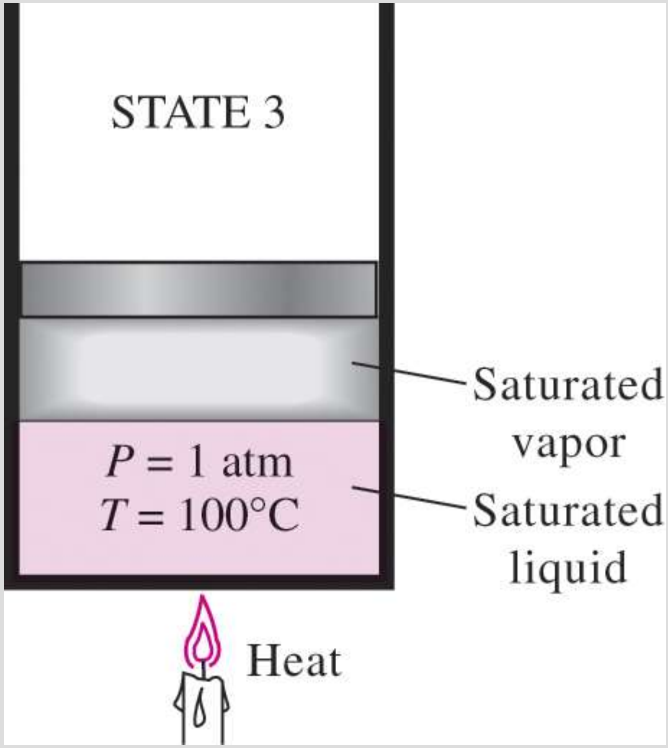


Phase Change of A Pure Substance

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.

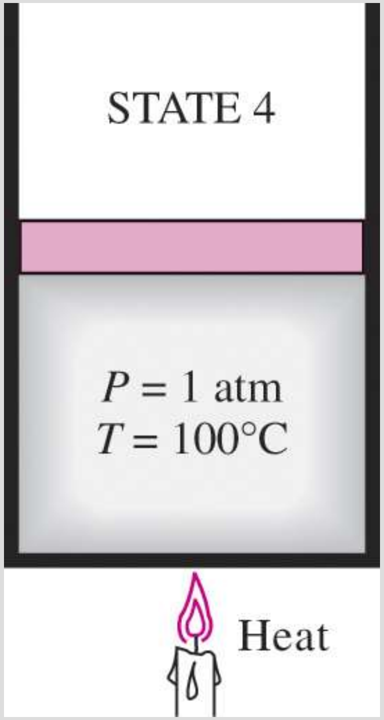


Phase Change of A Pure Substance

Saturated vapor

A substance is at the end of vaporization
OR
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.

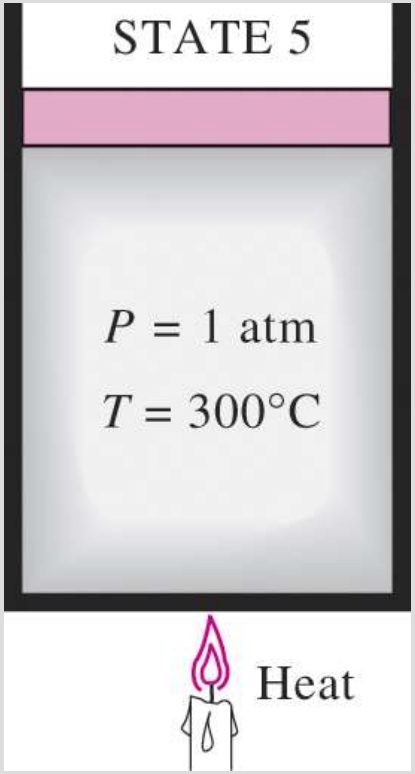


Phase Change of A Pure Substance

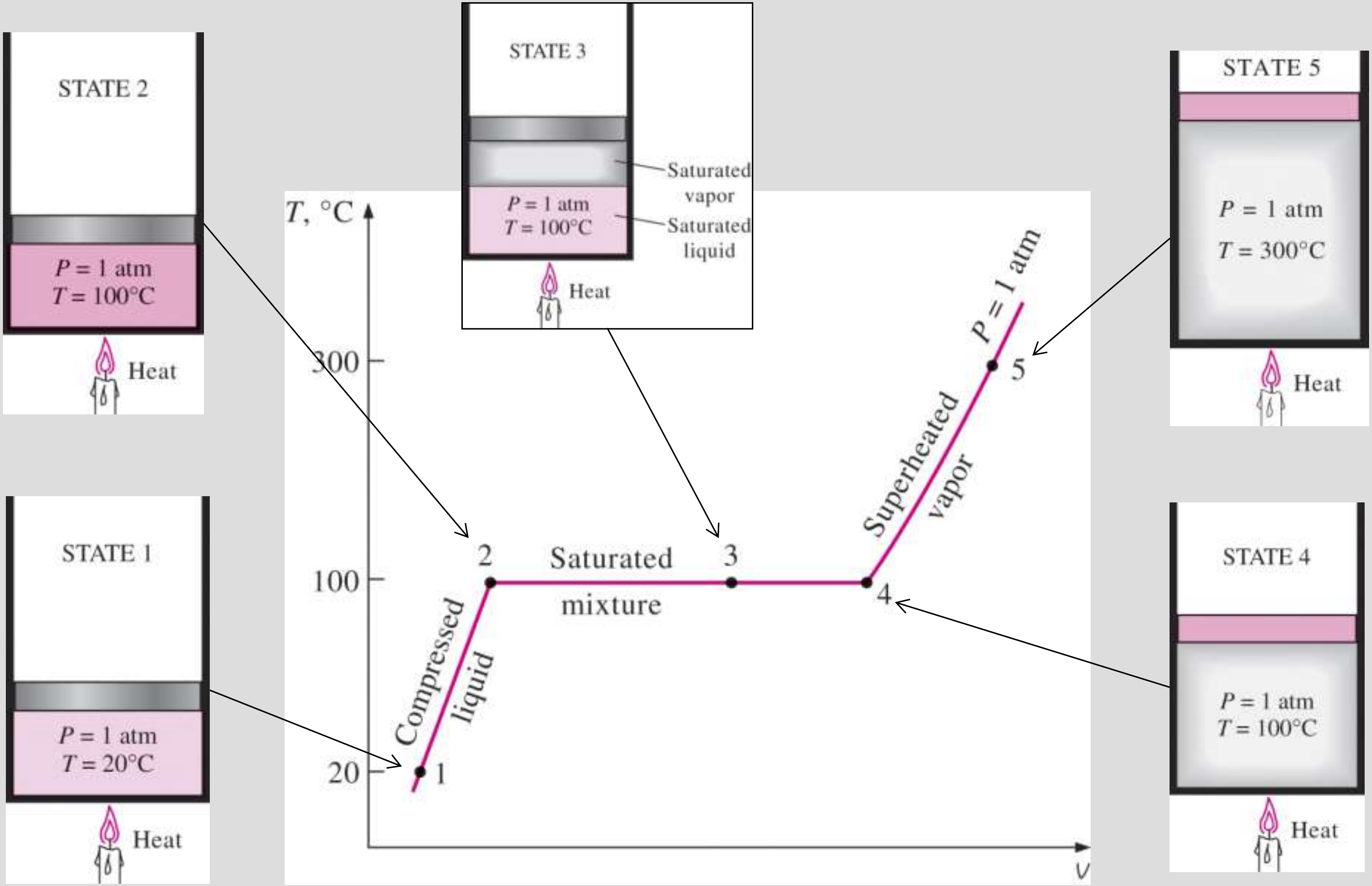
Superheated vapor

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.

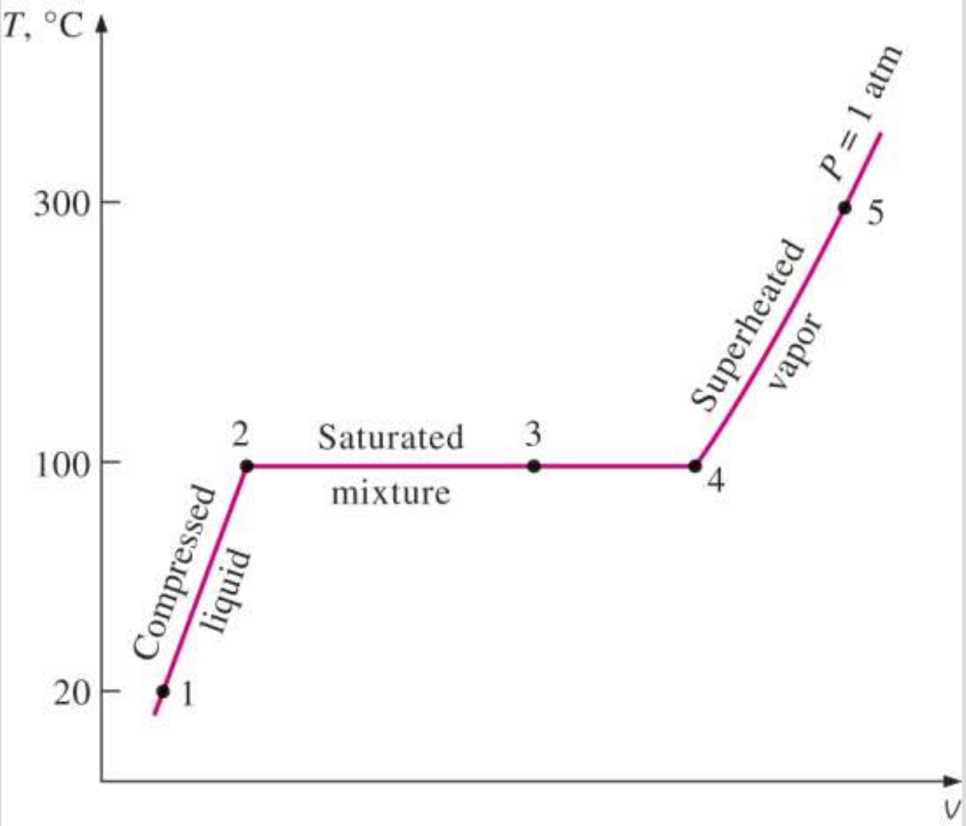


Phase Change of A Pure Substance



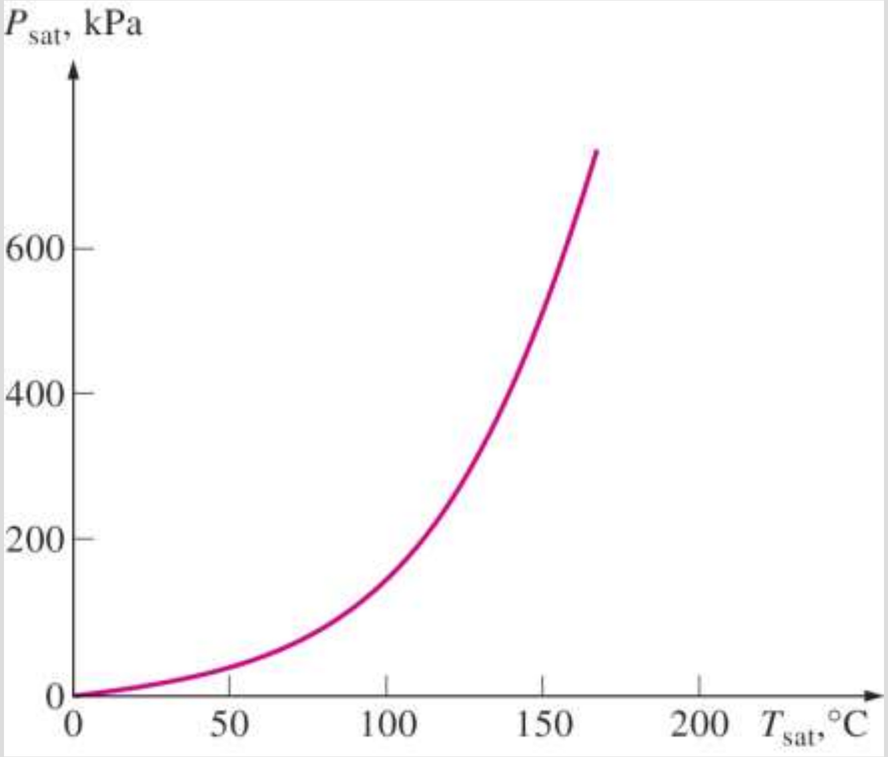
Phase Change of A Pure Substance

- 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.



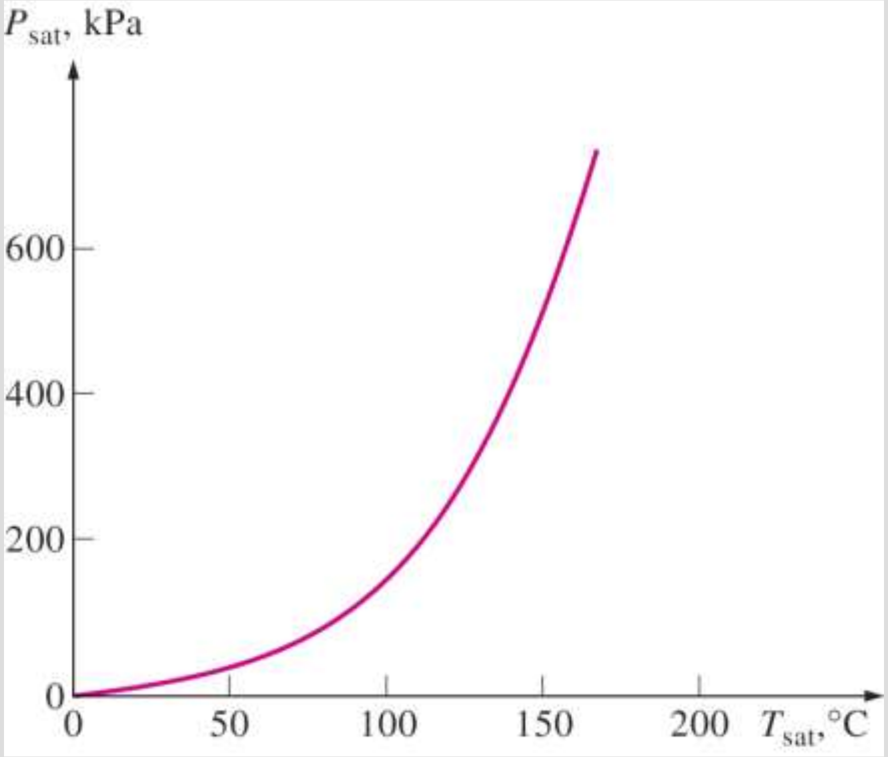
Saturation Temperature and Pressure

Saturation temperature T_{sat}

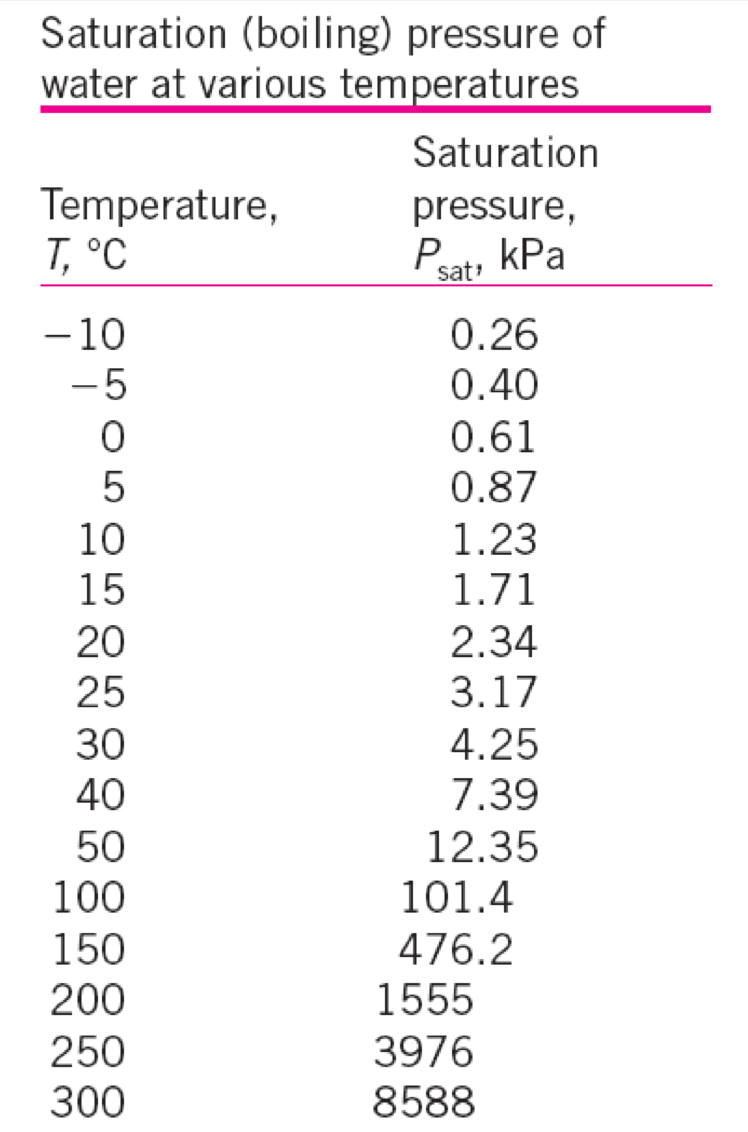
The temperature at which a pure substance changes phase at a given pressure.

Saturation pressure P_{sat}

The pressure at which a pure substance changes phase at a given temperature.

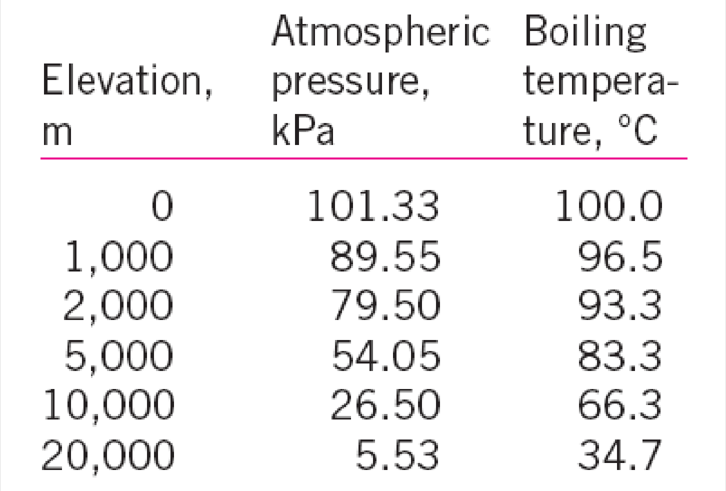


Saturation Temperature and Pressure



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



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

Latent Heat

- **Latent heat** is 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.

Latent Heat

- At 1 atm pressure, the latent heat of fusion of water is 334 kJ/kg and the latent heat of vaporization is 2257 kJ/kg.

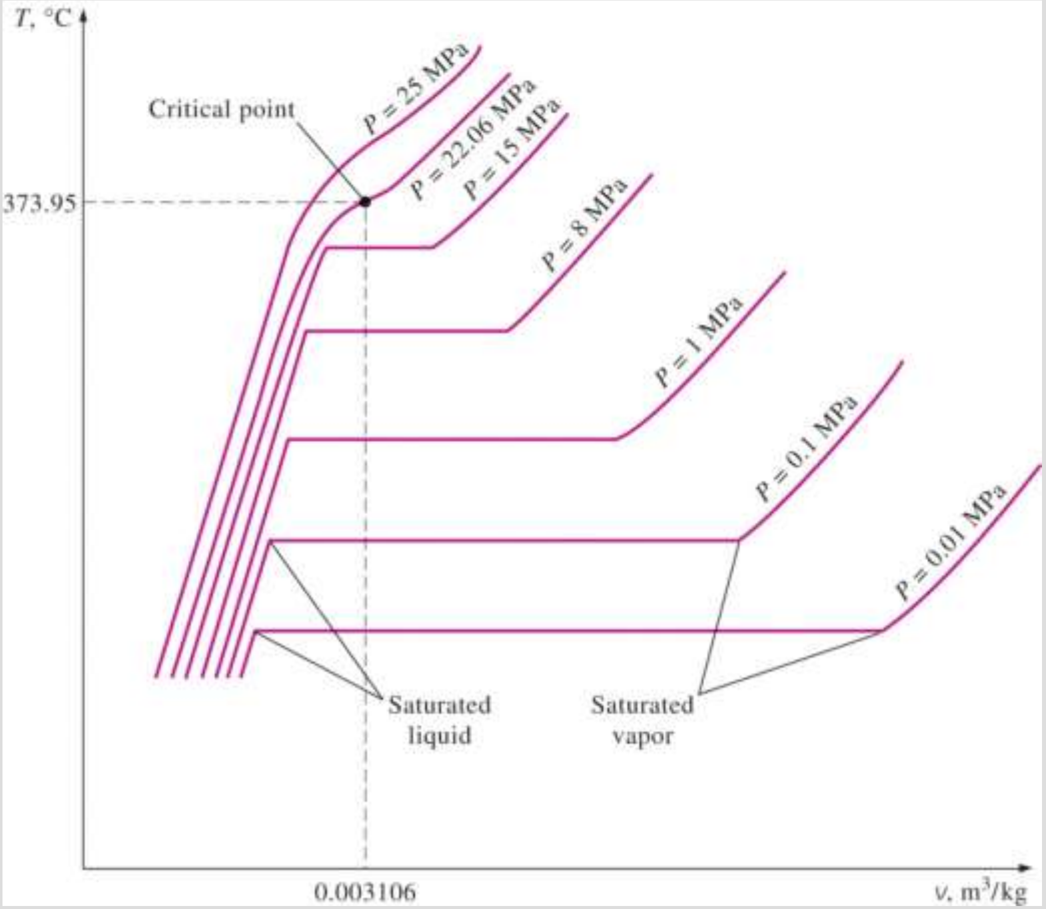
- The magnitudes of the latent heats depend on the temperature or pressure at which the phase change occurs.

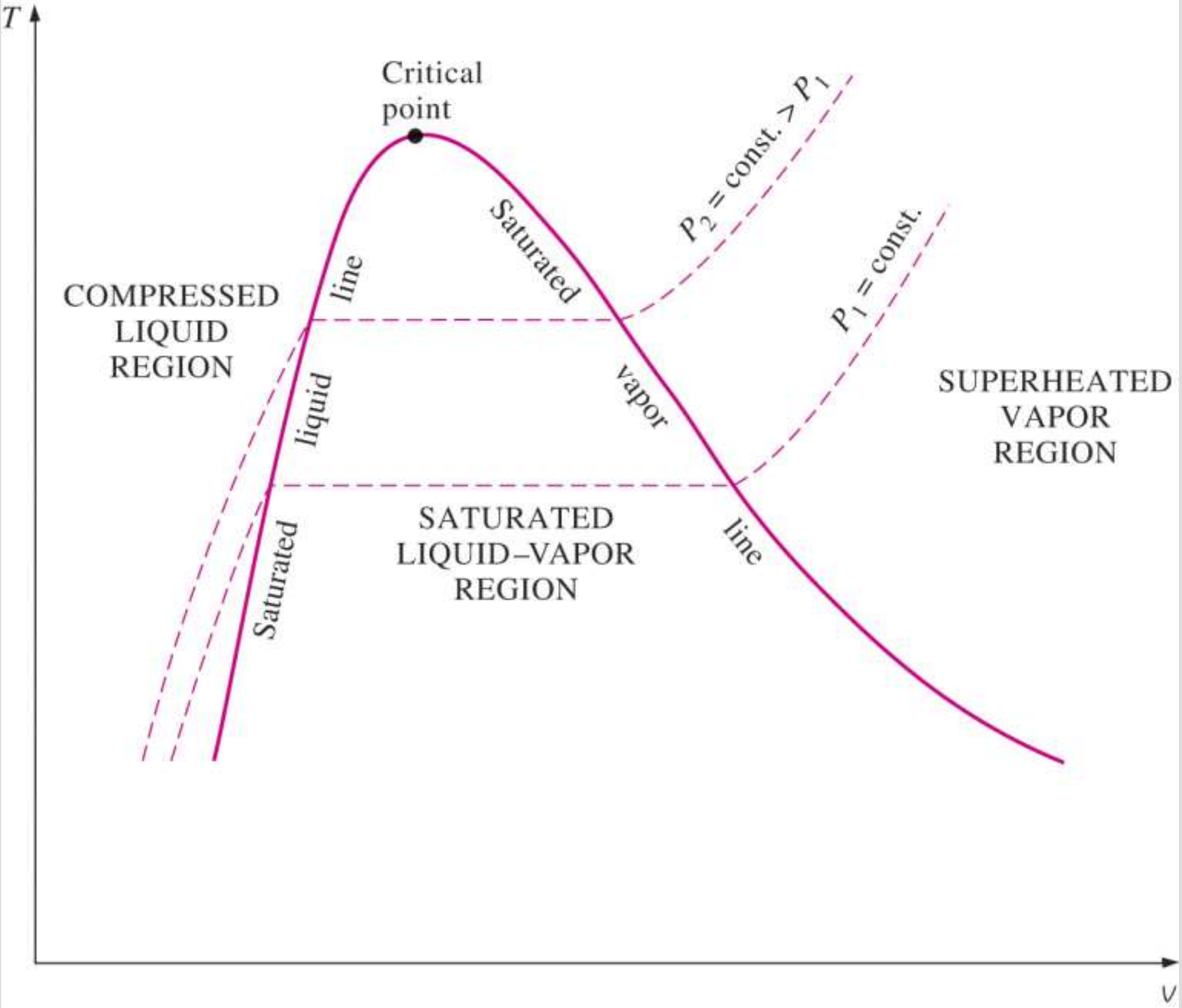
Temperature (°C)	Saturation Pressure (kPa)	Latent Heat of Vaporization (kJ/kg)
50	12.34	2382
100	101.3	2257
150	475.7	2114
200	1554	1940
250	3974	1715

Property Diagrams for Phase-Changing Substances

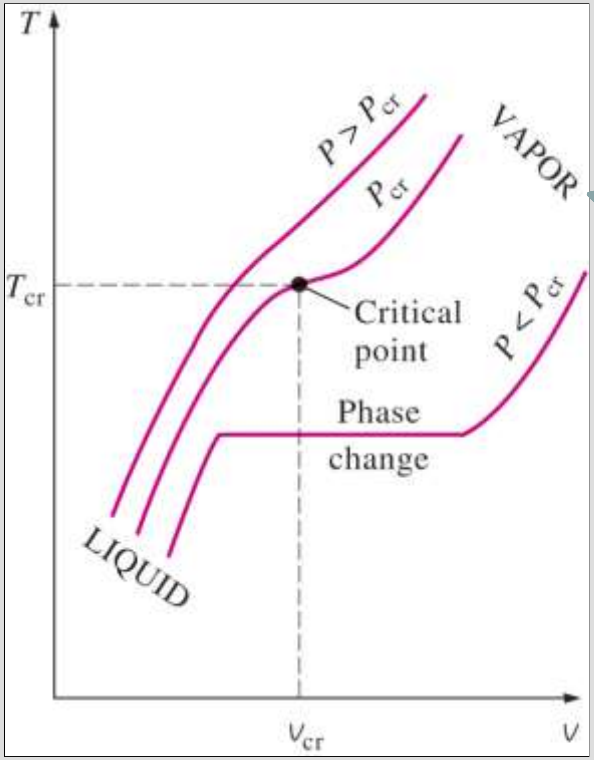
- The variations of properties during phase-change processes are best studied and understood with the help of property diagrams.

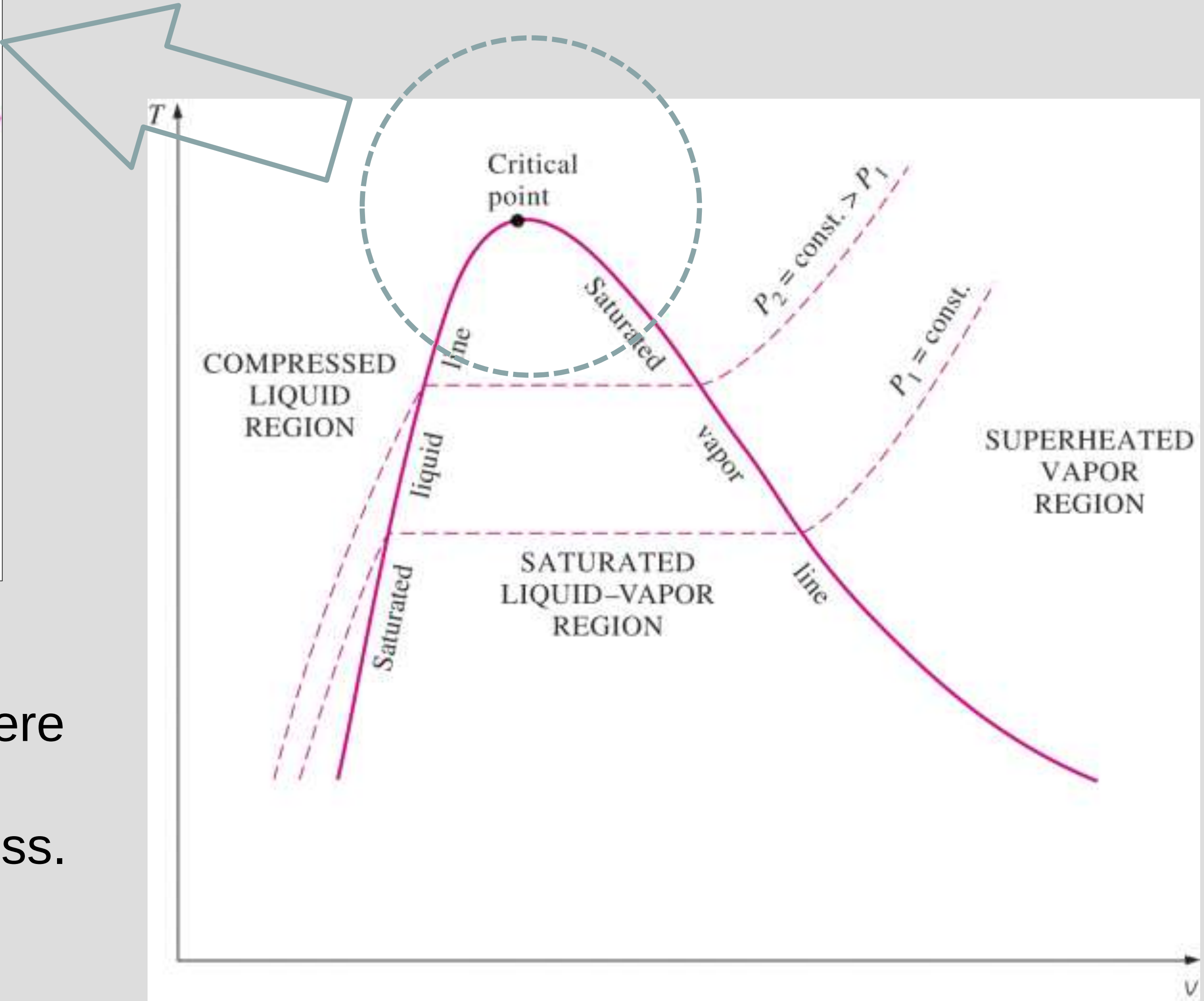
- The ***critical point*** is the point at which the saturated liquid and saturated vapor states are identical.




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

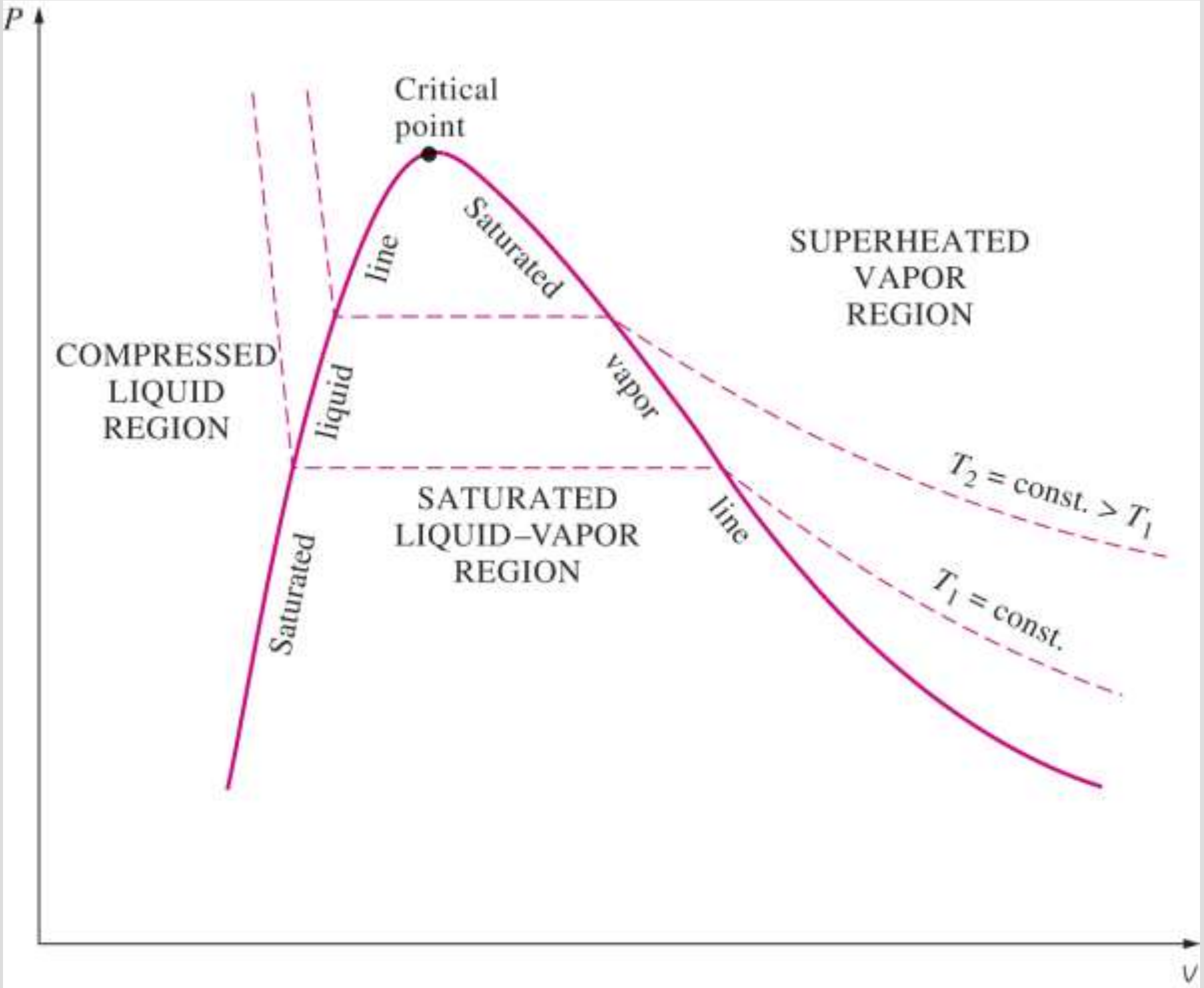
Property Diagrams for Phase-Changing Substances

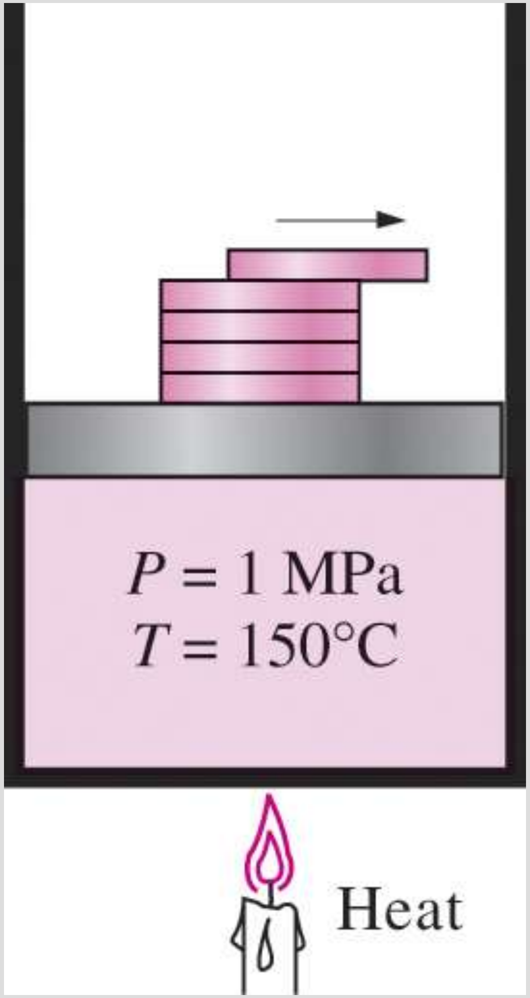




At supercritical pressures ($P > P_{cr}$), there is no distinct phase-change (boiling) process.

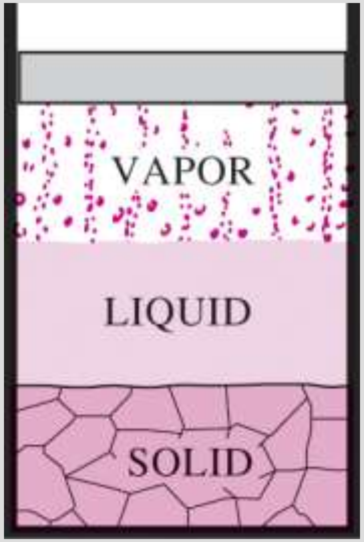
Property Diagrams for Phase-Changing Substances



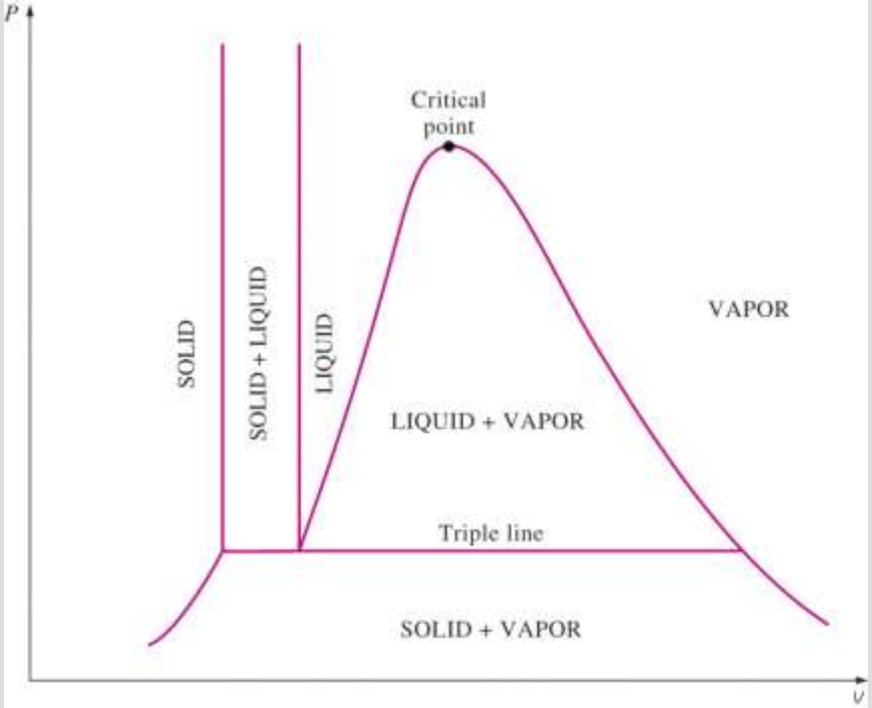


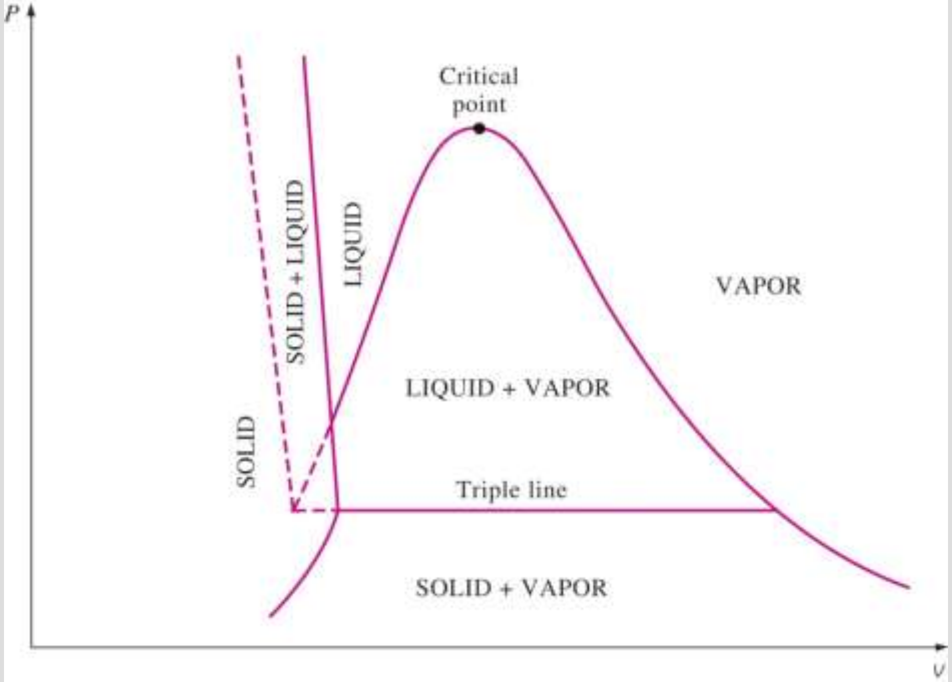
Extending the Diagrams to Include the Solid Phase

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

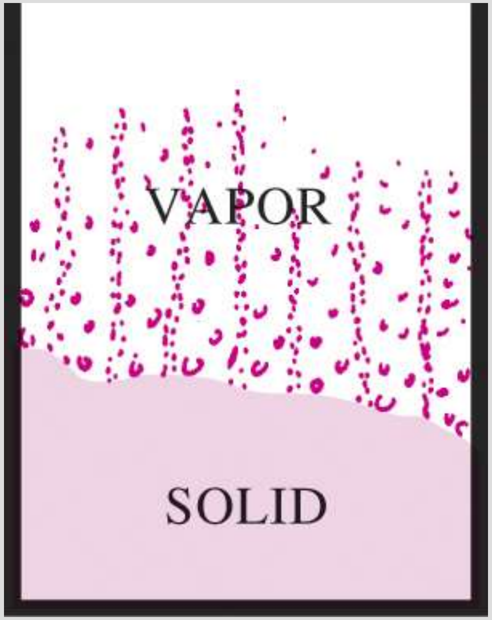


At triple-point pressure and temperature, a substance exists in three phases in equilibrium.



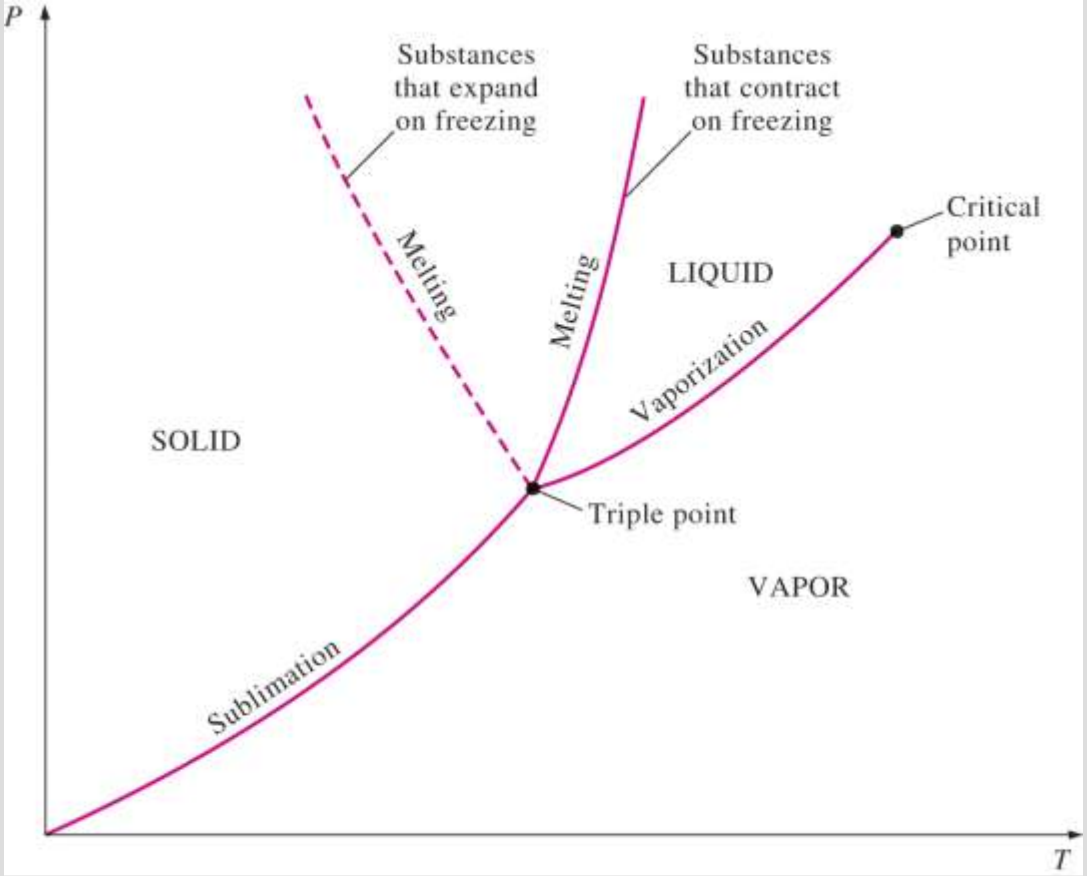


Sublimation: Passing from the solid phase directly into the vapor phase.



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.
- 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.

Why Determine Properties?

- Properties are needed to solve the laws of thermodynamics.
- Example: First law of thermodynamics

$$E_{\text{in}} - E_{\text{out}} = \Delta E_{\text{system}} = \Delta U + \Delta \text{KE} + \Delta \text{PE}$$

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

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

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

- Specific internal energy (*u*) is important in calculations related to the first law of thermodynamics.

Enthalpy

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

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

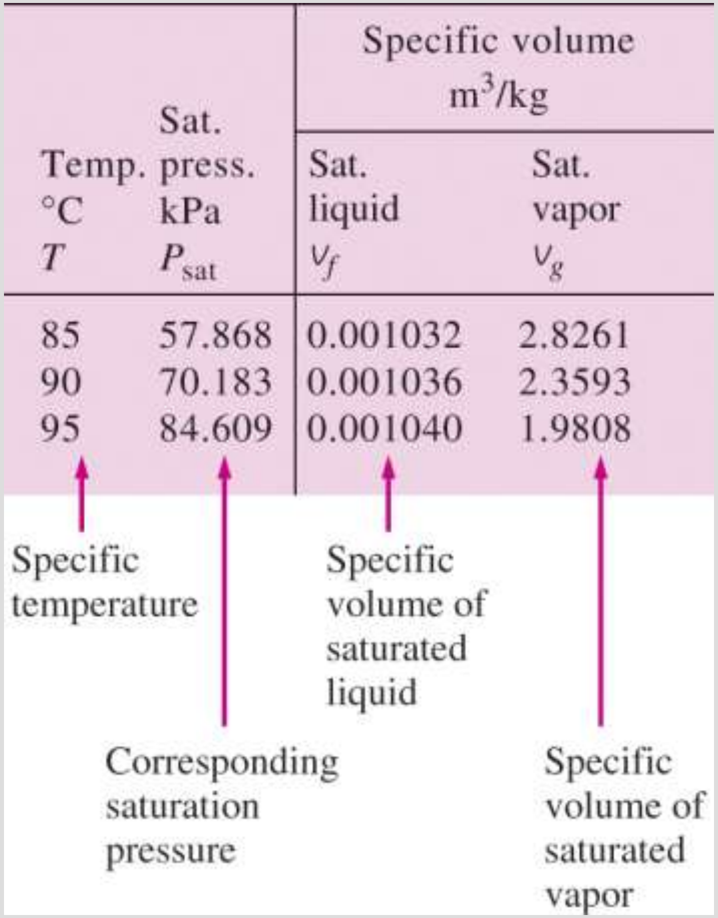
Specific Enthalpy: $h = u + Pv \qquad (\text{kJ/kg})$

- Enthalpy is frequently encountered in the analysis of control volumes.
- It will be seen later that enthalpy is an important of energy transfer by mass (E_{mass})

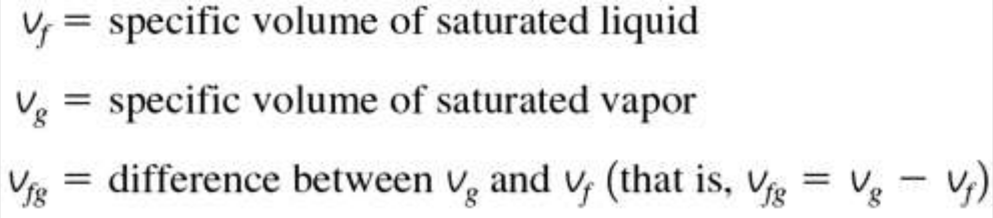
$$E_{\text{in}} - E_{\text{out}} = (Q_{\text{in}} + W_{\text{in}} + E_{\text{mass,in}}) - (Q_{\text{out}} + W_{\text{out}} + E_{\text{mass,out}}) = \Delta E_{\text{system}}$$

Saturated Liquid and Saturated Vapor States

Table A-4
Saturated Water – Temperature Table



		Specific volume m^3/kg	
Temp. °C T	Sat. press. kPa P_{sat}	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



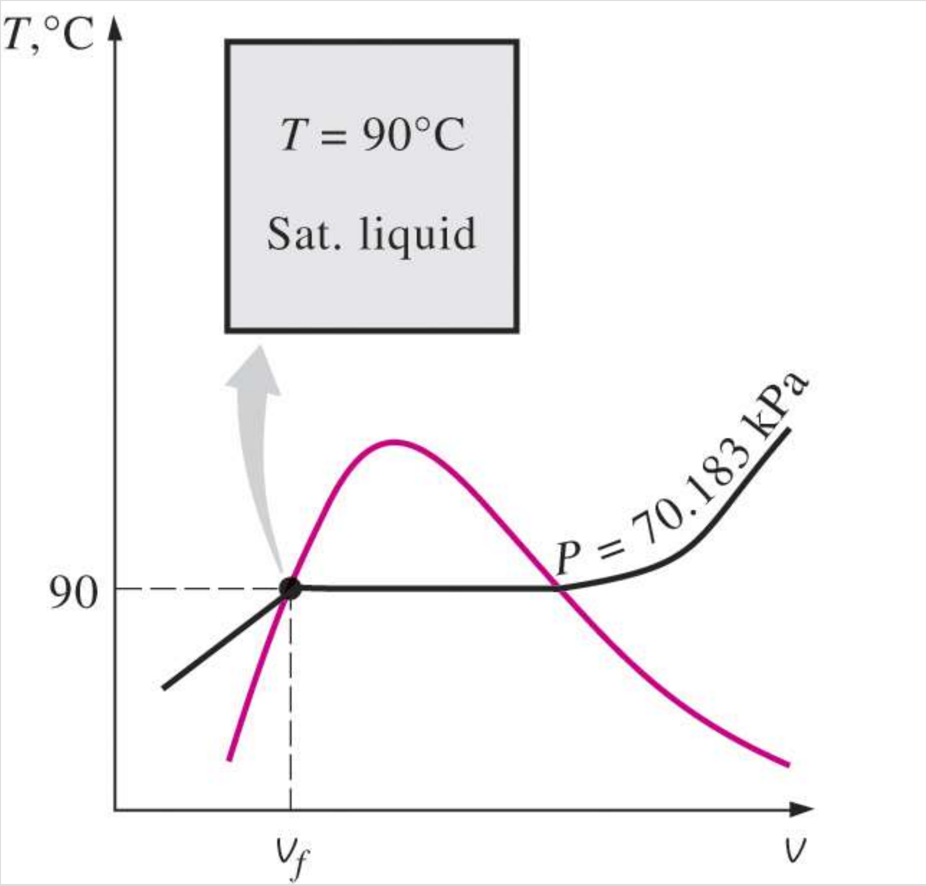
v_f = specific volume of saturated liquid

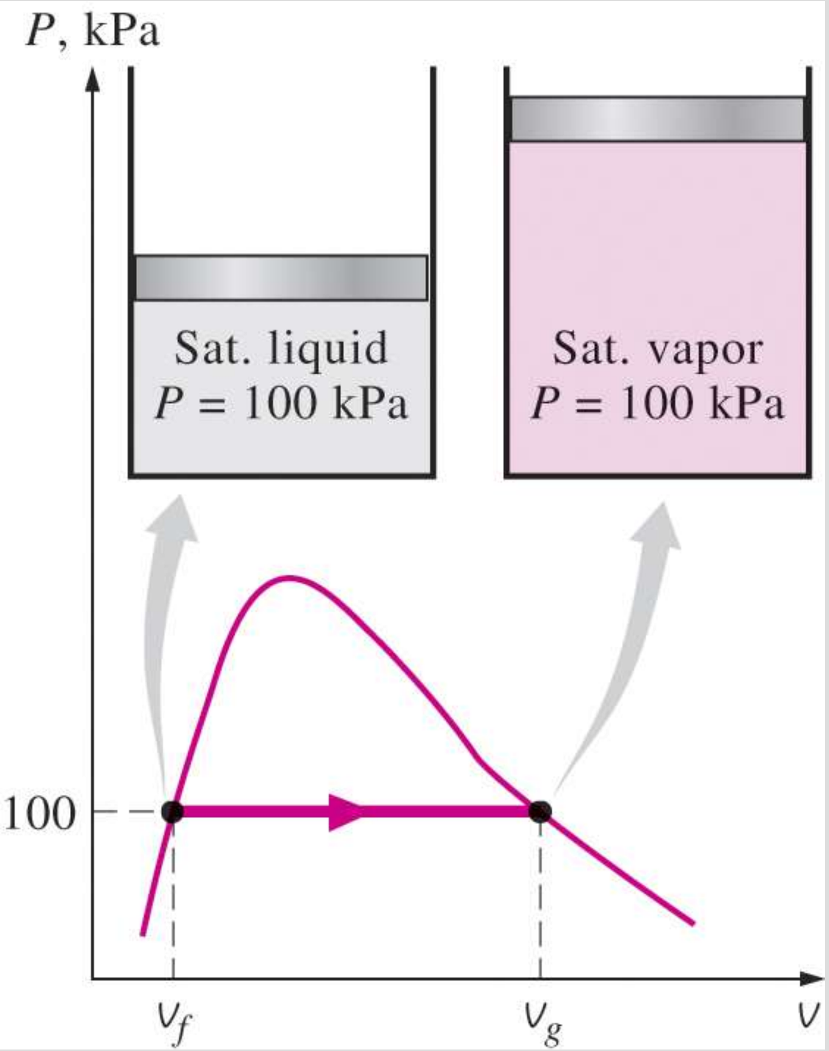
v_g = specific volume of saturated vapor

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

- 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

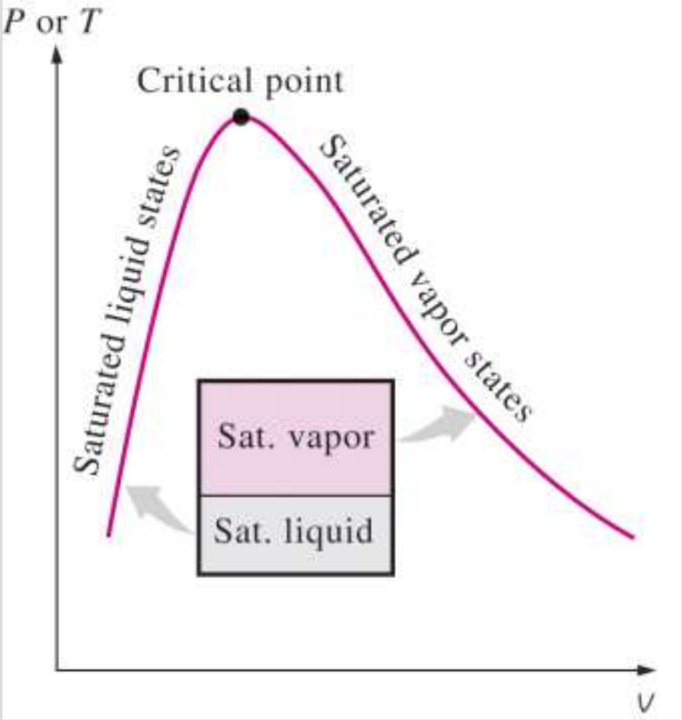
- During boiling, the temperature of a substance remains the same.
- This means that pressure and temperature are not independent during this period.
- Pressure and temperature cannot be used to specify the state in this case.
- Other properties are needed, e.g. v, u, or h
- How do we find v, u, or h?

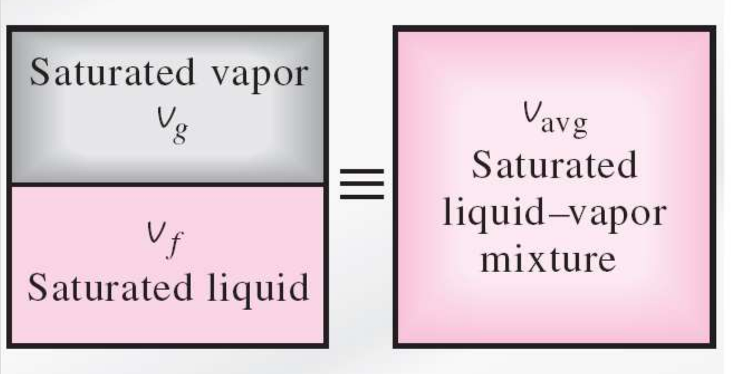
Saturated Liquid–Vapor Mixture

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

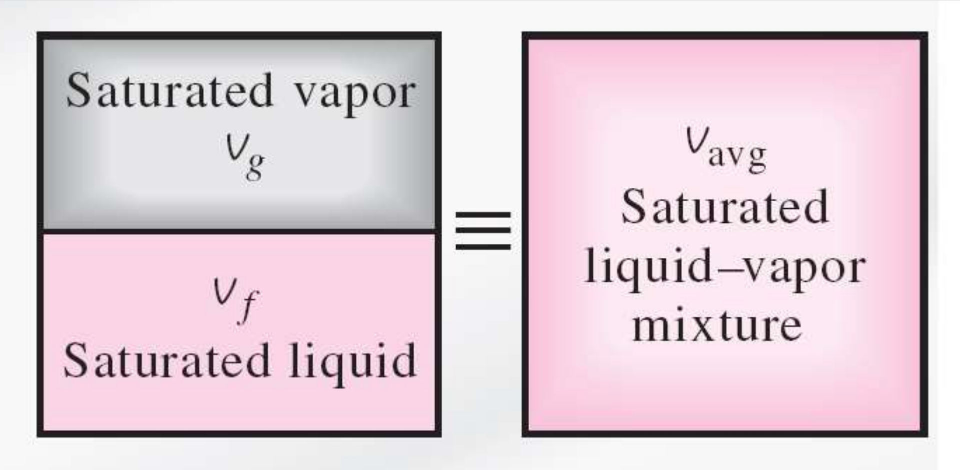
$$m_{\text{total}} = m_{\text{liquid}} + m_{\text{vapor}}$$

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

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

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

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



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

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

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

$$v_{avg} = v_f + x \, v_{fg}$$

Saturated Liquid–Vapor Mixture

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

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

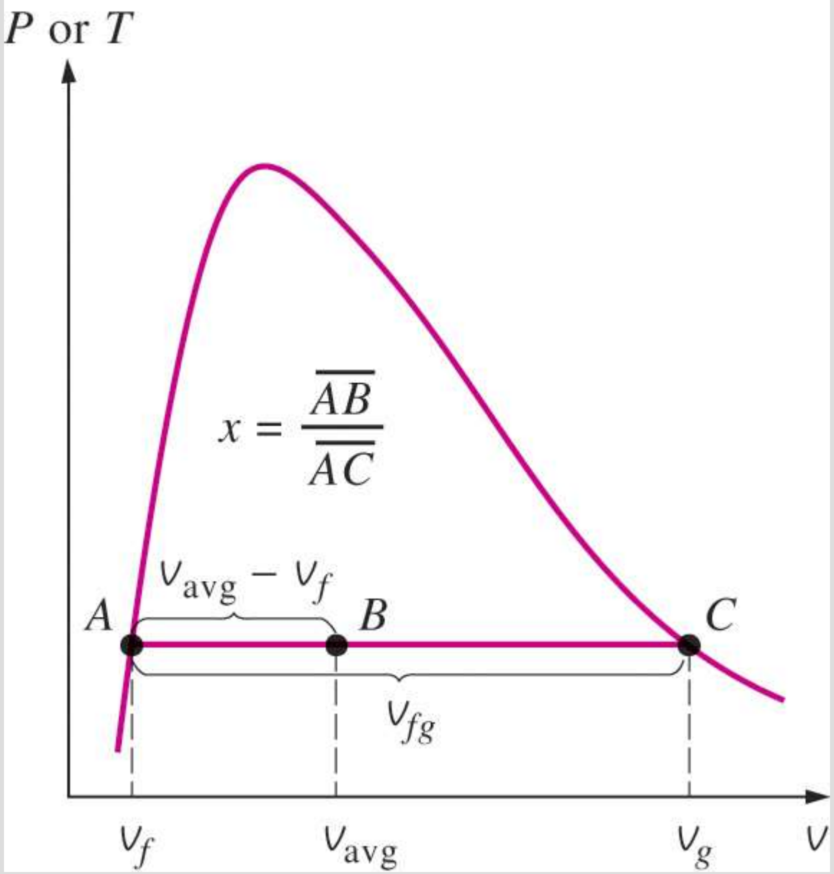
$$h_{avg} = h_f + x\,h_{fg}$$

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

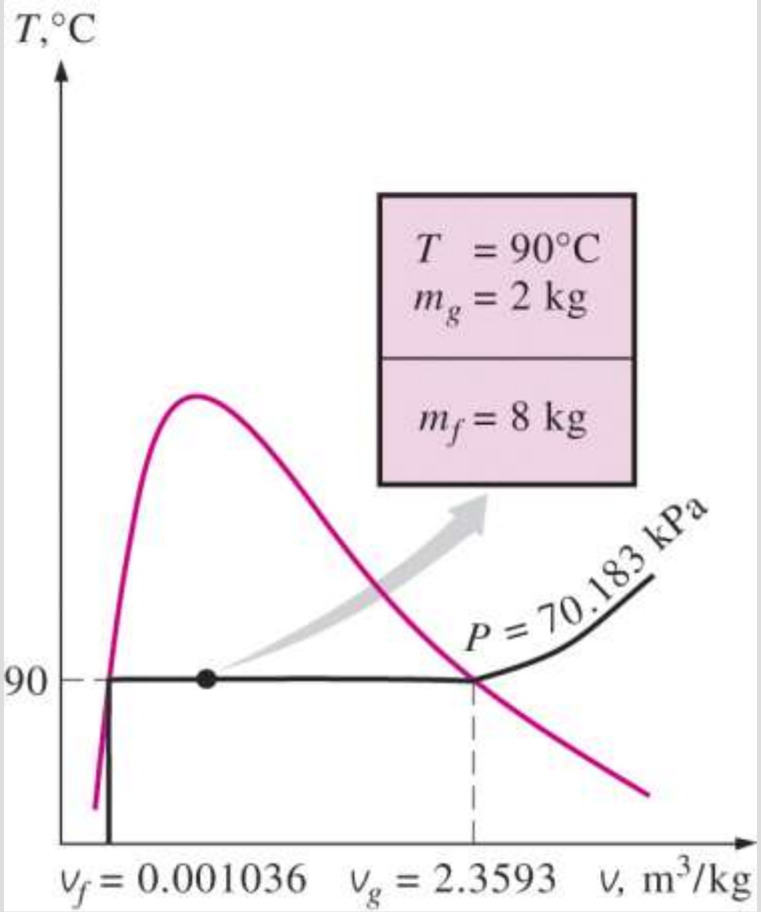
$$x = \frac{v_{\text{avg}} - v_f}{v_{fg}}$$

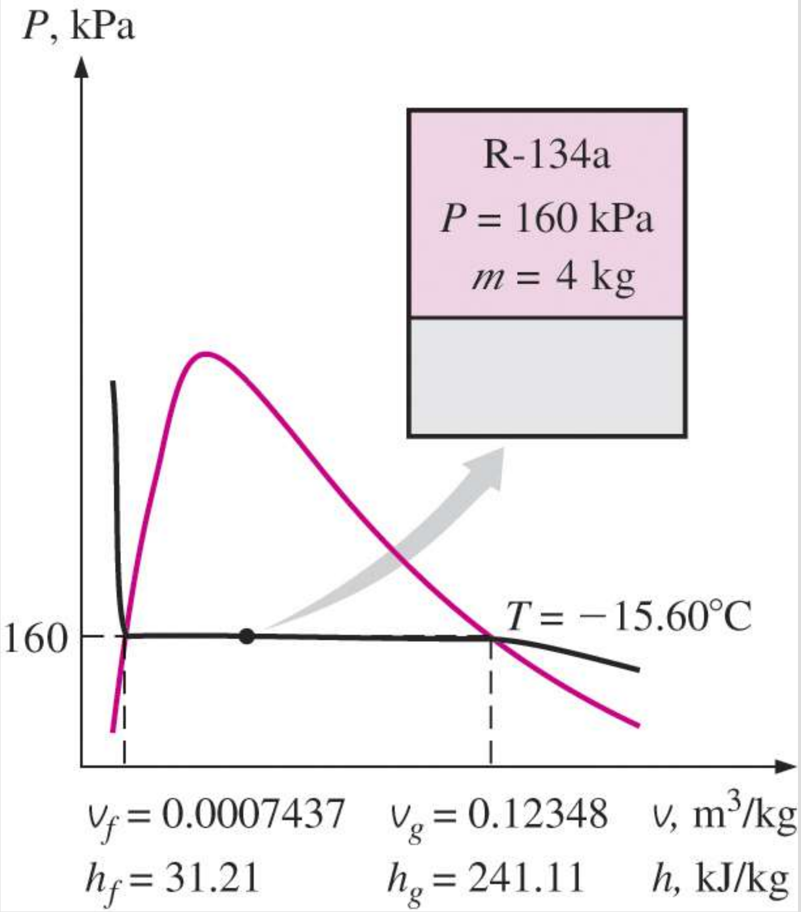
$$x = \frac{u_{\text{avg}} - u_f}{u_{fg}}$$

$$x = \frac{h_{\text{avg}} - h_f}{h_{fg}}$$



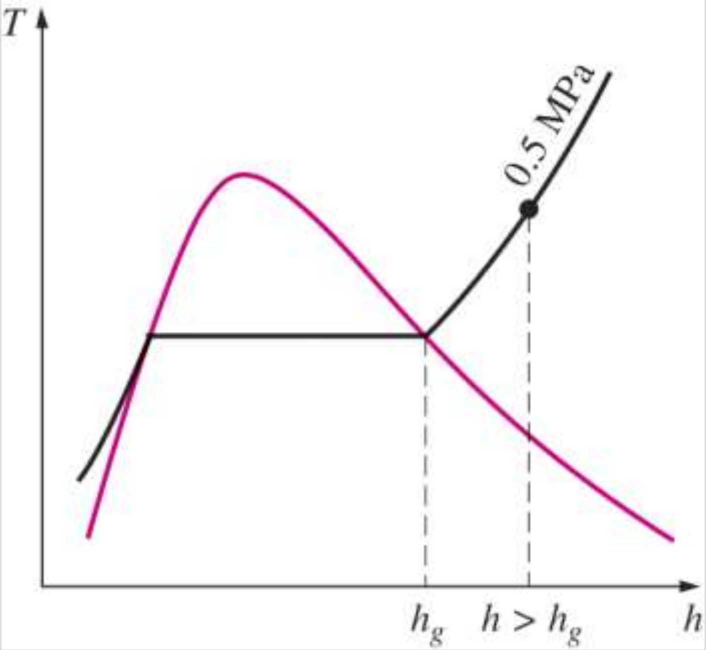
Saturated Liquid–Vapor Mixture





Superheated Vapor

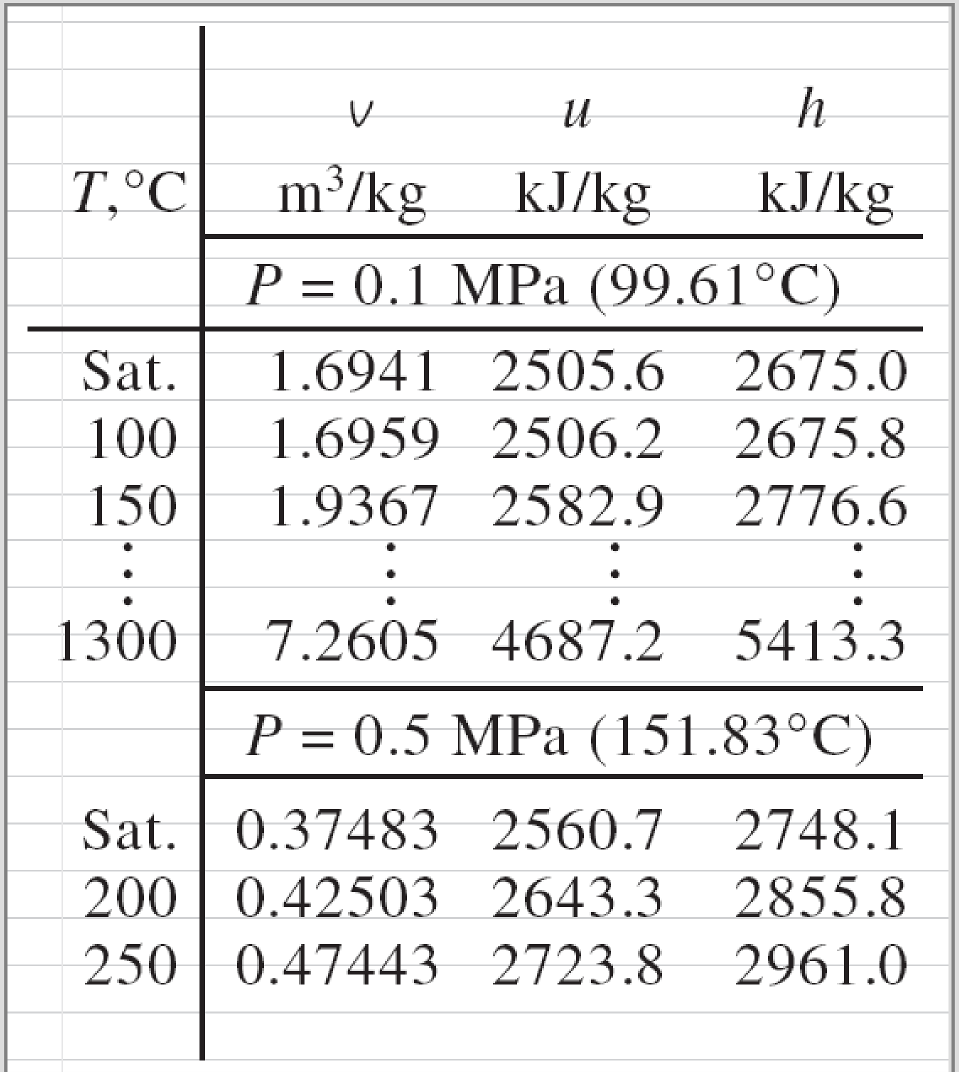
- In the region to the right of the saturated vapor line, a substance exists as superheated vapor.
- In this region, temperature and pressure are independent properties.



- The superheated region is characterized by:
  - **Higher temperatures ($T > T_{sat}$ at a given P)**
  - **Low pressures ($P < P_{sat}$ at given T)**
  - **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

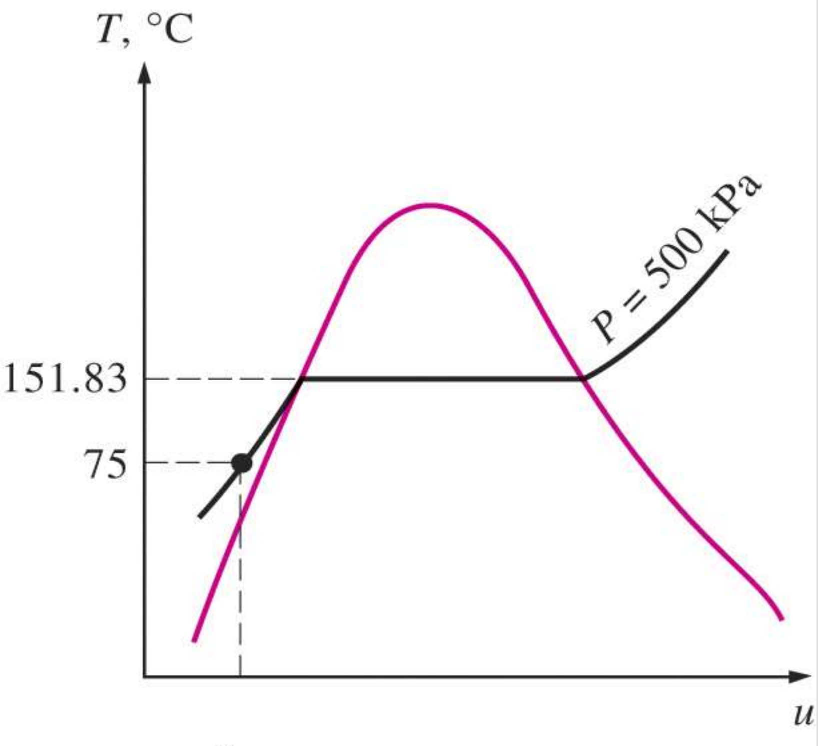
Table A-6
Superheated water



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)**
  - **Higher pressure ($P > P_{sat}$ at a given T)**
  - **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)**

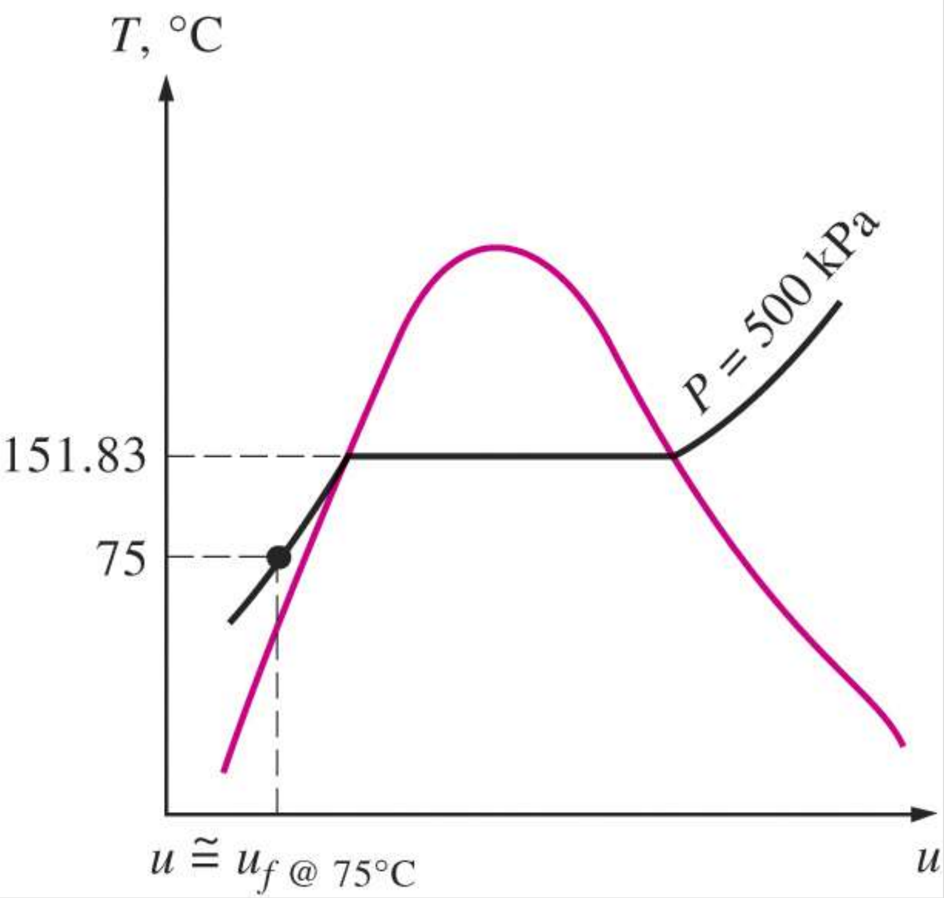
Compressed Liquid

- 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)

The Ideal-Gas Equation of State

- An ***equation of state*** is 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.

$$Pv = RT \longrightarrow PV = mRT \longrightarrow \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

- *R* is called the ***gas constant***
- Note: T must be in kelvin
- This equation predicts the *P-v-T* behavior of a gas quite accurately within some properly selected region.
- It is an easier alternative to looking up *P*, *v*, and *T* from tables
  - Problem: limited to the gas phase (superheated region only)

The Gas Constant

- The gas constant is fixed for each gas.
- It can be found from:

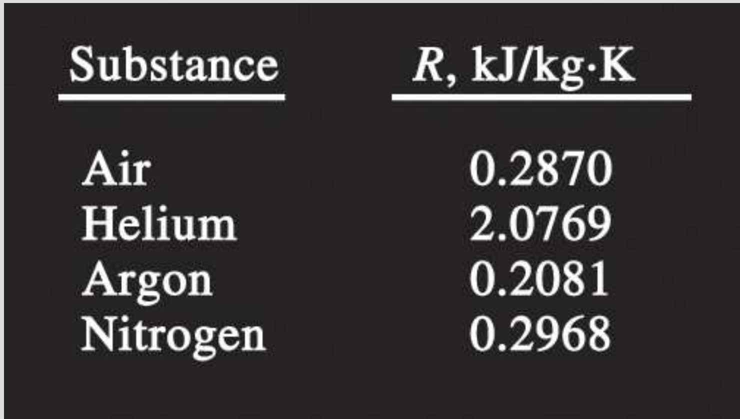
$$R = \frac{R_u}{M}$$

where:

R_u: universal gas constant (8.314 kJ/kmol.K)

M: molar mass (kg/kmol)

- Listing of the gas constant for numerous gases can be found in textbooks.



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

OTHER EXPRESSIONS OF THE IDEAL-GAS EQUATION OF STATE

$$V = mv \longrightarrow \boxed{PV = mRT}$$

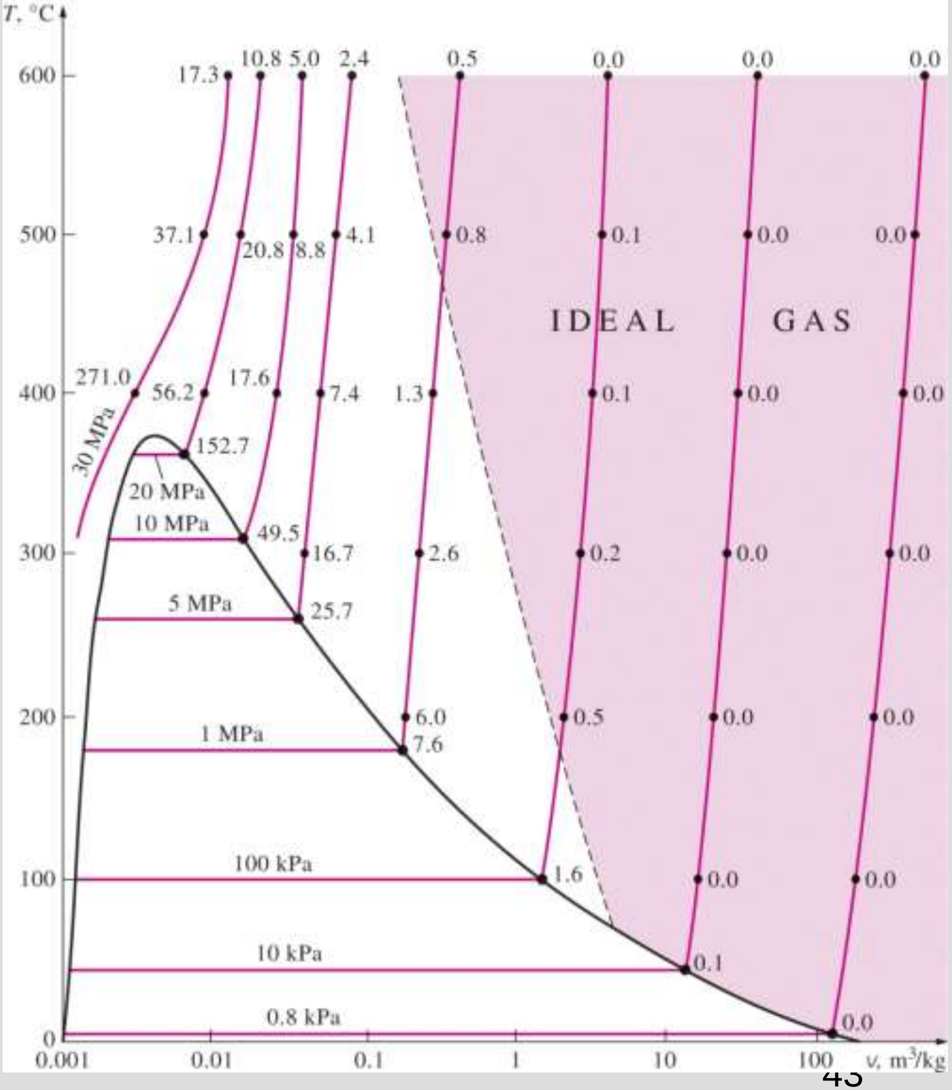
Mass = Molar mass × Mole number

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

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

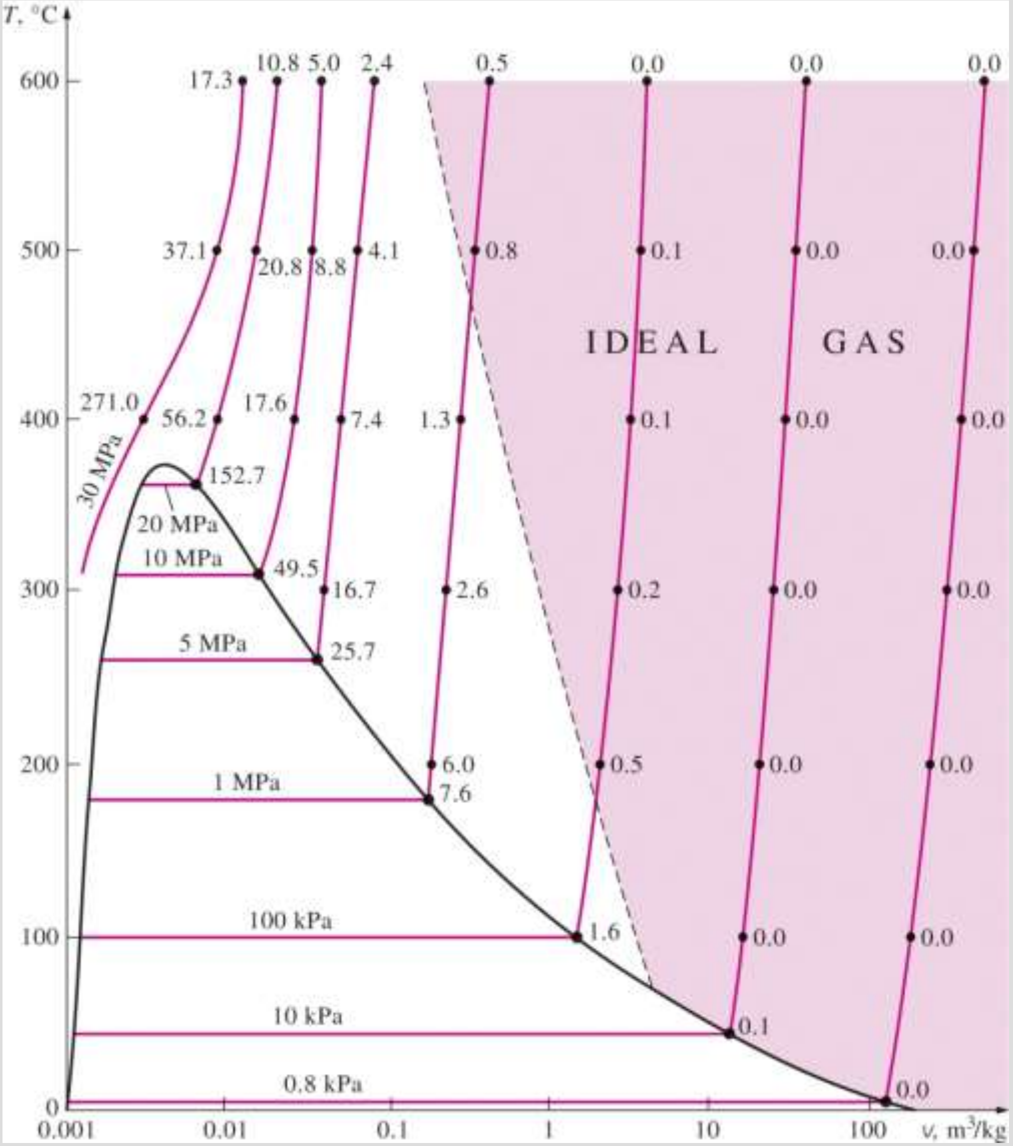
Validity of the Ideal-Gas Equation of State

- 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, the ideal gas assumption yields unacceptable errors, particularly in the vicinity of the critical point and the saturated vapor line.



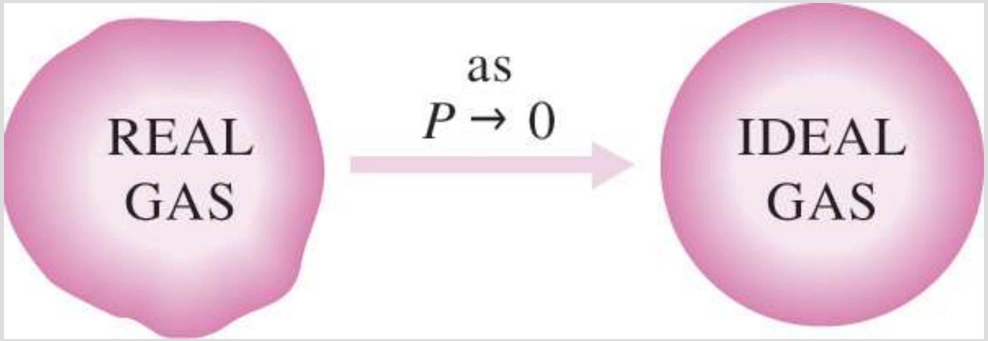
Percentage of error ($[|v_{table} - v_{ideal}|/v_{table}] \times 100$)

WHEN CAN A GAS BE CONSIDERED IDEAL?

- Gases behave as an ideal gas at low densities (i.e., low pressure, high temperature).
- At very low pressures, all gases approach ideal-gas behavior (regardless of their temperature).

What is the criteria for low pressure and high temperature?

- The pressure or temperature of a gas is high or low relative to its ***critical temperature or pressure***.

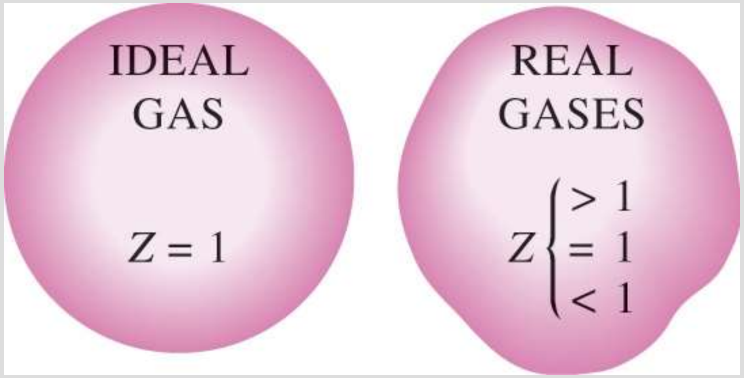


COMPRESSIBILITY FACTOR

- The ***Compressibility factor (Z)*** is a factor that accounts for the deviation of real gases from ideal-gas behavior at a given temperature and pressure.

$$Pv = ZRT \quad \Rightarrow \quad Z = \frac{Pv}{RT} \qquad\qquad Z = \frac{v_{\text{actual}}}{v_{\text{ideal}}}$$

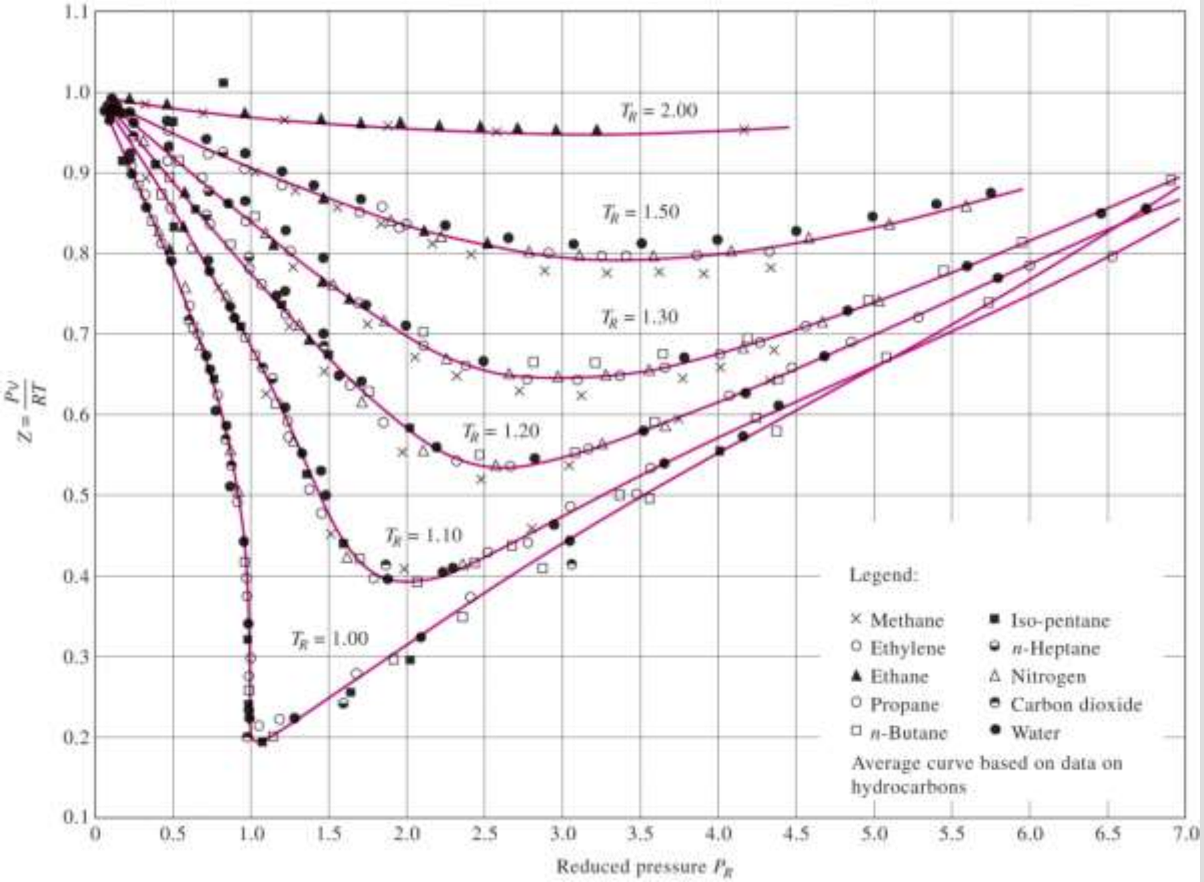
- The farther away Z is from unity, the more the gas deviates from ideal-gas behavior.
- The compressibility factor is unity for ideal gases.



COMPRESSIBILITY FACTOR

Reduced pressure: $P_R = \dfrac{P}{P_{cr}}$

Reduced temperature: $T_R = \dfrac{T}{T_{cr}}$



Other Equations of State

Many 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

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

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

Other Equations of State

Beattie-Bridgeman Equation of State

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

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

Benedict-Webb-Rubin Equation of State

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

Accuracy of Other Equations of State