Thermodynamics I
Chapter 2
Properties of Pure Substances

Mohsin Mohd Sies

Fakulti Kejuruteraan Mekanikal, Universiti Teknologi Malaysia

Properties of Pure Substances (Motivation)

To quantify the changes in the system, we have to be able to describe the substances which make up the system.

The substance is characterized by its properties.

This chapter shows how this is done for two major behavioral classes of substance covered in this course; phase-change fluids, and gases.

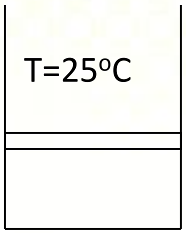
PURE SUBSTANCE

3 major phases of pure substances;

- Solid
- Liquid
- Gas
  - plasma

Phase Change of Pure Substances

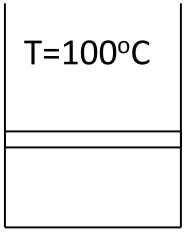
ex. Water at 1 atm of pressure



Not about to evaporate

Heat added → T ↑

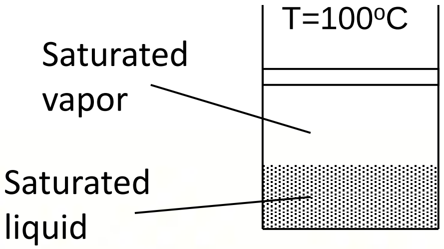
Compressed liquid phase



About to evaporate

Heat added → evaporation starts

Saturated liquid phase



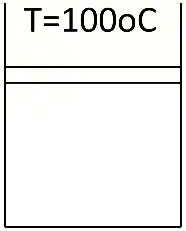
Heat added → continues evap.
→ **T unchanged**

Wet steam or

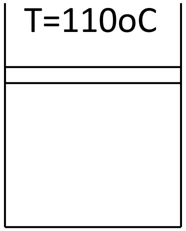
Saturated liquid-vapor mixture

Phase Change of Pure Substances (ctd.)

ex. Water at 1 atm of pressure



All liquid evaporated
(*about to condense*)
Heat removed → *condensation*
Saturated vapor phase



Not about to condense
Heat added → T ↑
Superheated vapor phase

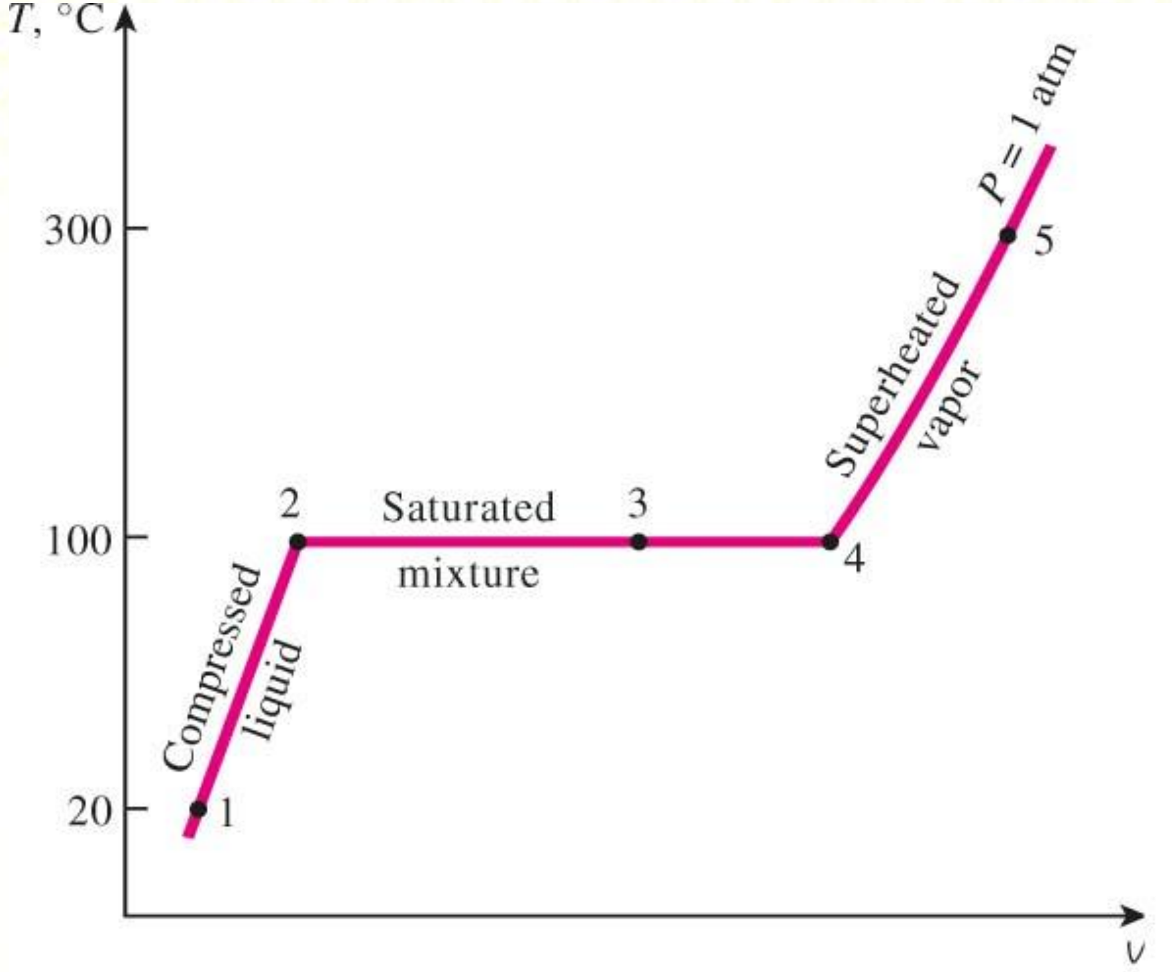
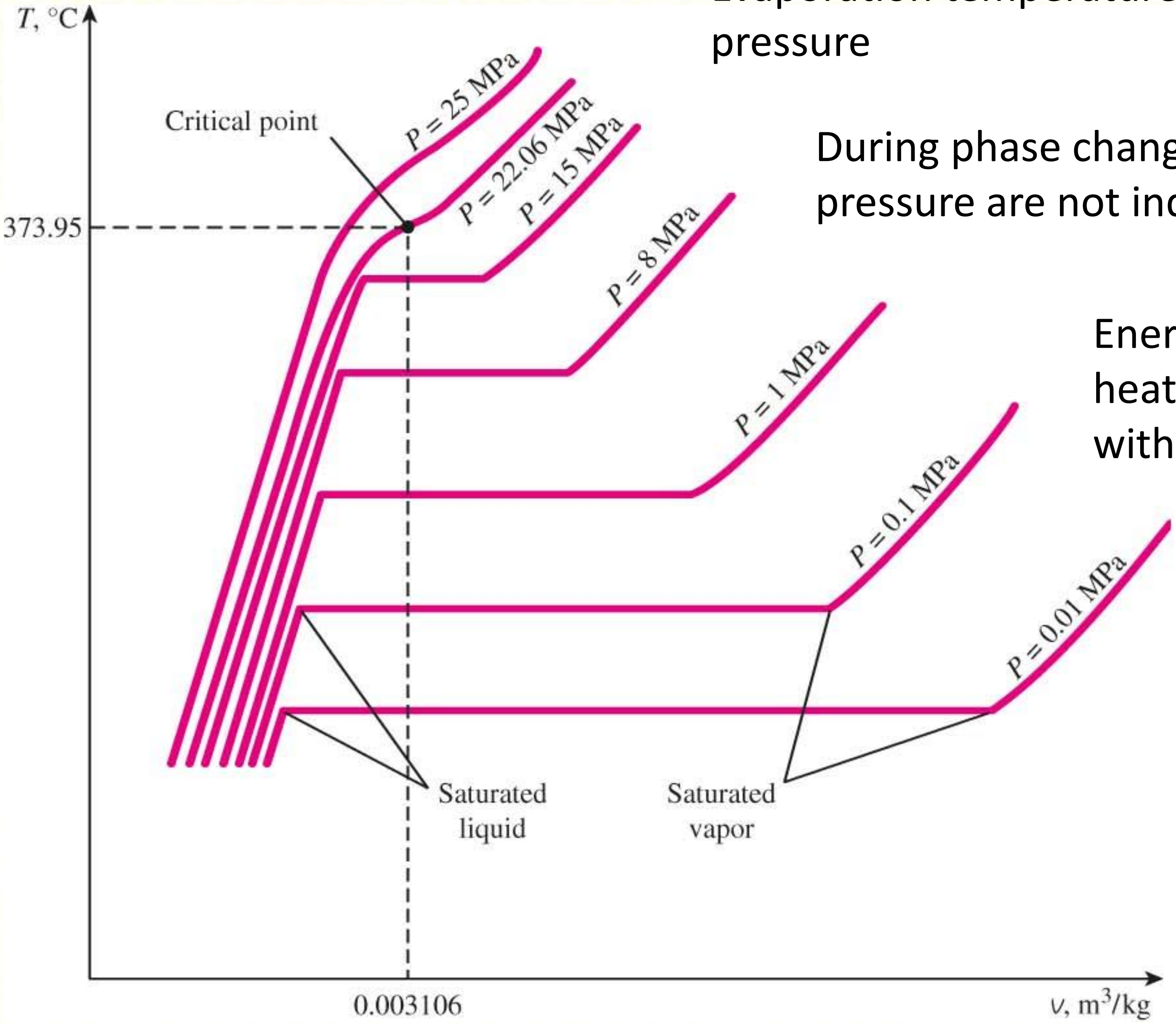


FIGURE 3–11

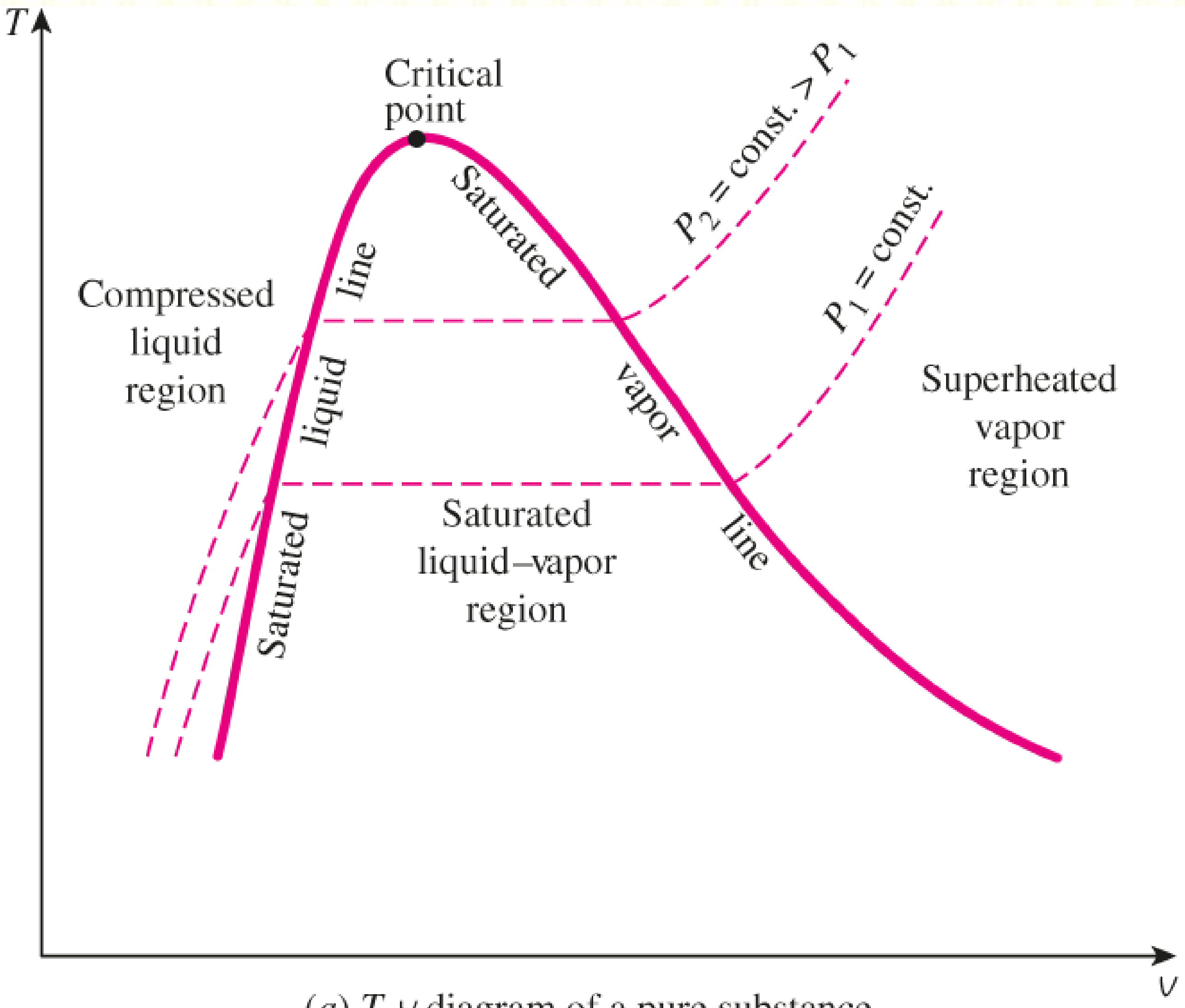
T-v diagram for the heating process of water at constant pressure.



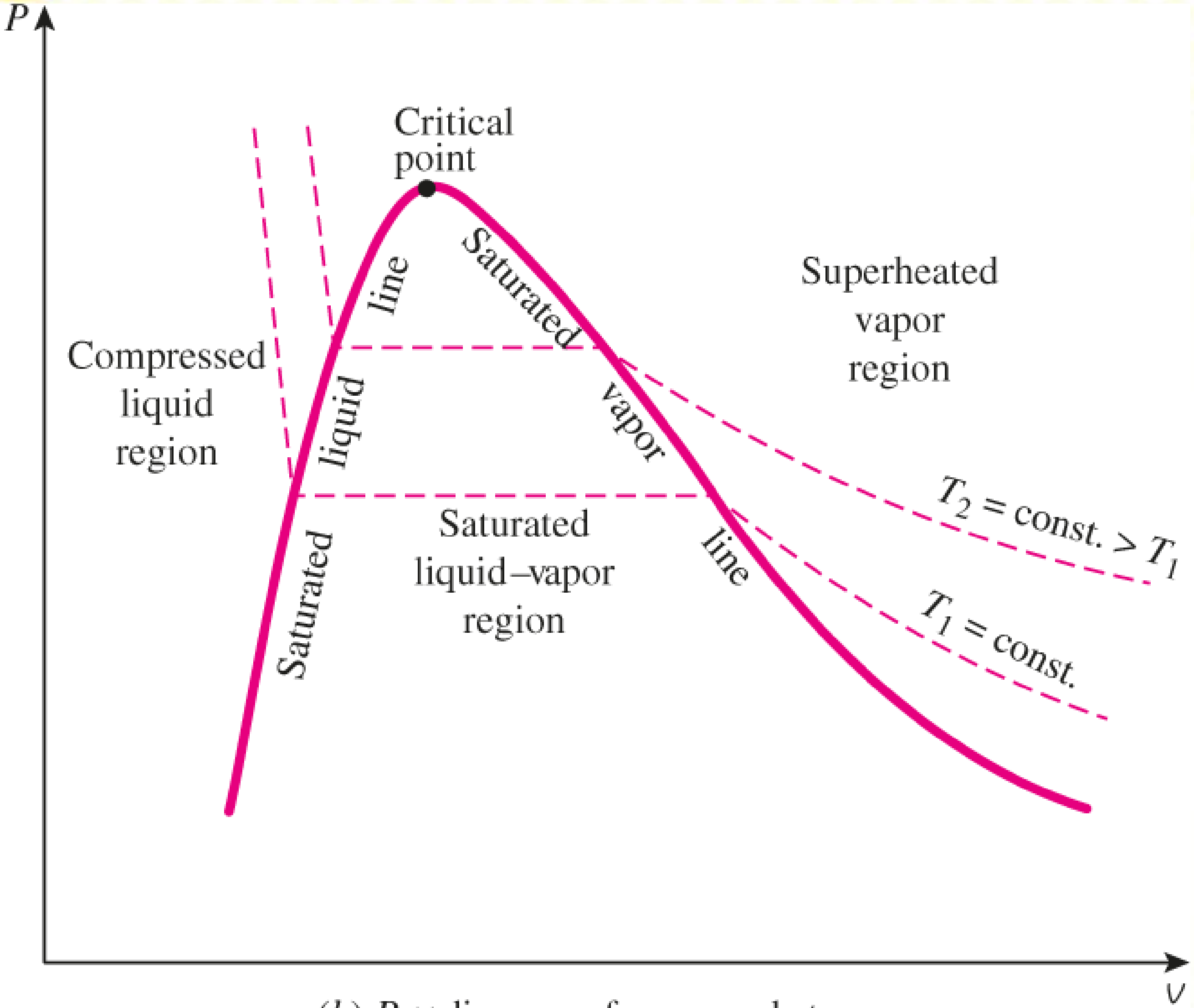
Evaporation temperature changes with pressure

During phase change, temperature and pressure are not independent T_{sat} <-> P_{sat}

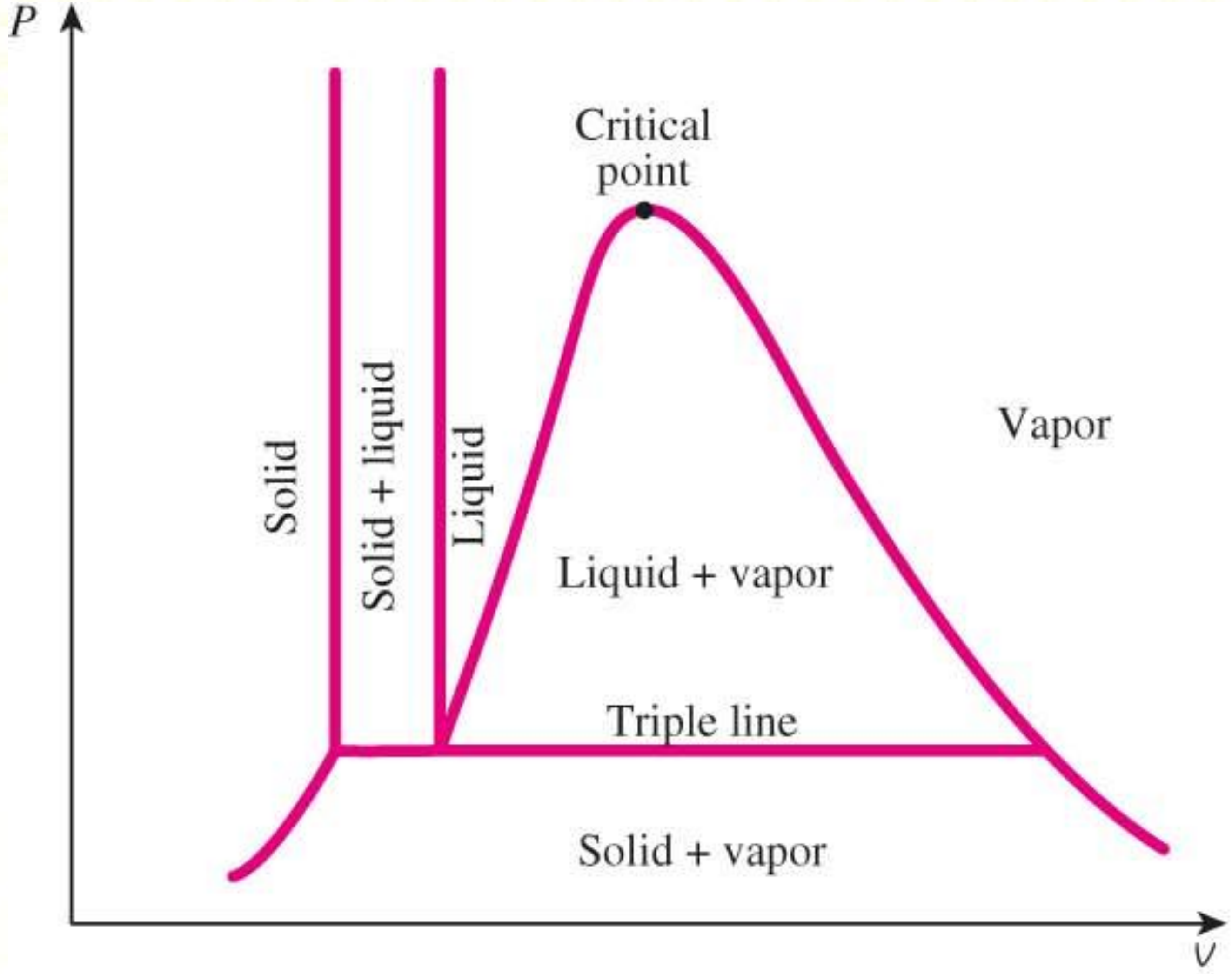
Energy needed to vaporize (latent heat of vaporization) decreases with increasing pressure



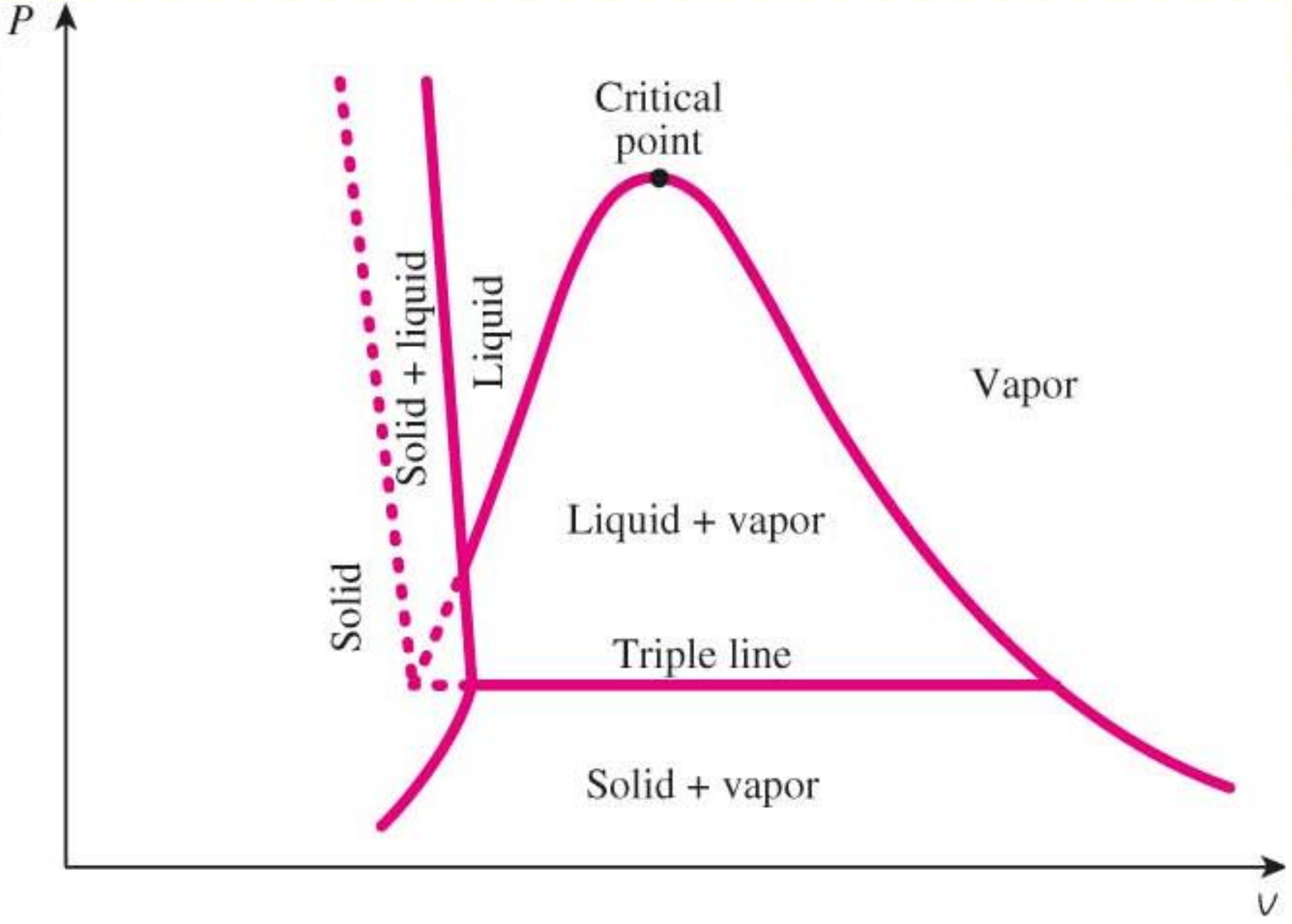
(*a*) *T*-v diagram of a pure substance



(*b*) *P*-v diagram of a pure substance



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



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

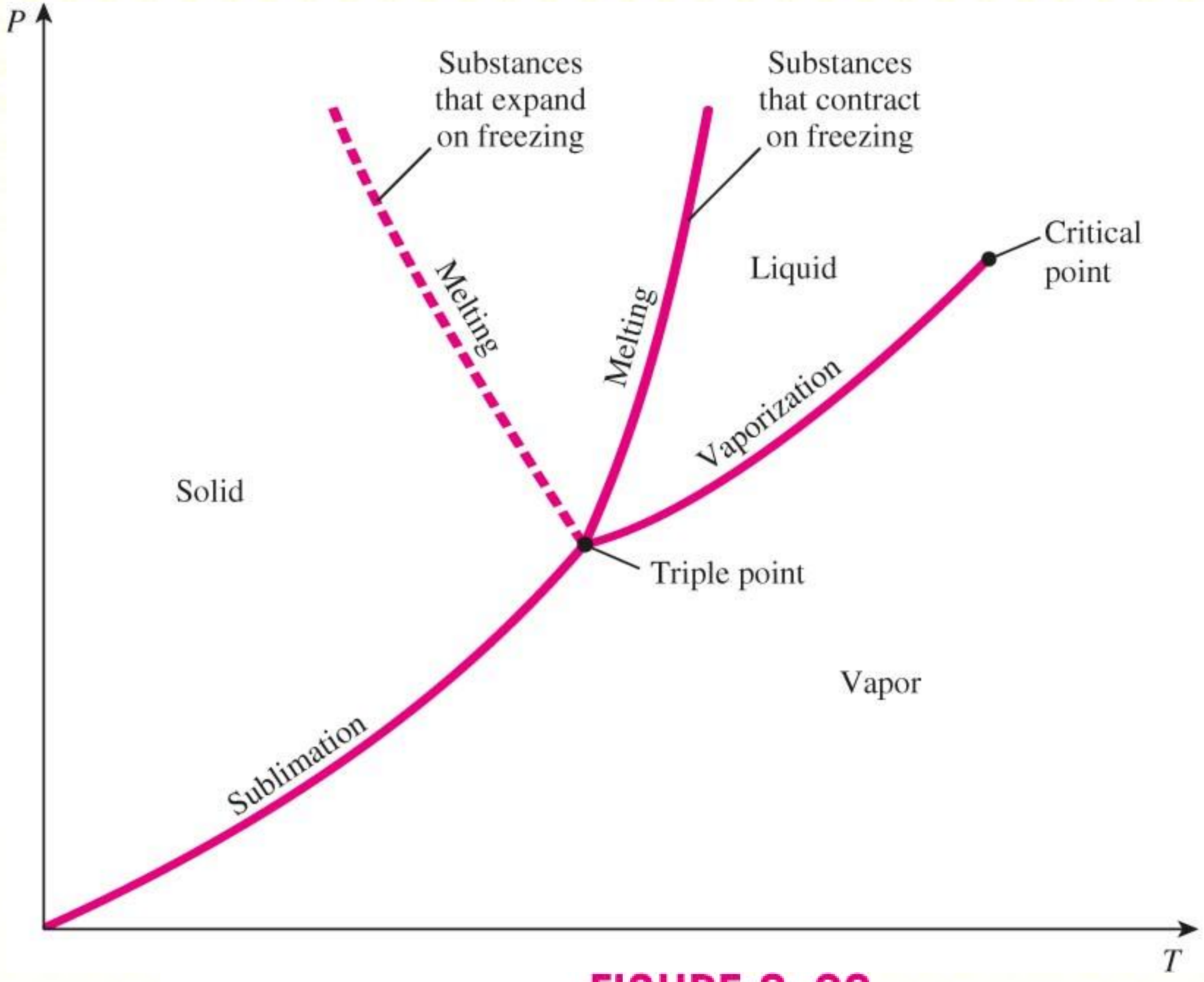


FIGURE 3–23

P-T diagram of pure substances.

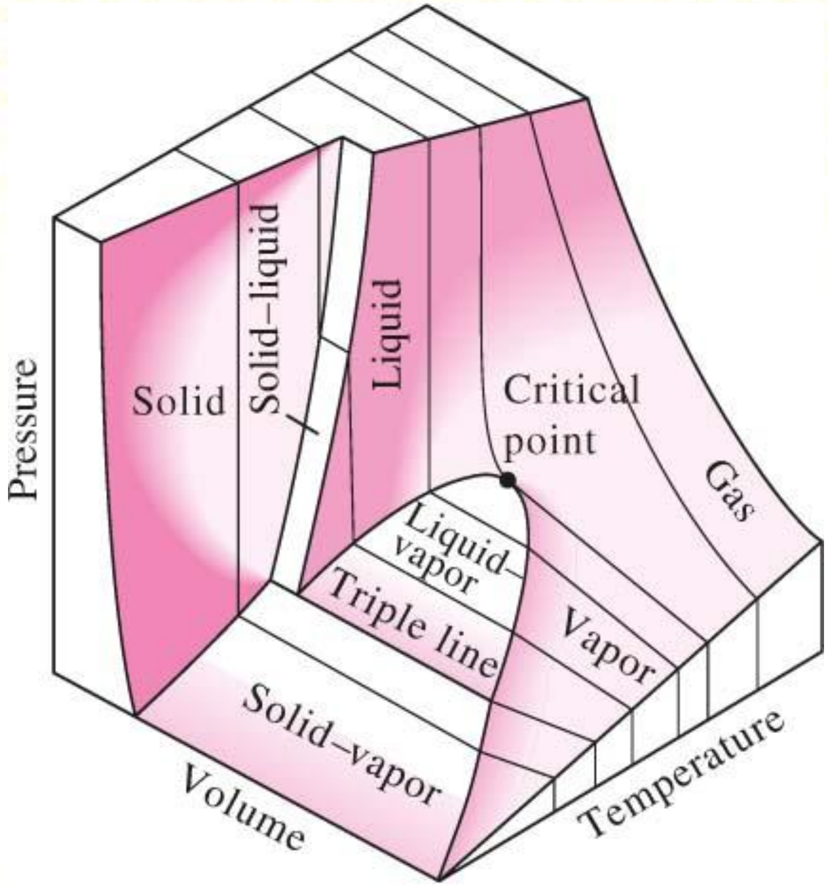


FIGURE 3–24

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

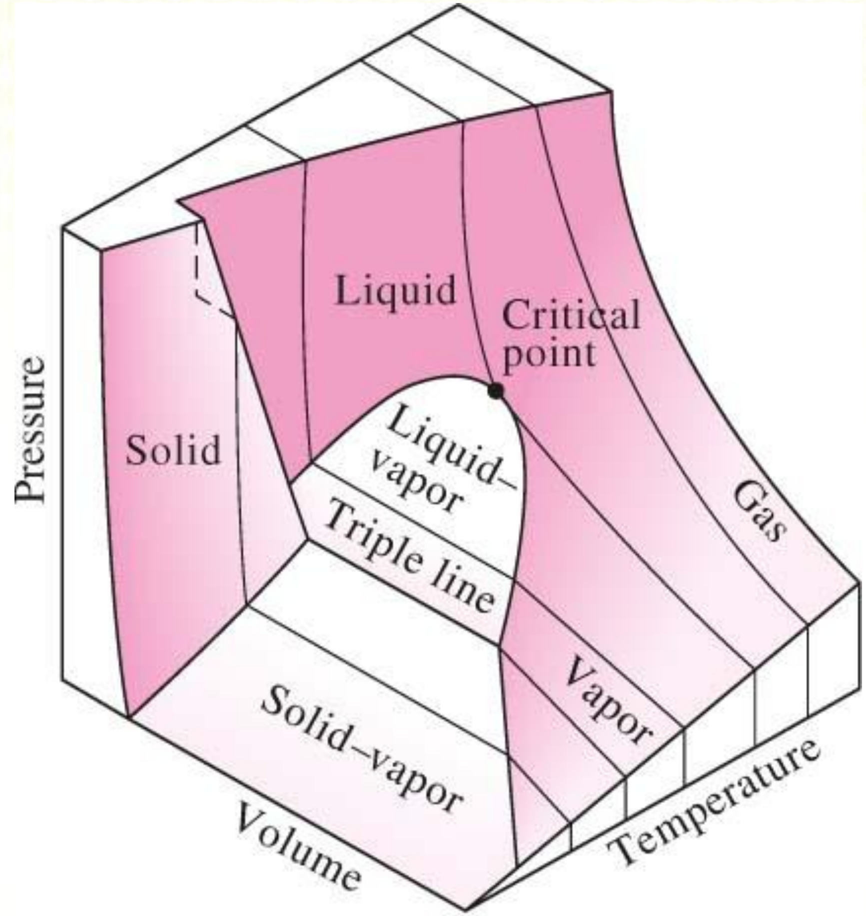
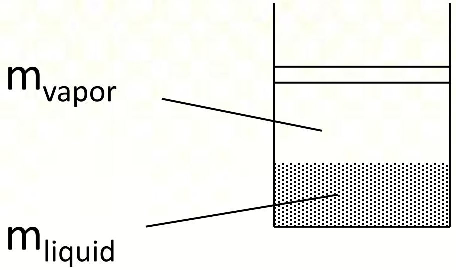


FIGURE 3–25
P-v-T surface of a substance that *expands* on freezing (like water).

QUALITY, x (*2 phase condition)*



Saturated liquid-vapor mixture condition

x is a thermodynamic property

x exists only in the liquid-vapor *mixture* region

$$\text{Degree of evaporation} = \text{Dryness fraction} = \text{quality} \equiv \frac{m_{vapor}}{m_{total}} = x$$

$$\mathbf{0 \leq x \leq 1}$$

(wet)	(dry)
100% liquid	100% vapor

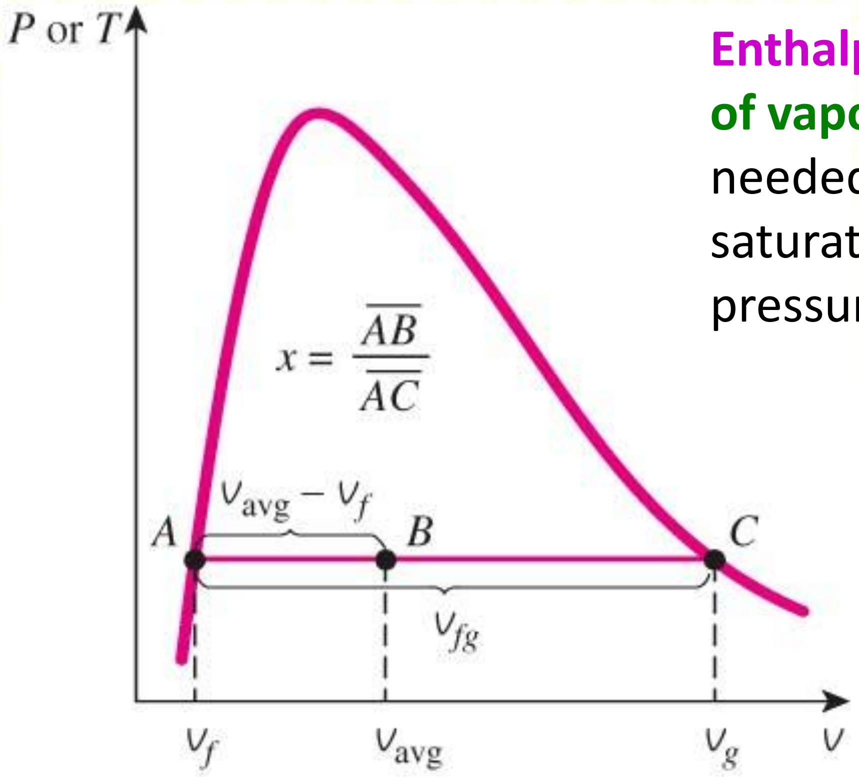


FIGURE 3–34

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

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.

Quality (cont.)

$$x = \frac{m_g}{m_g + m_f} \qquad 1 - x = \frac{m_f}{m_g + m_f}$$

$$x \equiv \frac{m_g}{m_g + m_f}$$

$$= \frac{v - v_f}{v_g - v_f} \qquad = \frac{h - h_f}{h_g - h_f}$$

$$= \frac{u - u_f}{u_g - u_f} \qquad = \frac{s - s_f}{s_g - s_f}$$

Some Additional Thermodynamic Properties

Internal Energy, U [kJ]

Specific Internal Energy, u [kJ/kg]

Enthalpy, H [kJ]

$H \equiv U + PV$

Specific Enthalpy, h [kJ/kg]

$h = u + Pv$

Entropy, S [kJ/K]

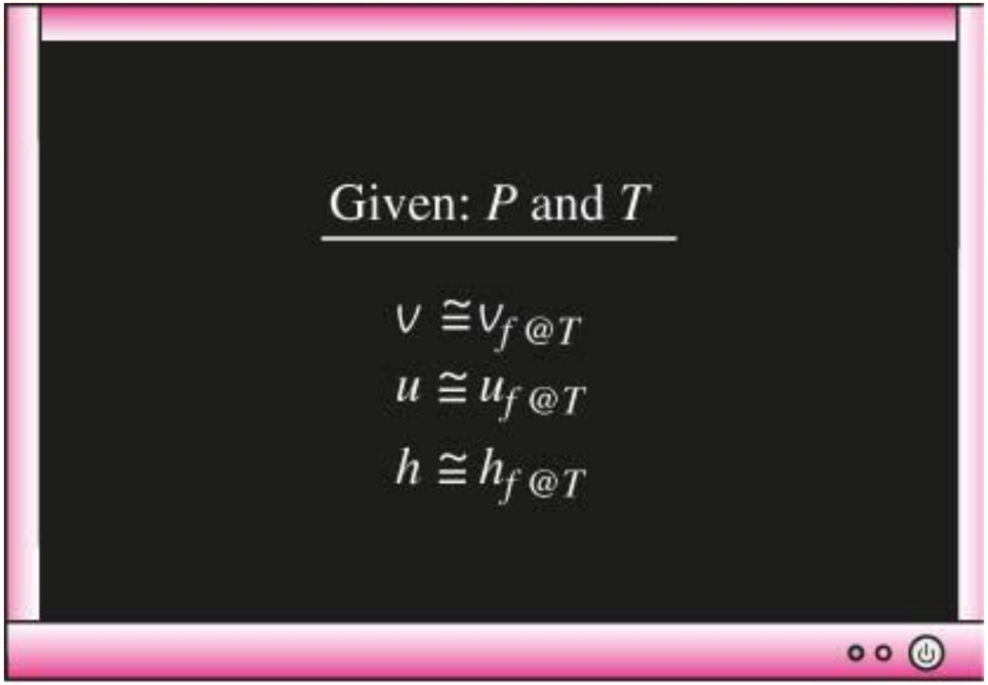
Specific Entropy, s [kJ/kg.K]

PROPERTY TABLES

3 types of tables
- Compressed liquid table
- Saturated table
- Superheated table

Saturated tables
- Temperature table – T in easy to read numbers
- Pressure table – P in easy to read numbers

Compressed Liquid Approximation



Given: P and T

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

FIGURE 3–40

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

Choosing which table to use

!!!!Determine state (phase) first!!!!

How? Compare the given properties against the saturated table

(ex. given h & T)

If $h_f \leq h \leq h_g$ at the given T

→Mixture phase

→ use saturated table

If $h > h_g$ at the given T

→ Superheated phase

→ use superheated table

If $h < h_f$ at the given T

→ Compressed liquid phase

→ use saturated table

$$h \approx h_f \Big|_T$$

Choice of tables (cont.)

If P & T is given

$P \leftrightarrow T_{sat}$

$T \leftrightarrow P_{sat}$

$\left.\begin{array}{l} P > P_{sat} \text{ at the given } T \\ T < T_{sat} \text{ at the given } P \end{array}\right\}$ Compressed liquid

$\left.\begin{array}{l} P < P_{sat} \text{ at the given } T \\ T > T_{sat} \text{ at the given } P \end{array}\right\}$ Superheated vapor

Choice of tables (additional)

(ex. given h & P)

If $h_f \leq h \leq h_g$ at the given P

→Mixture phase

→ use saturated table

If $h > h_g$ at the given P

→ Superheated vapor phase

→ use superheated vapor table

If $h < h_f$ at the given P

→ Compressed liquid phase

→ use saturated table

P ↔ Tsat

$$h \neq h_f\big|_P$$

$$h \approx h_f\big|_{Tsat}$$

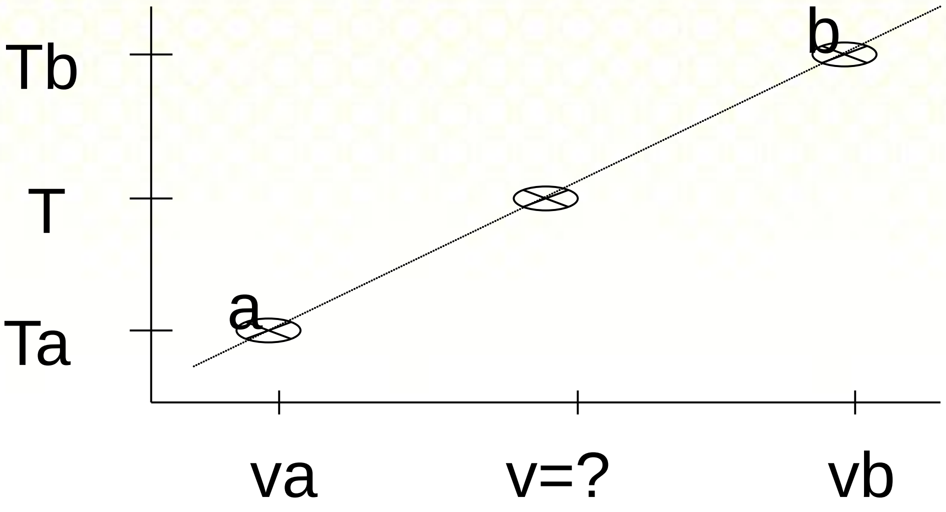
Notes on Using Property Tables

Some tables do not list ***h*** (or ***u***)
→ ***u*** (or ***h***) can be obtained from **h = u + Pv**

Values for compressed liquid is taken as the same as that of saturated liquid at the same **temperature**

ex. T=25^{o}C, P=1 bar (compressed liquid)

Interpolation

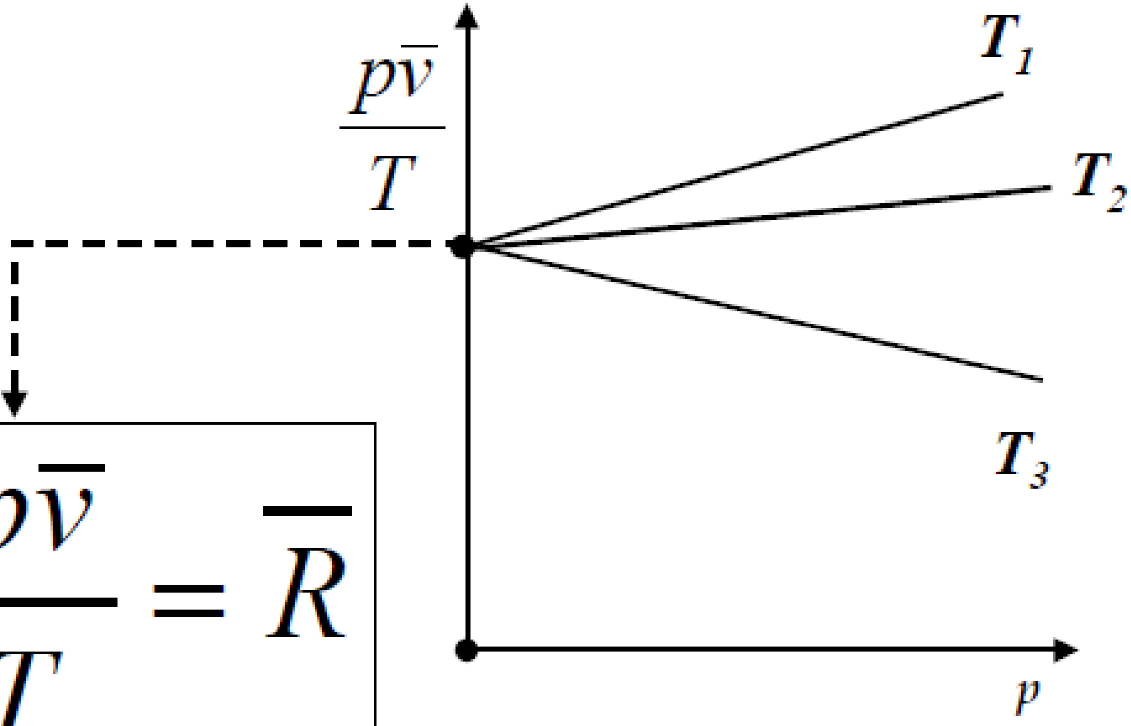


Assume a & b connected by a straight line

Employ concept of slope $\frac{\Delta y}{\Delta x} = \text{constant}$

$$\frac{\Delta v}{\Delta T} = \frac{v - v_a}{T - T_a} = \frac{v_b - v_a}{T_b - T_a}$$

Ideal Gas
(Initial Observations)



$$\boxed{\lim_{p\to 0}\frac{p\bar{v}}{T}=\bar{R}}$$

IDEAL GAS

(for pressures much lower than critical pressure)

Equation of *state* for ideal gas

$$\boxed{PV = mRT}$$

R = Gas Constant [kJ/kg.K]

(constant for a gas, value depends on type of gas)

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

$$M = \text{Molecular mass}\left[\frac{kg}{kmol}\right]$$

$$R_u = \text{Universal Gas Constant} = 8.314\left[\frac{kJ}{kmol.K}\right]$$

$$R = \frac{P_1V_1}{T_1m_1} = \frac{P_2V_2}{T_2m_2}$$

Can be used to relate between different states

Ideal gas **u, h, c_p, c_v** relationship

Constant Volume Specific Heat Capacity **c_v**

$$\boxed{c_v = \frac{du}{dT}}$$

Constant Pressure Specific Heat Capacity, **c_p**

$$\boxed{c_p = \frac{dh}{dT}}$$

$$du = c_v dT$$

$$dh = c_p dT$$

$$c_p = c_v + R$$

$$\frac{c_p}{c_v} = k = \text{specific heat ratio}$$

$$c_p = \frac{kR}{k-1}$$

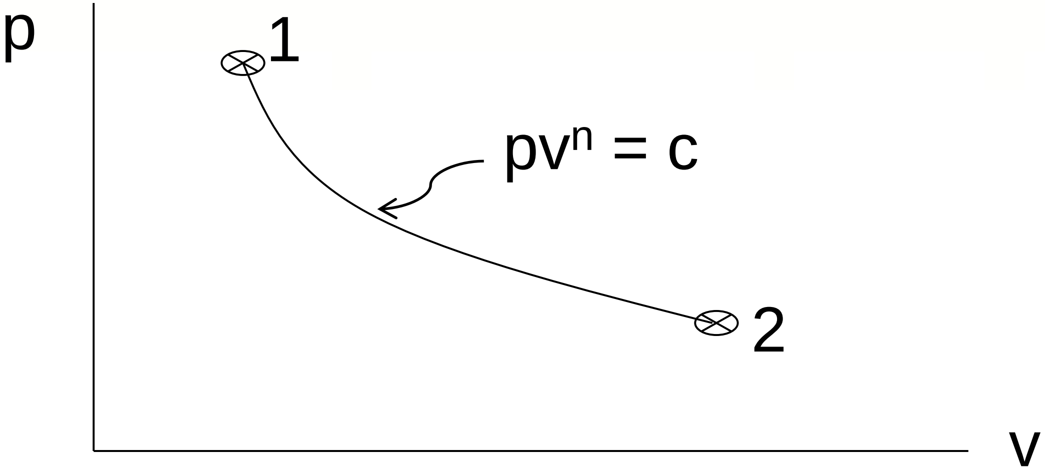
$$c_v = \frac{R}{k-1}$$

POLYTROPIC PROCESS

-Processes that obey/follow the path

$$\boxed{pv^n = c}$$

n = polytropic index $-\infty \leq n \leq \infty$



$p_1v_1^n = p_2v_2^n$ Can be used to relate between two states

Some special cases for polytropic processes

$n = 1$	isothermal
$n = 0$	isobaric
$n = \pm\infty$	const. volume

Ideal Gas & Polytropic Process combined

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}} = \left(\frac{v_1}{v_2}\right)^{n-1}$$

Can be used to relate between two states

Real Gases & Compressibility Factor

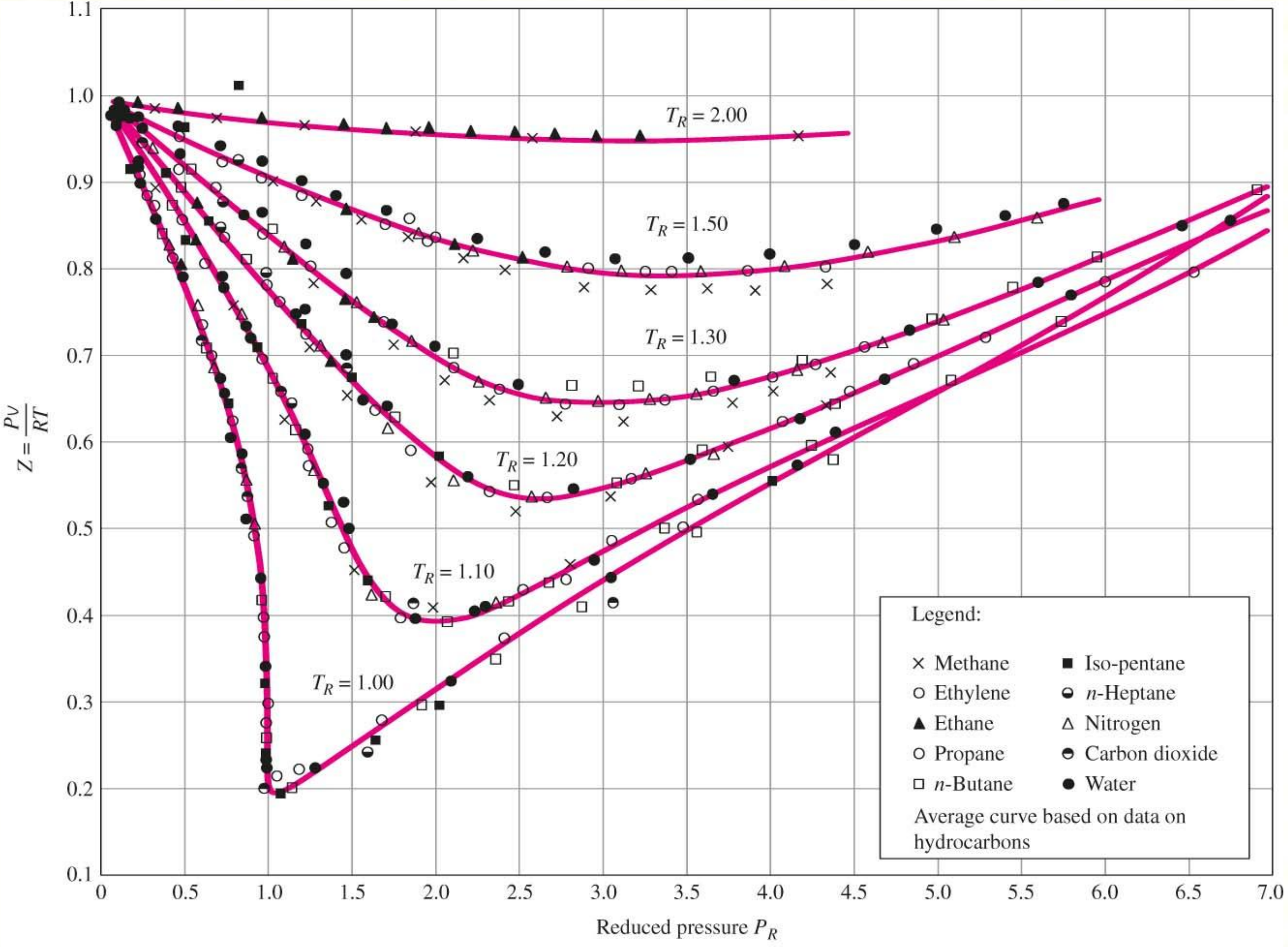
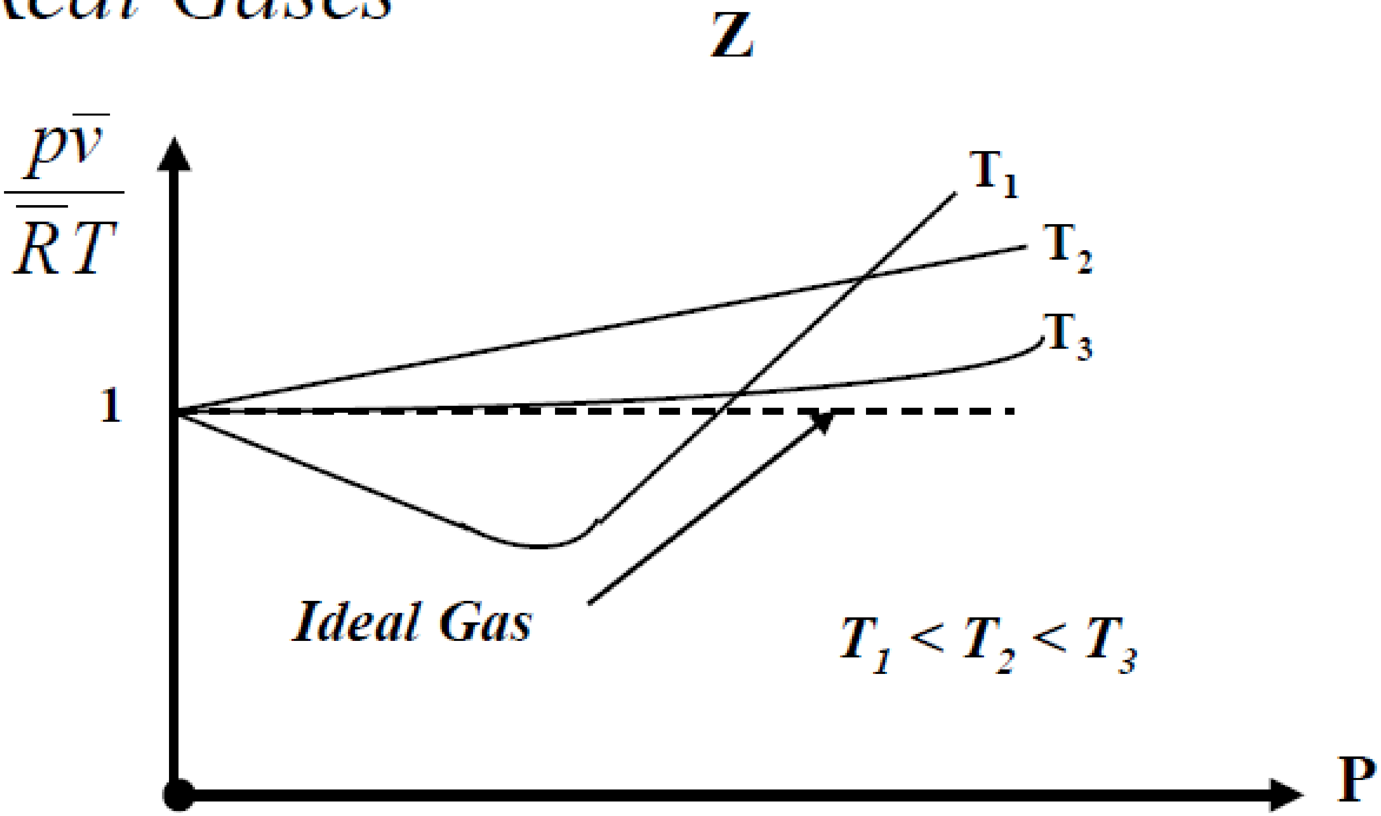


FIGURE 3–49

Comparison of *Z* factors for various gases.

Source: Gour-Jen Su, "Modified Law of Corresponding States," Ind. Eng. Chem. *(international ed.) 38 (1946), p. 803.*

Real Gases



Compressibility Factor

$$Z = \frac{Pv}{RT} = \frac{v}{RT/P} = \frac{v_{\mathrm{actual}}}{v_{\mathrm{ideal}}}$$

Reduced temperature

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

Pseudo-reduced specific volume

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

Reduced pressure

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

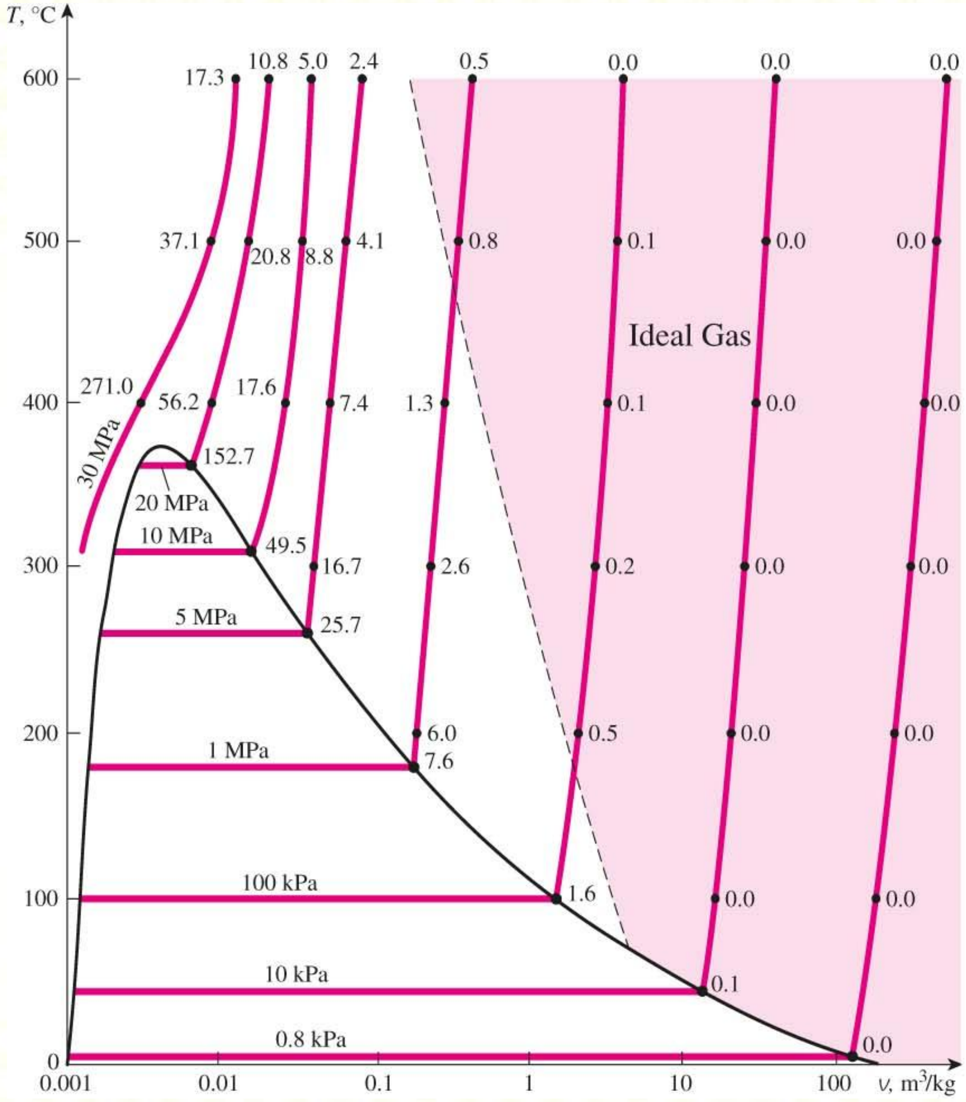


FIGURE 3–47

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

H2O (Water, Steam)

Property Tables !!!

Ideal Gas

Air,
N2 , He,
etc.

$pV = mRT$

& other relations

$h = cpT$

$u = cvT$

etc.

Other Equations of State

Van der Waal’s :

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

Beattie-Bridgeman :

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

Benedict-Webb-Rubin :

$$P=\frac{R_uT}{\bar{v}}+\left(B_0R_uT-A_0-\frac{C_0}{T^2}\right)\frac{1}{\bar{v}^2}+\frac{bR_uT-a}{\bar{v}^3}+\frac{a\alpha}{\bar{v}^6}+\frac{c}{\bar{v}^3T^2}\left(1+\frac{1}{\bar{v}^2}\right)e^{-\left(\gamma/\bar{v}^2\right)}$$

Virial equations of state:

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

The apparent and the implied

Some examples…

The Apparent	The Implied
Rigid tank Frictionless cylinder, freely moving piston	Constant volume (V=c) Constant pressure (p=c)