

Thermodynamics I

Chapter 2

Properties of Pure Substances

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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.

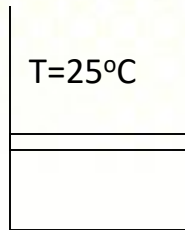
PURE SUBSTANCE

3 major phases of pure substances;

- Solid
- Liquid
- Gas
 - plasma

Phase Change of Pure Substances

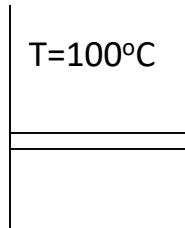
ex. Water at 1 atm of pressure



Not about to evaporate

Heat added $\longrightarrow T \uparrow$

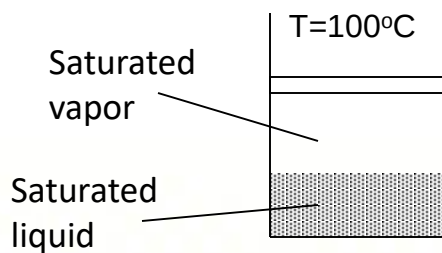
Compressed liquid
phase



About to evaporate

Heat added $\longrightarrow$ evaporation starts

Saturated liquid phase



Heat added $\longrightarrow$ continues evap.
 $\longrightarrow T$ unchanged

Wet steam or
Saturated liquid-vapor mixture

Phase Change of Pure Substances (ctd.)

ex. Water at 1 atm of pressure

T=100oC

All liquid evaporated
(*about to condense*)
Heat removed $\longrightarrow$ *condensation*
Saturated vapor phase

T=110oC

Not about to condense
Heat added $\longrightarrow$ T $\uparrow$
Superheated vapor phase

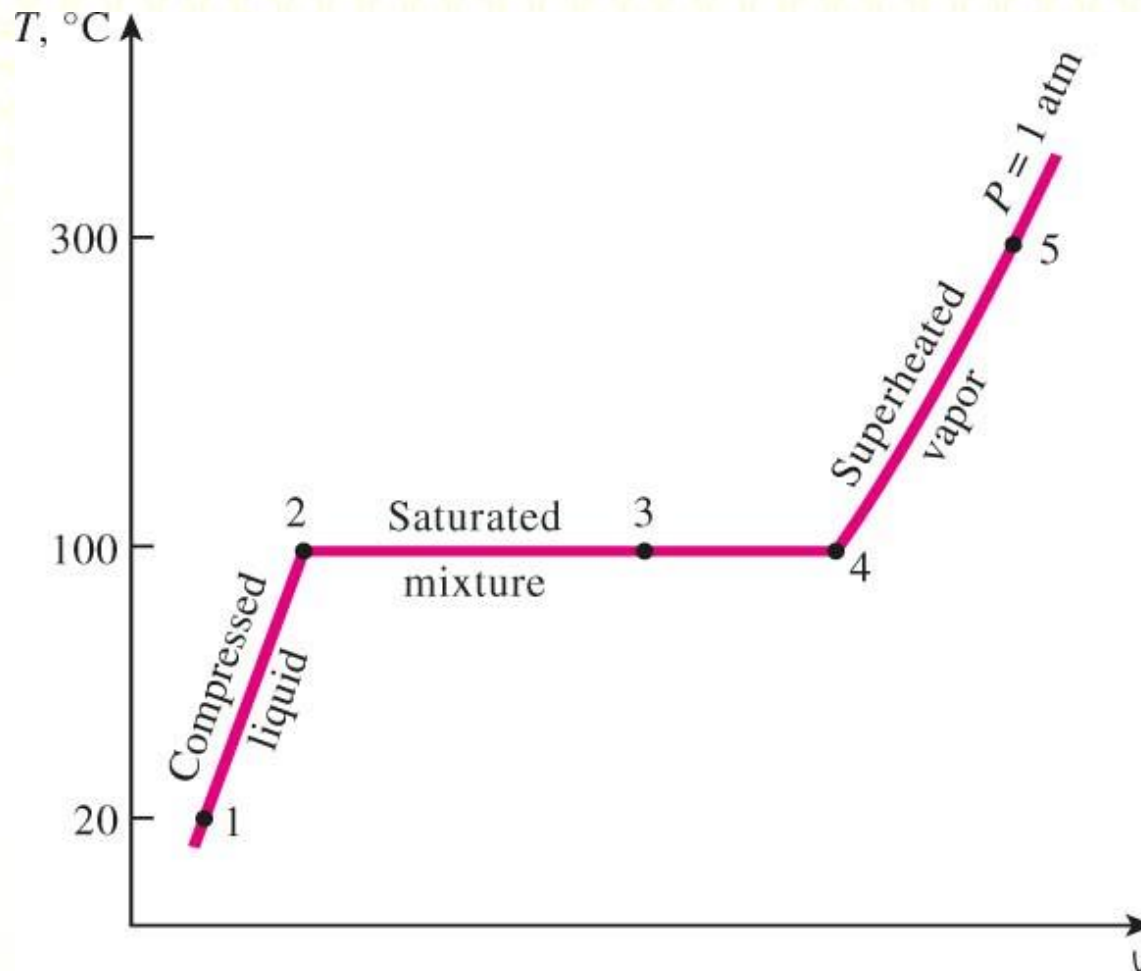
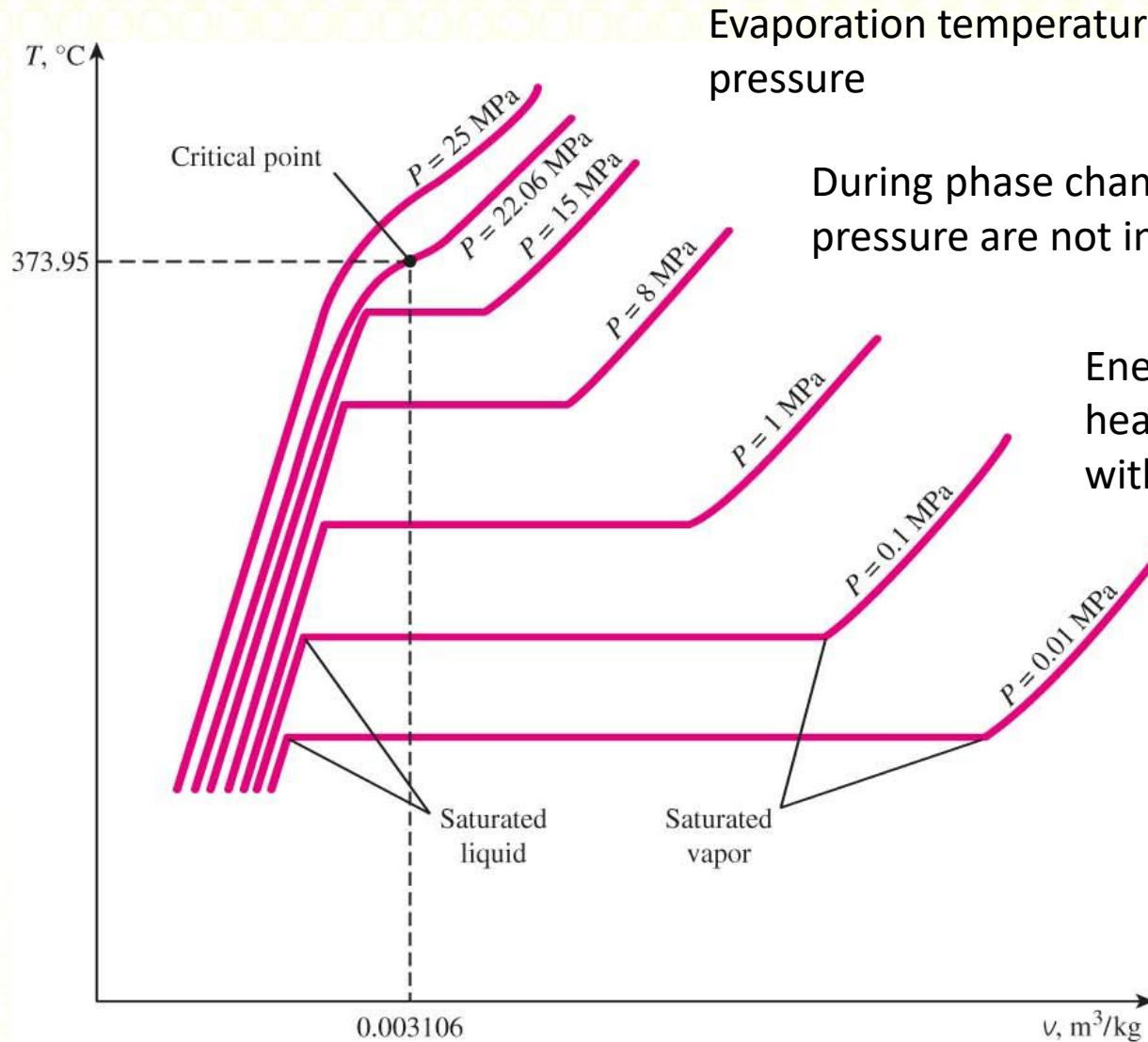


FIGURE 3–11

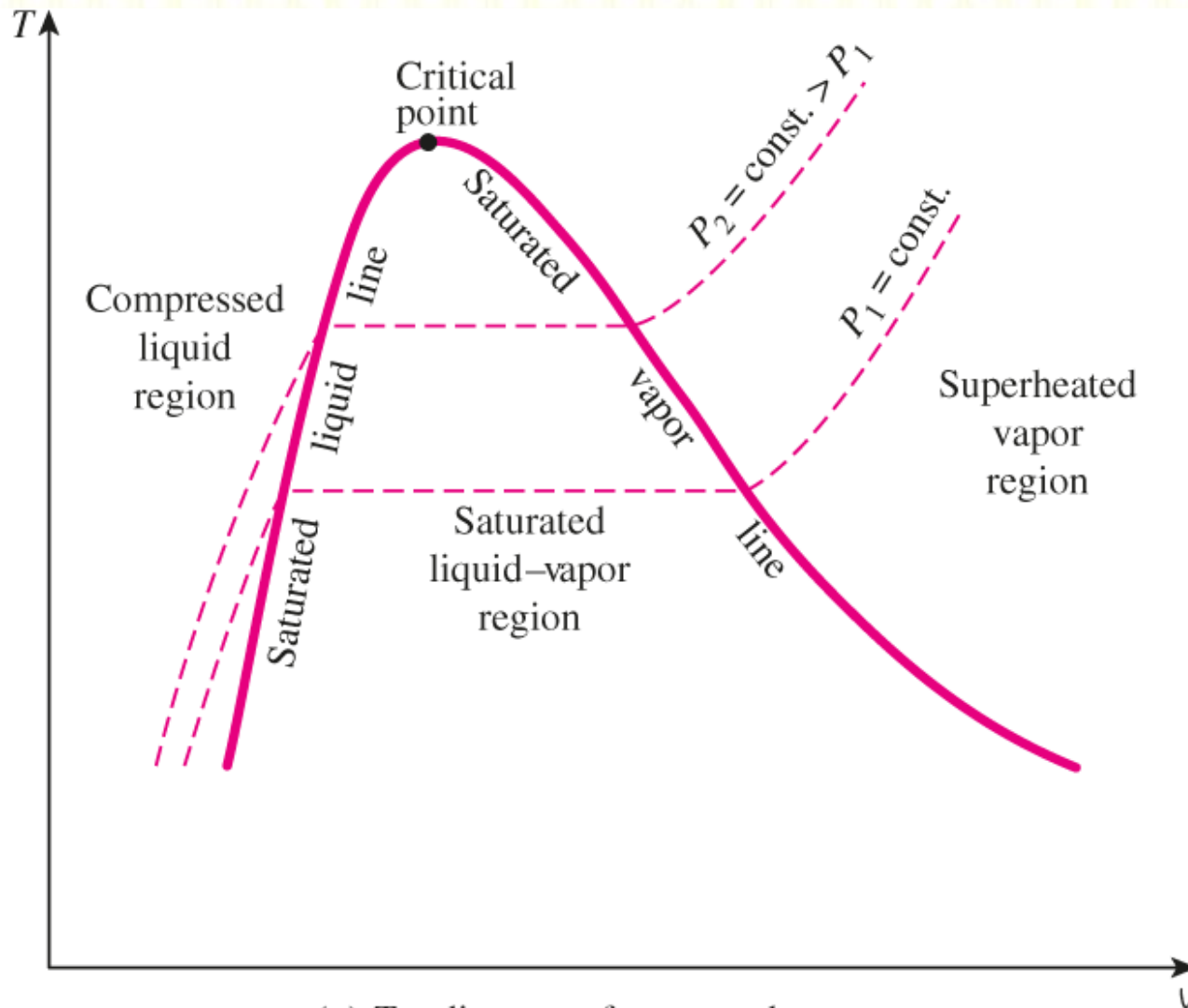
T - v diagram for the heating process of water at constant pressure.



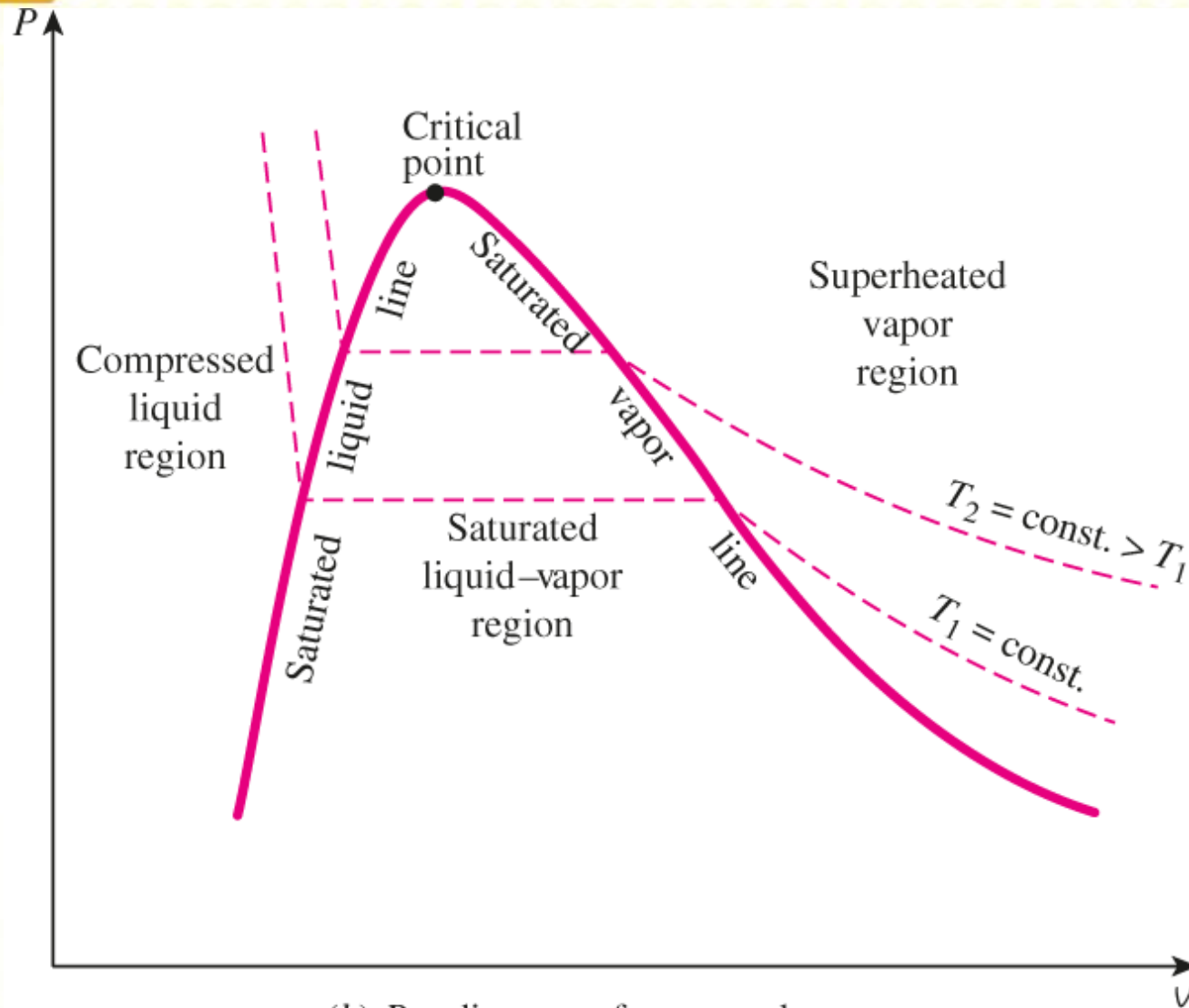
Evaporation temperature changes with pressure

During phase change, temperature and pressure are not independent $T_{\text{sat}} \leftrightarrow P_{\text{sat}}$

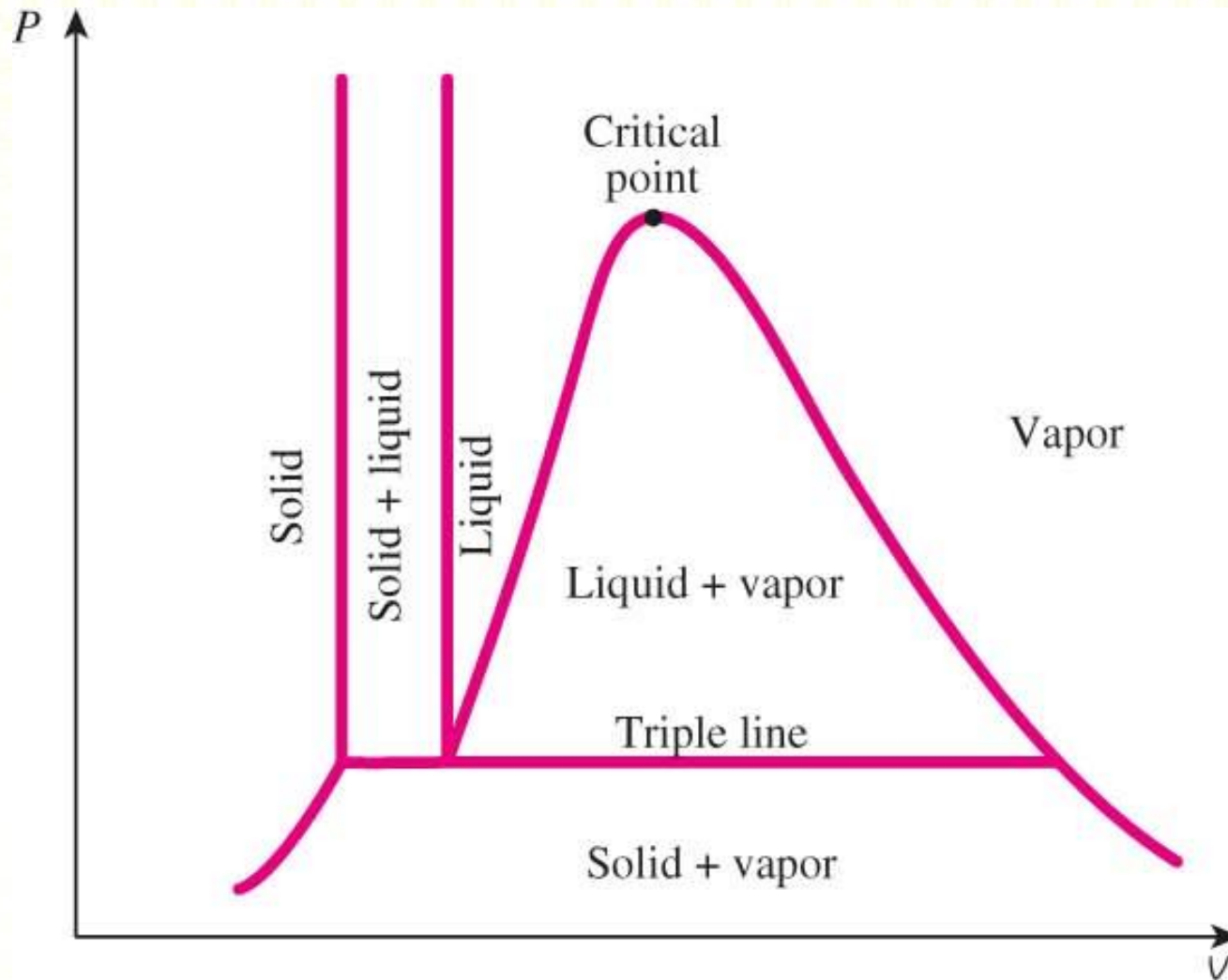
Energy needed to vaporize (latent heat of vaporization) decreases with increasing pressure



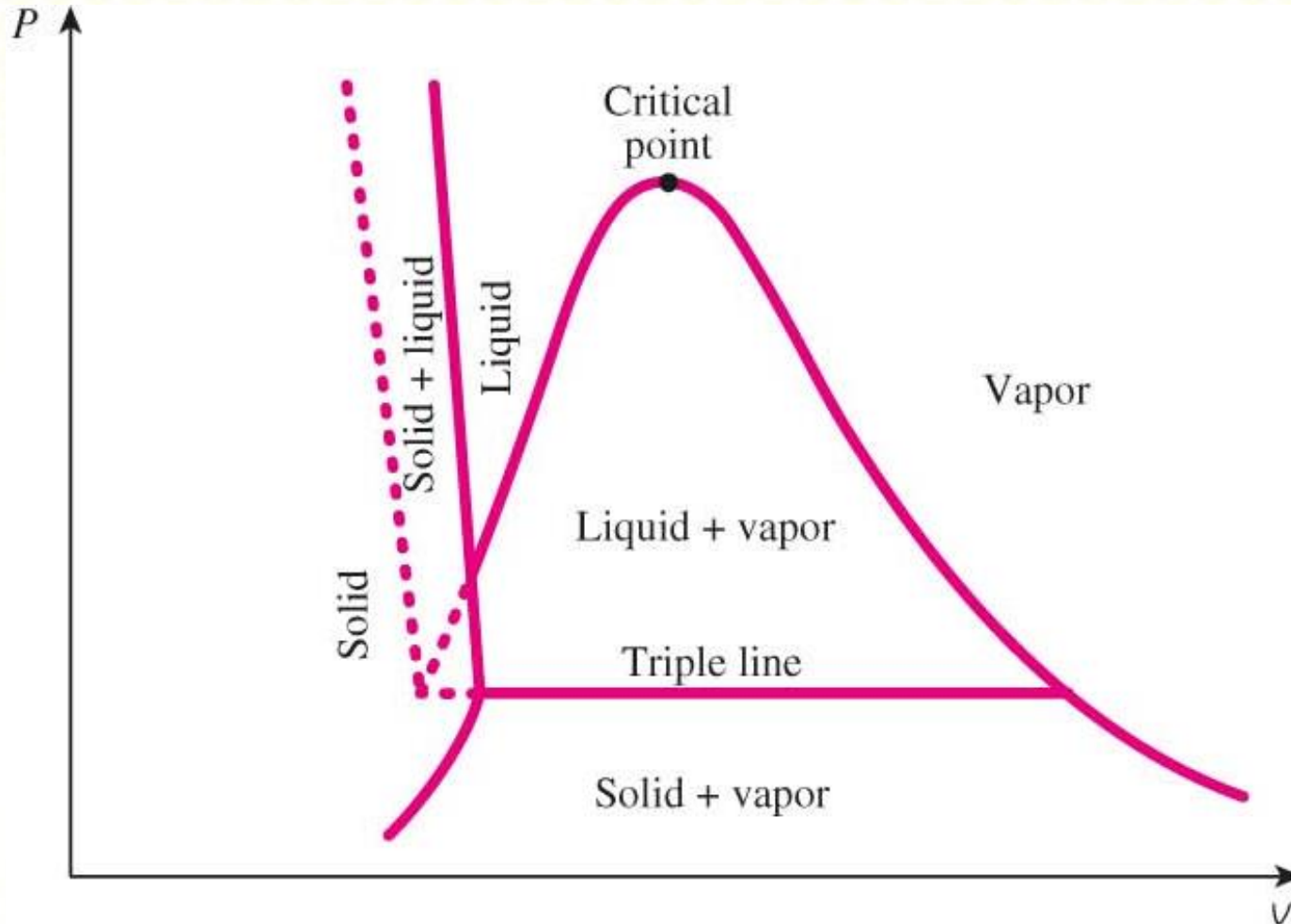
(a) T - v diagram of a pure substance



(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)

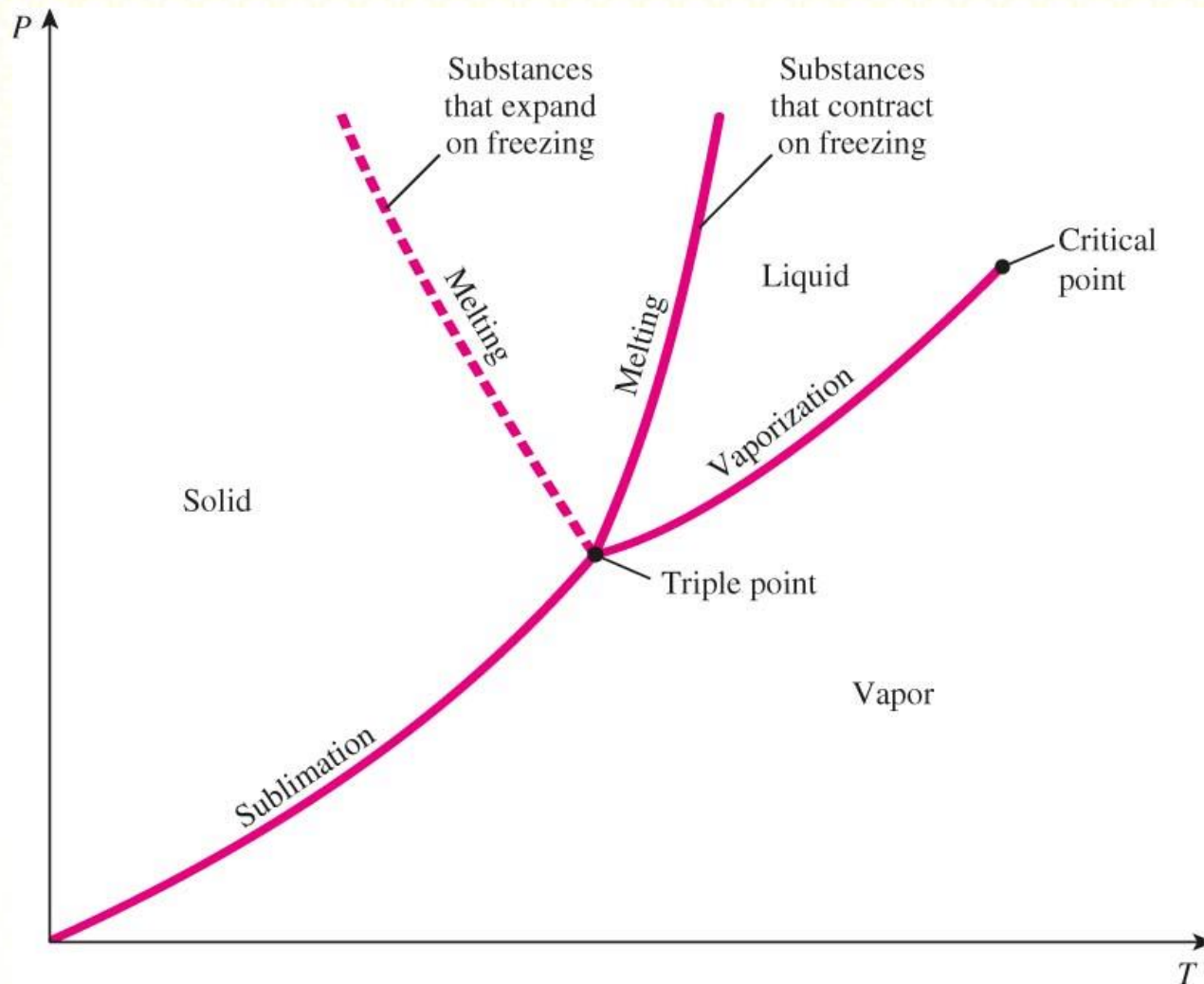


FIGURE 3-23

P - T diagram of pure substances.

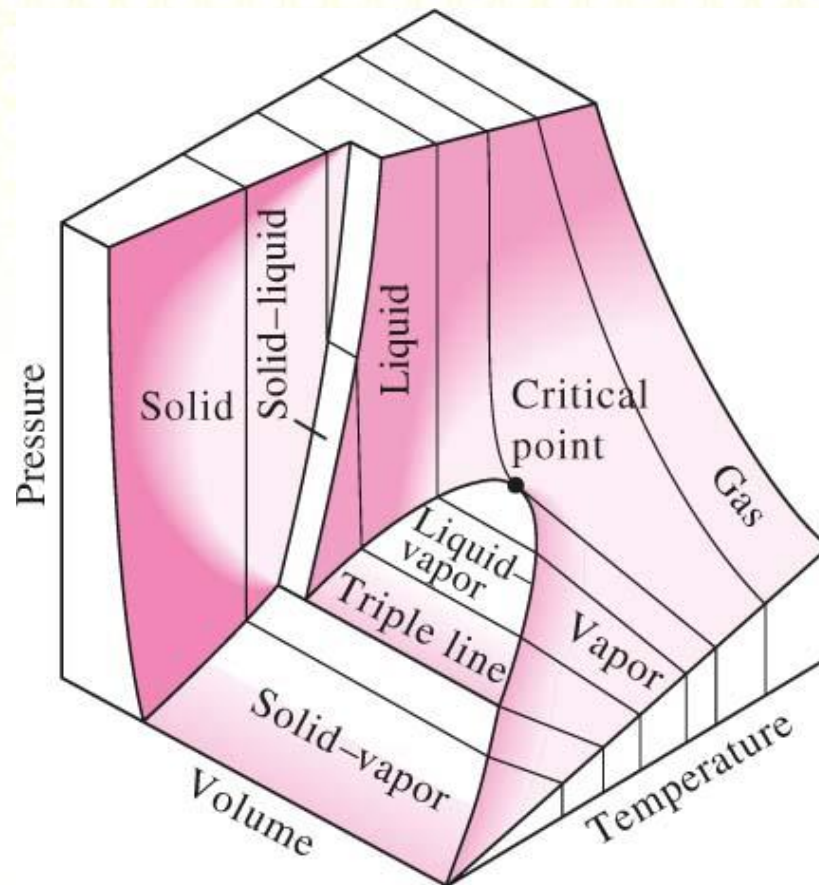


FIGURE 3–24

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

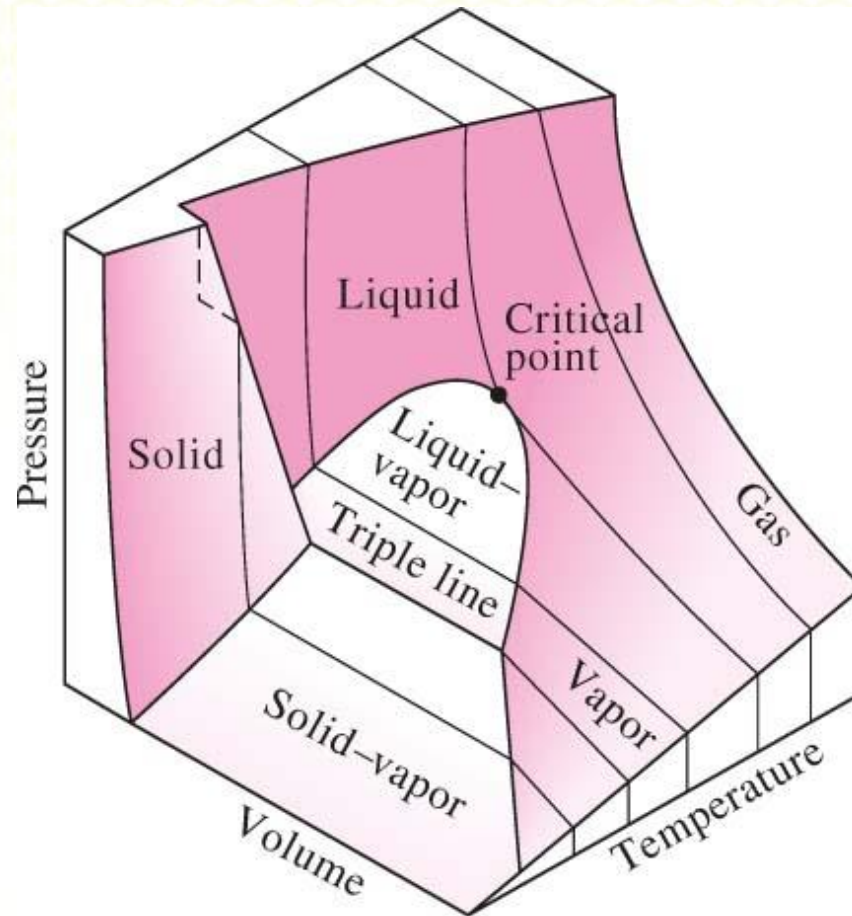
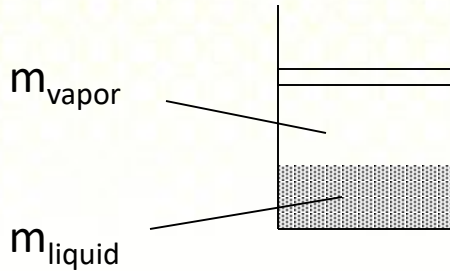


FIGURE 3–25

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



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

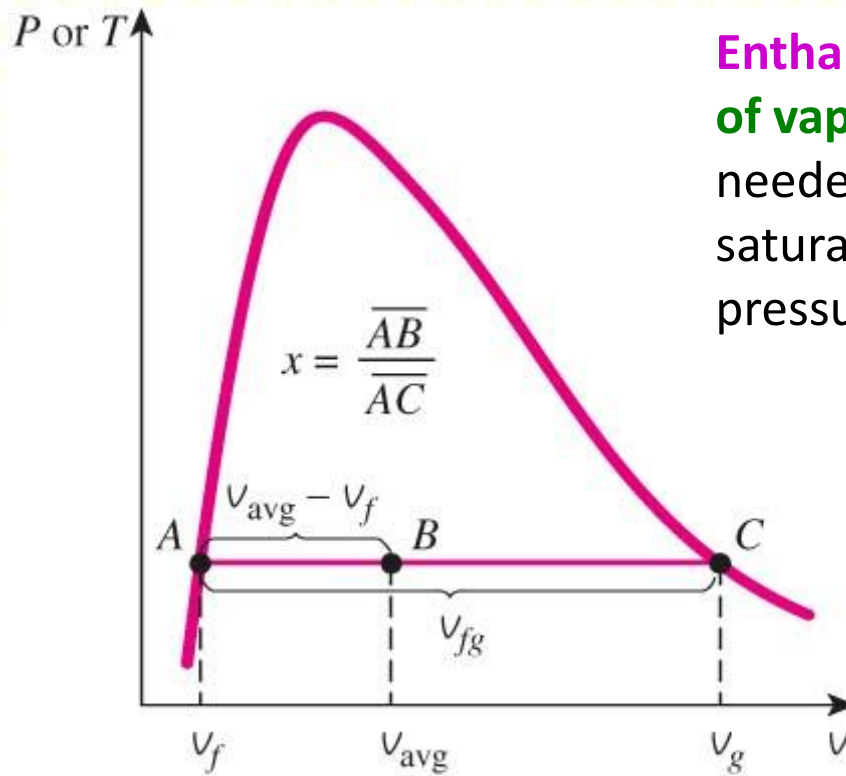
$$0 \leq x \leq 1$$

(wet)

100% liquid

(dry)

100% vapor



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.

FIGURE 3–34

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

Quality (cont.)

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

$$\begin{aligned} x &\equiv \frac{m_g}{m_g + m_f} \\ &= \frac{v - v_f}{v_g - v_f} &= \frac{h - h_f}{h_g - h_f} \\ &= \frac{u - u_f}{u_g - u_f} &= \frac{s - s_f}{s_g - s_f} \end{aligned}$$

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

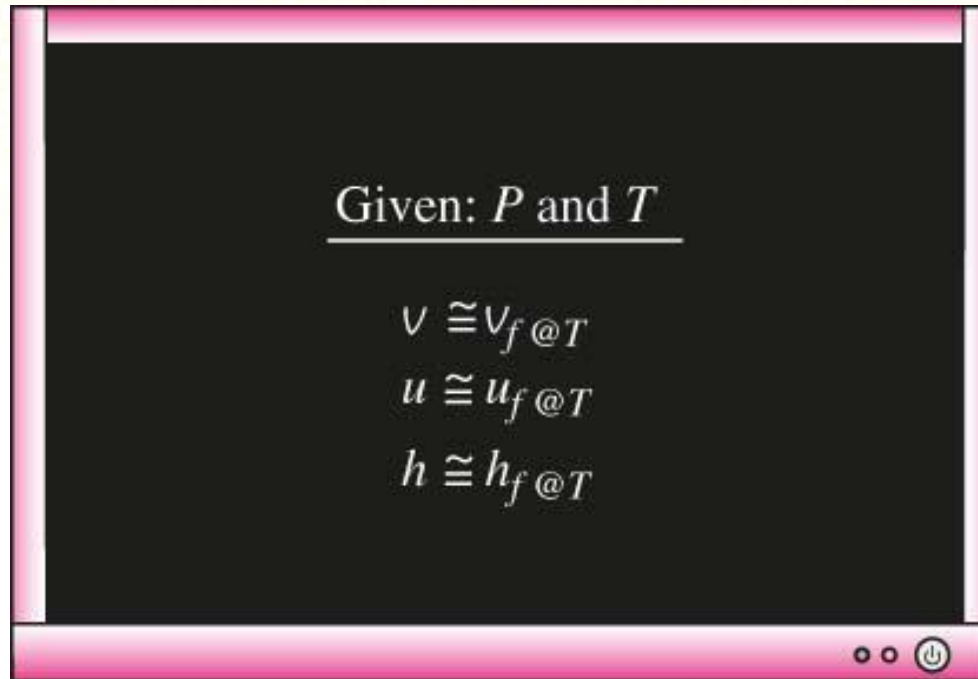


FIGURE 3–40

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

Because liquid is more sensitive to changes of temperature than that of pressure

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

$$P \leftrightarrow T_{\text{sat}}$$

$$T \leftrightarrow P_{\text{sat}}$$

$P > P_{\text{sat}}$ at the given T

$T < T_{\text{sat}}$ at the given P

$P < P_{\text{sat}}$ at the given T

$T > T_{\text{sat}}$ at the given P

Compressed
liquid

Superheated vapor

Best determined by simple sketching of
the p - v or T - v diagram

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

$$P \leftrightarrow T_{sat}$$

$$h \neq h_f|_P$$

$$h \approx h_f|_{T_{sat}}$$

Notes on Using Property Tables

Some tables do not list ***h*** (or ***u***)

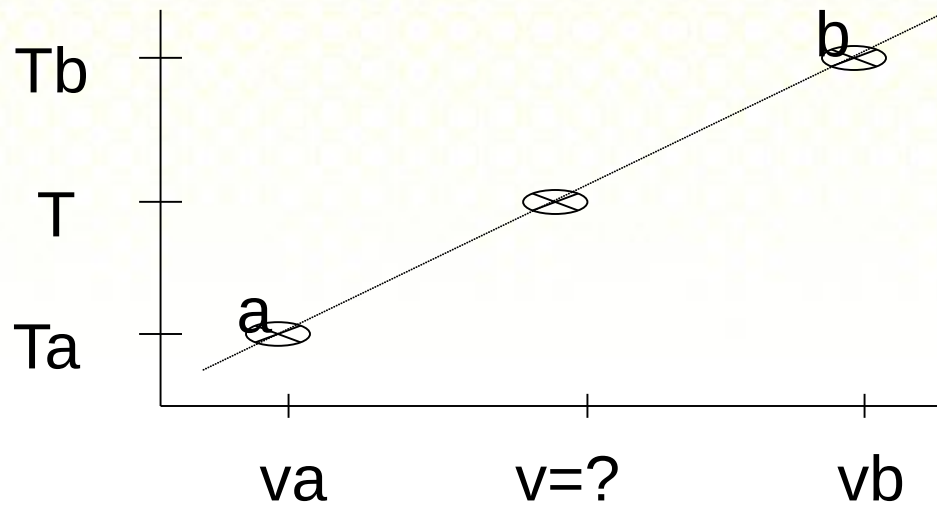
→ ***u*** (or ***h***) can be obtained from **$h = u + Pv$**

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

ex. $T=25^{\circ}\text{C}$, $P=1$ bar (compressed liquid)

$$h_{25^{\circ}\text{C},1\text{b}} \approx h_f @ T=25^{\circ}\text{C}$$

Interpolation (*Linear Interpolation*)

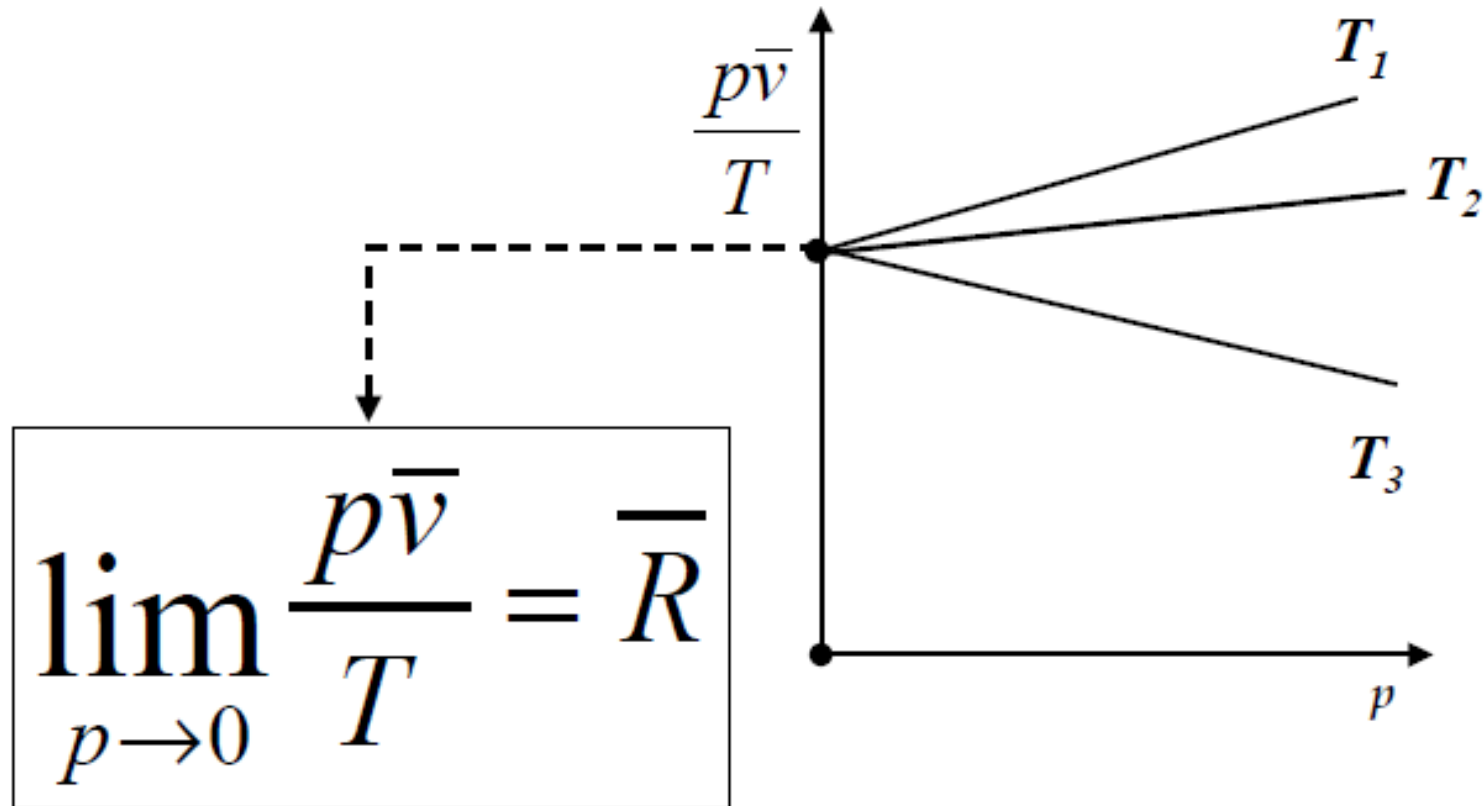


Assume a & b
connected by a
straight line

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)



IDEAL GAS

(for pressures much lower than critical pressure)

Equation of state for ideal gas

$$PV = mRT$$

R = Gas Constant [kJ/kg.K]
(constant for a gas, value
depends on type of gas)

$$P \frac{V}{m} = RT \quad Pv = RT$$

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

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

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

$$R = \frac{P_1 V_1}{T_1 m_1} = \frac{P_2 V_2}{T_2 m_2}$$

Can be used to relate between
different states

Ideal gas u , h , c_p , c_v relationship

Constant Volume Specific Heat Capacity c_v

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

Constant Pressure Specific Heat Capacity, c_p

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

$$du = c_v dT$$

$$dh = c_p dT$$

$$c_p = c_v + R$$

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

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

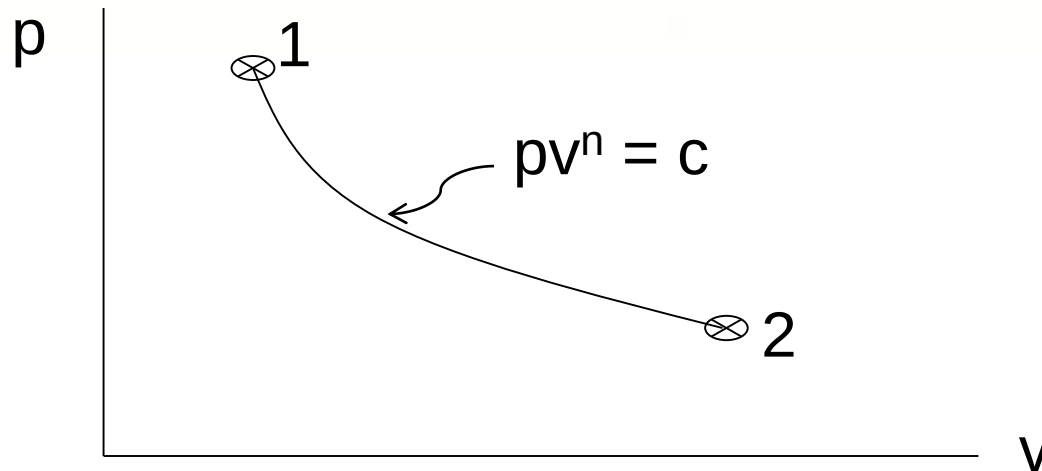
$$c_v = \frac{R}{k - 1}$$

POLYTROPIC PROCESS

-Processes that obey/follow the path

$$pv^n = c$$

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



$$p_1 v_1^n = p_2 v_2^n$$

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

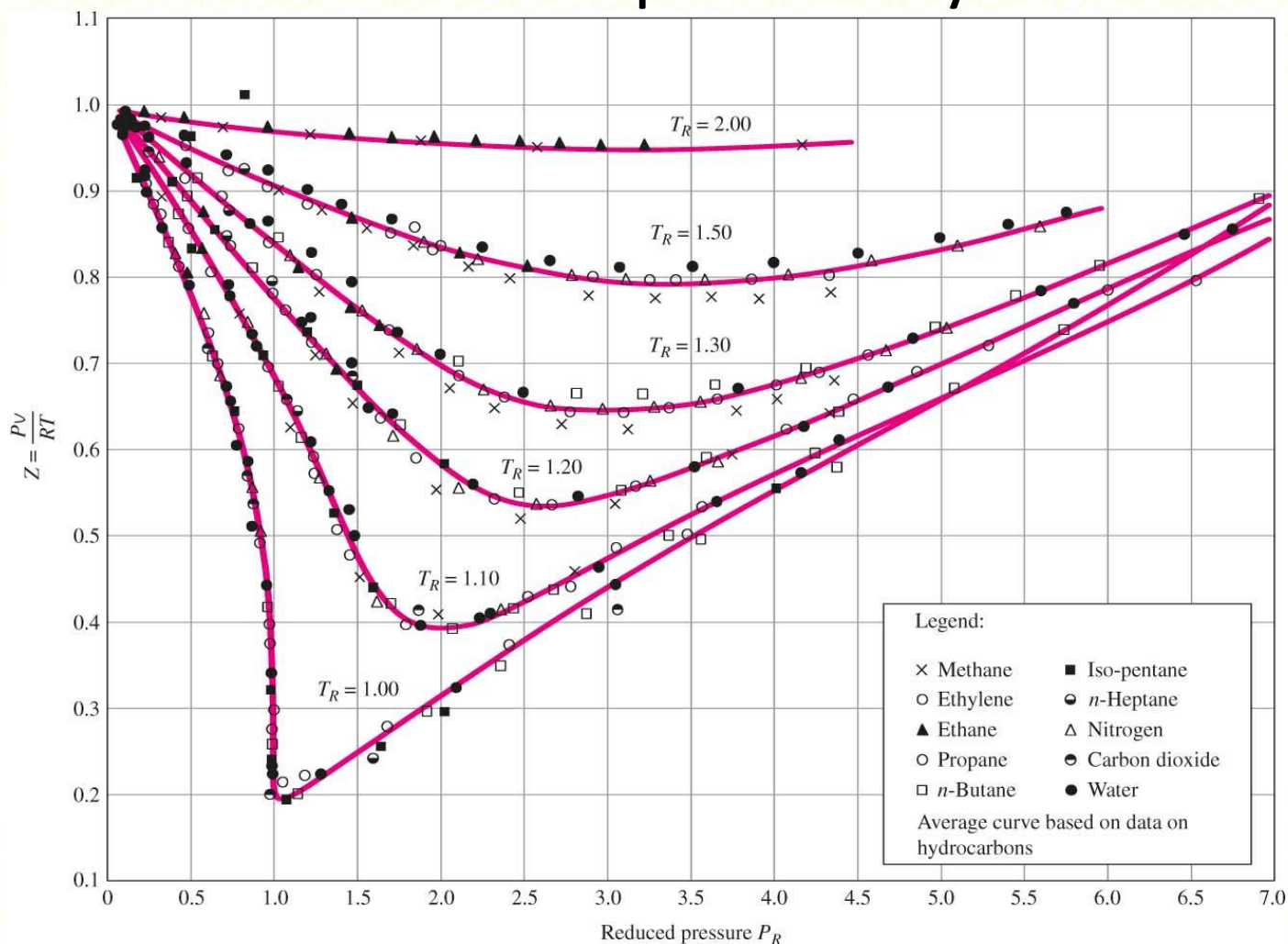
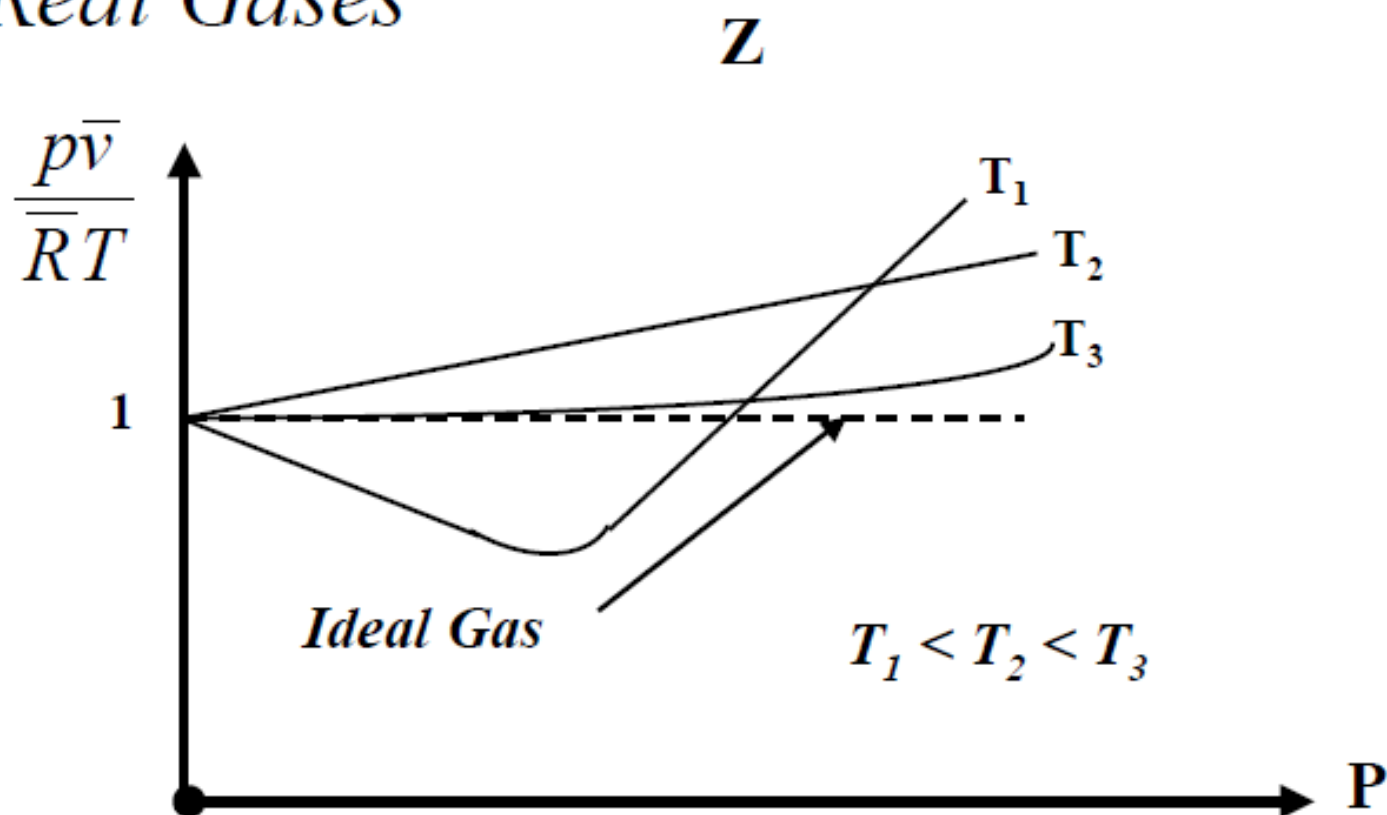


FIGURE 3-49

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

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

Reduced temperature

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

Reduced pressure

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

Pseudo-reduced specific volume

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

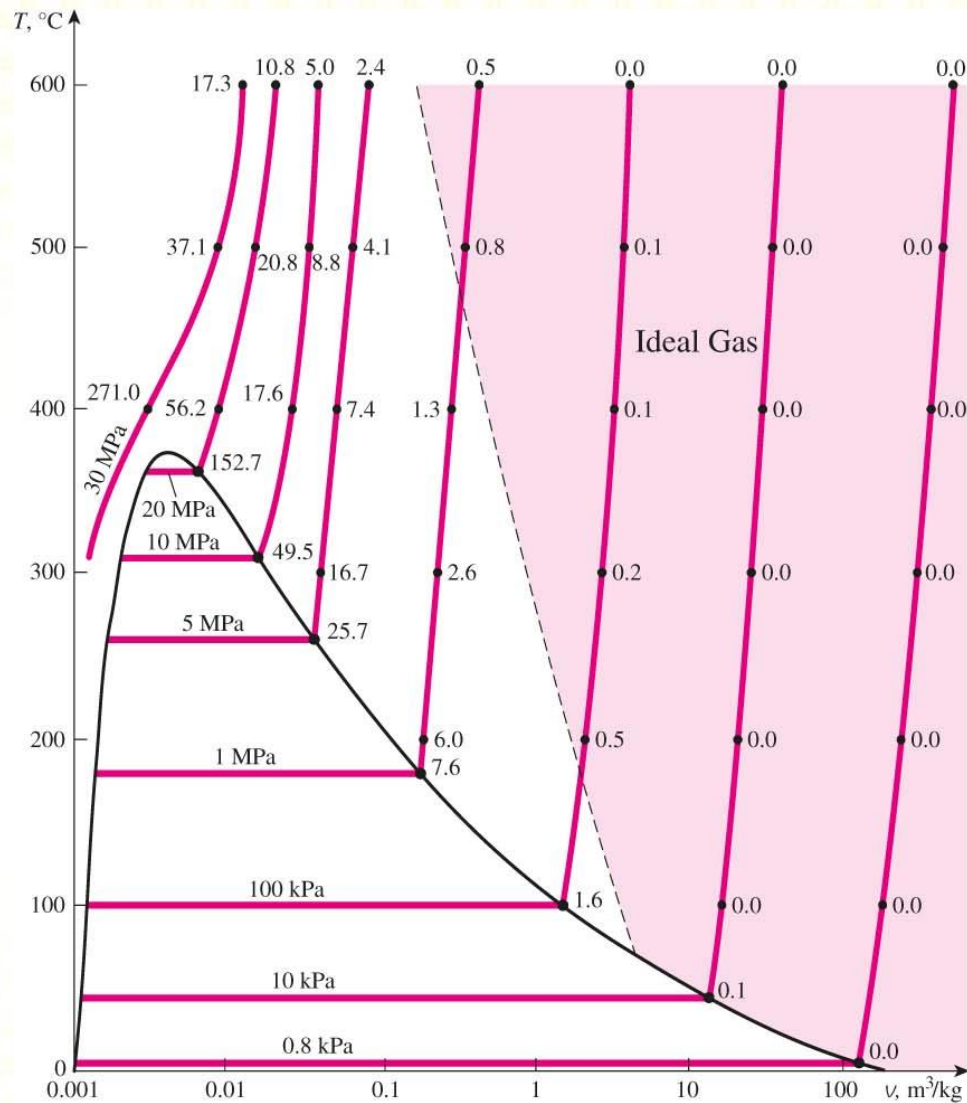


FIGURE 3-47

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



$$pV = mRT$$

& other relations

$$h = cpT$$

$$u = cvT$$

etc.

[Air,
N₂ , He,
etc.

Other Equations of State

Van der Waal's :

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

Beattie-Bridgeman :

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

Benedict-Webb-Rubin :

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

Virial equations of state:

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

The apparent and the implied

Some examples...

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