

LECTURE # 6



Chapter 3 (Session #1): **Properties of Pure Substances**

CHAPTER 3



PROPERTIES OF PURE SUBSTANCES

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PROPERTIES OF PURE SUBSTANCES



OUTCOMES:

- Understand the physics of phase change processes for a pure substance
- Be able to plot the T - v , P - v , and P - T property diagrams for a pure substance
- Be able to evaluate the properties of a pure substance using tables of property data
- Understand the concept of an ideal gas and use the ideal gas Equation of State in solving problems

Definition

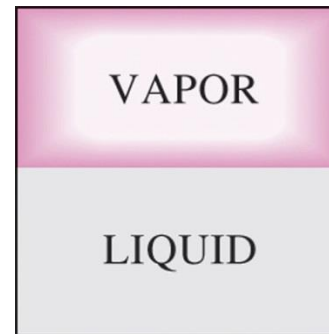


- **A “Pure Substance” is a particular chemical species**
 - A pure substance can exist in one of three phases (gas, liquid, solid) or a combination thereof depending on the state
 - One-constituent system of one or more phases depending on conditions [Example H_2O : ice, liquid water & steam (vapor)]

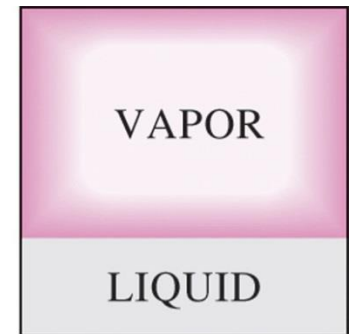
DEFINITION – PURE SUBSTANCE

❑ **Pure substance:** A substance that has a fixed chemical composition throughout.

- Air is a mixture of several gases; it is considered to be a pure substance only if it a gas. (why?)
- Nitrogen is a pure substance whether it is only a gas or a mixture of liquid and gas



(a) H_2O

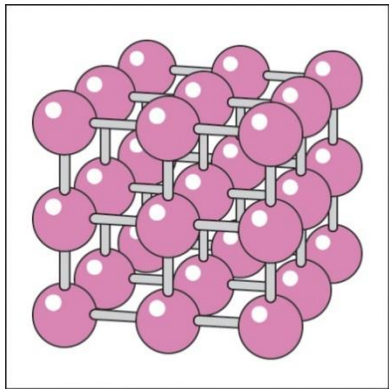


(b) AIR

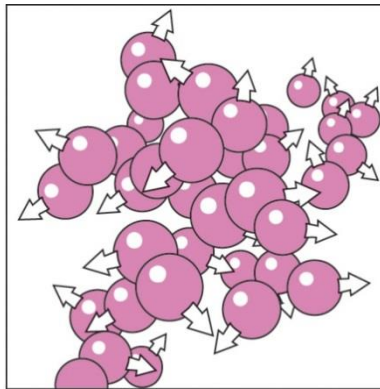
A mixture of liquid and gaseous water (i.e. steam) is a pure substance, but a mixture of liquid and gaseous air is not (@ 1atm $T_{\text{sat, N}_2} \approx -196^\circ\text{C}$; $T_{\text{sat O}_2} \approx -183^\circ\text{C}$).

Phases of a Pure Substance

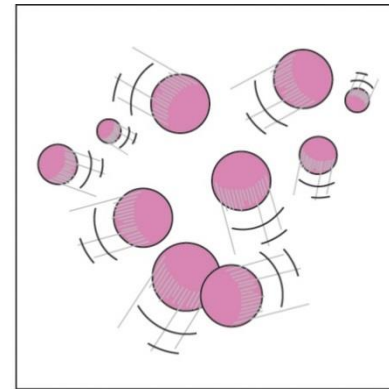
- A pure substance can exist in different phases depending on the arrangement of its molecules : (a) molecules are at relatively fixed positions in a solid, (b) groups of molecules move about each other in the liquid phase, and (c) molecules move about at random in the gas phase.



(a)



(b)



(c)

PROPERTY DIAGRAMS --

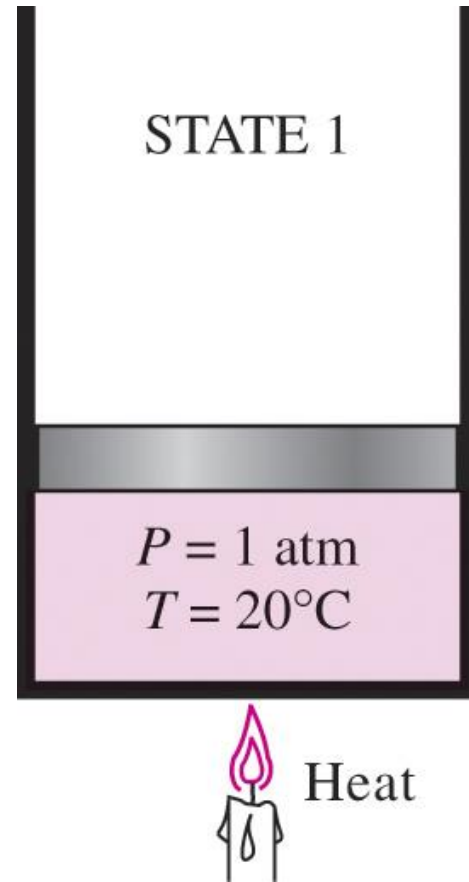
Phase Change Process



- **Experiment:** Isobaric heating of a pure substance
 - Water initially at 20 °C and 1 atm is to be heated at constant pressure

Isobaric Phase Change Process of a Pure Substance

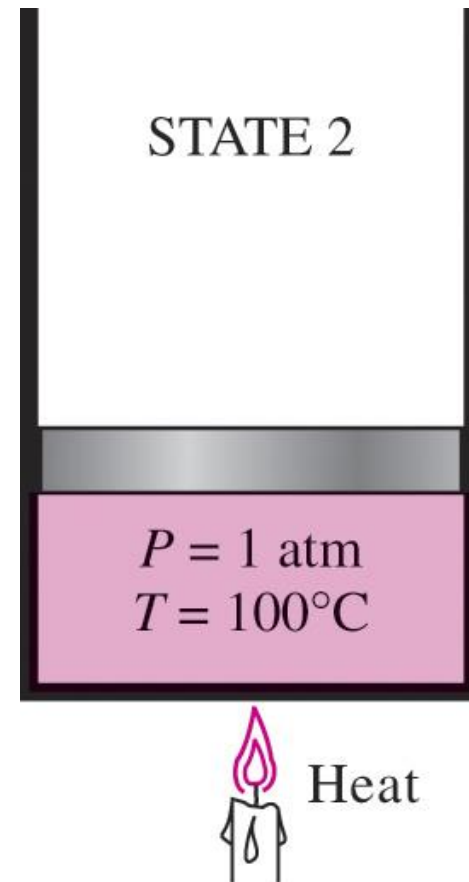
- ❑ **Compressed liquid (or “subcooled liquid”):** A substance that is *not about to vaporize*.
 - At 1 atm pressure and 20°C, water exists in the liquid phase (***compressed liquid***).



Isobaric Phase Change Process of a Pure Substance

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

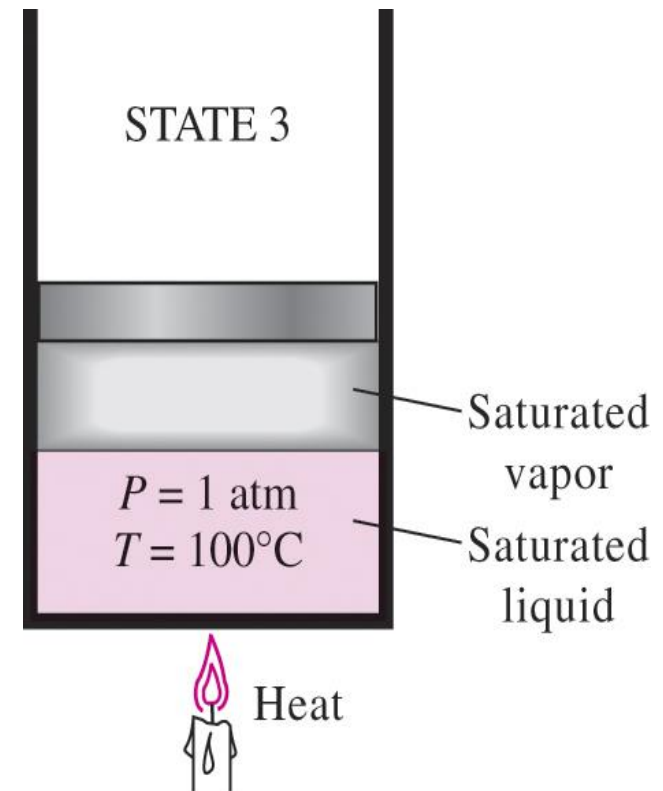
- At 1 atm pressure and 100°C, water exists as a liquid that is ready to vaporize (*saturated liquid*).



Isobaric Phase Change Process of a Pure Substance

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

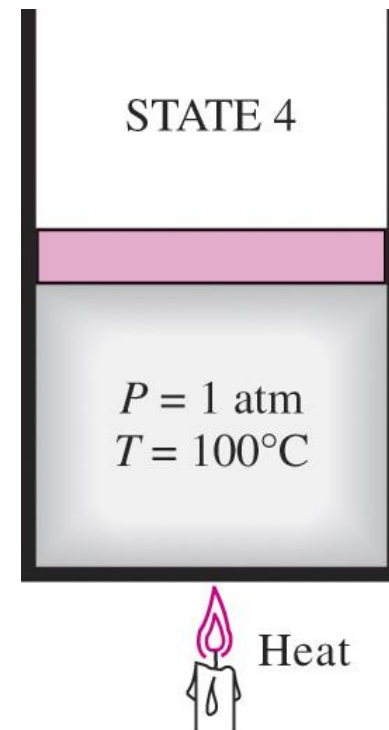
- As more heat is transferred, a larger fraction of the saturated liquid vaporizes
- “T” remains constant as long as “P” is kept constant (***saturated liquid–vapor mixture***)



Isobaric Phase Change Process of a Pure Substance

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

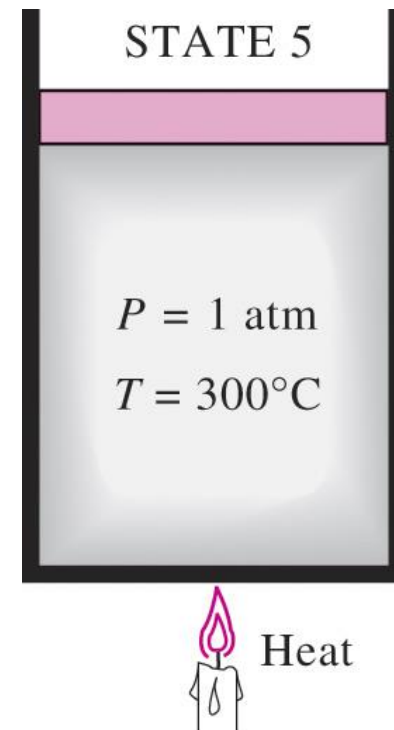
- At 1 atm pressure, the temperature remains constant at 100°C until all the liquid is vaporized (*saturated vapor*).

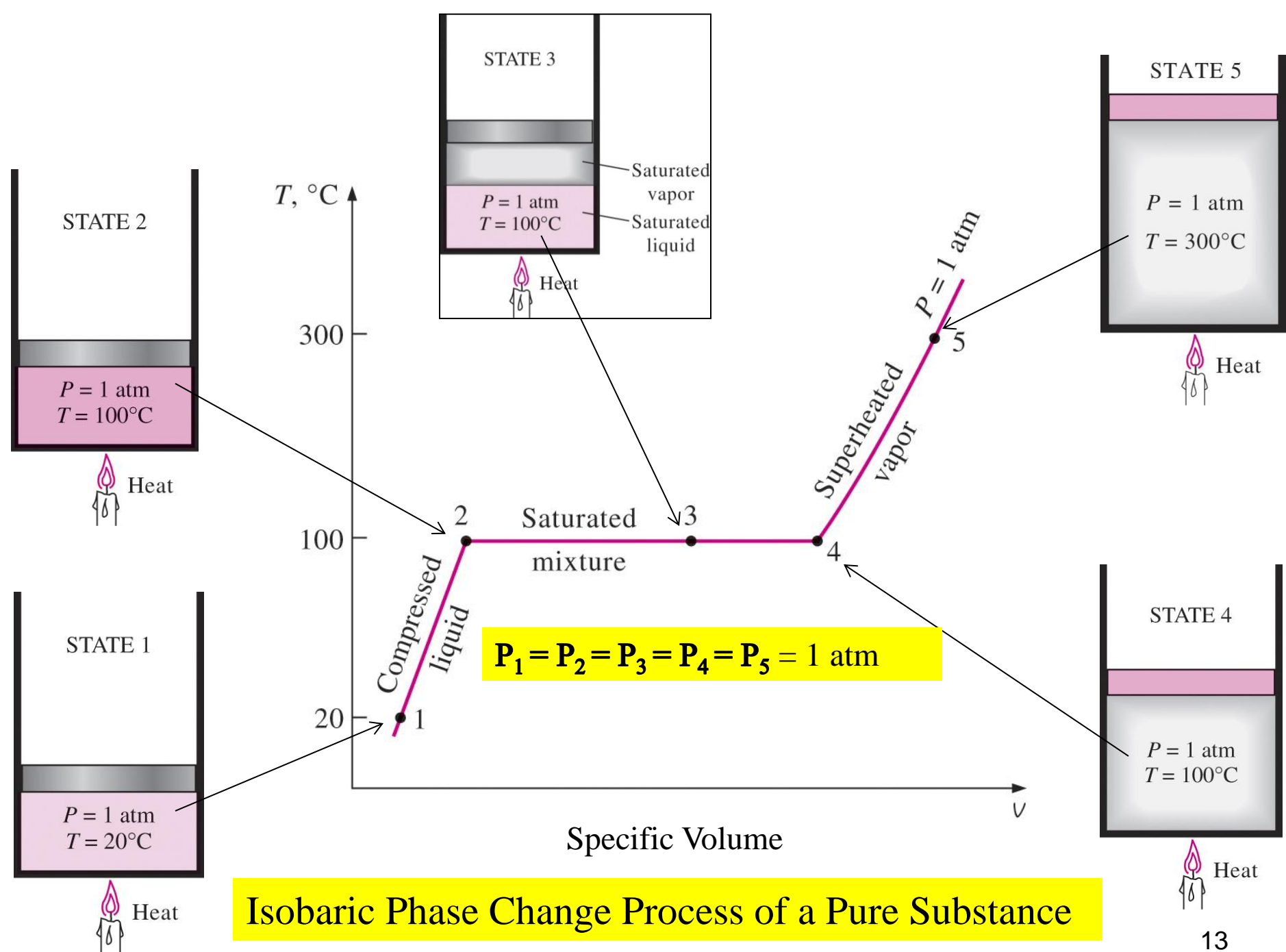


Isobaric Phase Change Process of a Pure Substance

❑ **Superheated vapor:** A vapor that is *not about to condense* (i.e., Temp is higher than that for saturated vapor).

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





Isobaric Phase Change Process of a Pure Substance

The T- ν Diagram -- Isobaric Process

❑ 1 ➡ 2: Compressed Liquid

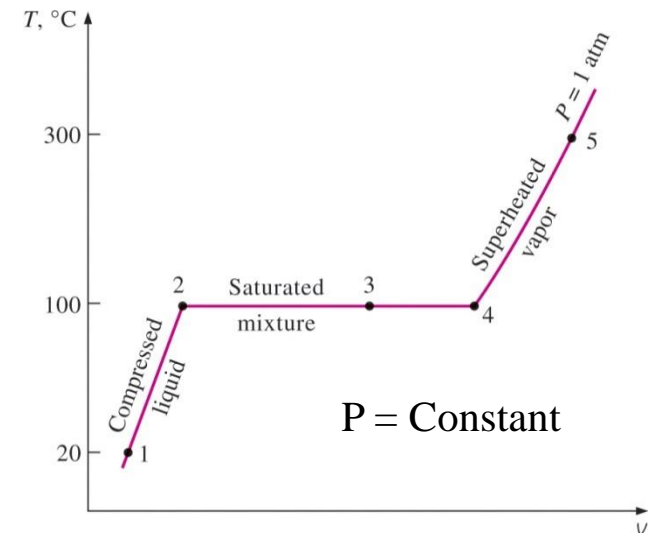
- Both T & ν increase with heat addition until the boiling point (saturation temp) is reached
- Liquid at state "2" is "saturated liquid"

❑ 2 ➡ 4: Saturated (Liquid-vapor) Mixture

- T remains constant while ν increases with heat addition
- State 3 is a saturated mixture of liquid and vapor
- Mass fraction of vapor increases until all "saturated liquid" is converted to "saturated vapor" (state 4)

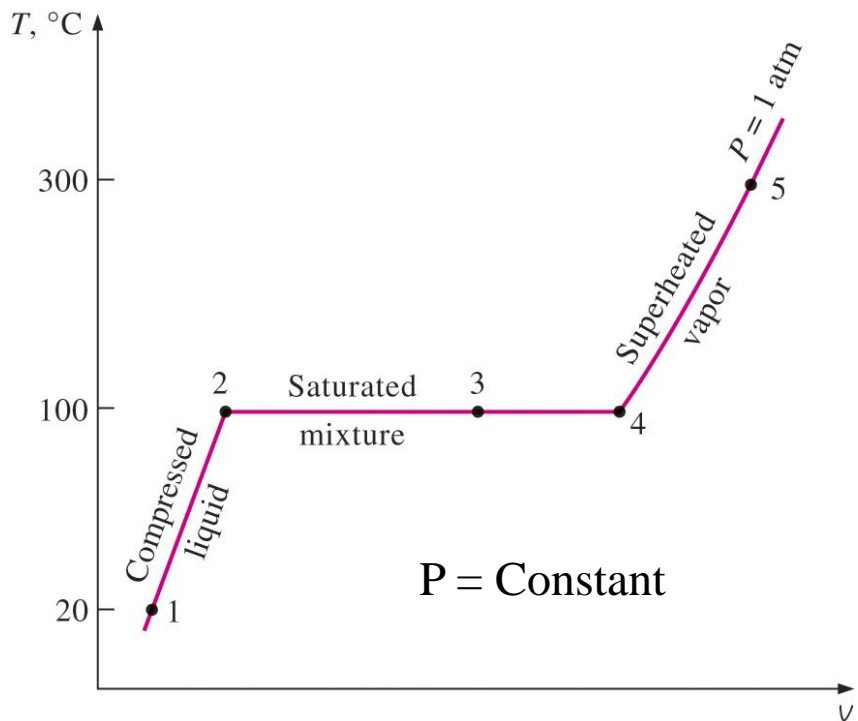
❑ 4 ➡ 5: Superheated Vapor

- Both T & ν increase with further heat addition



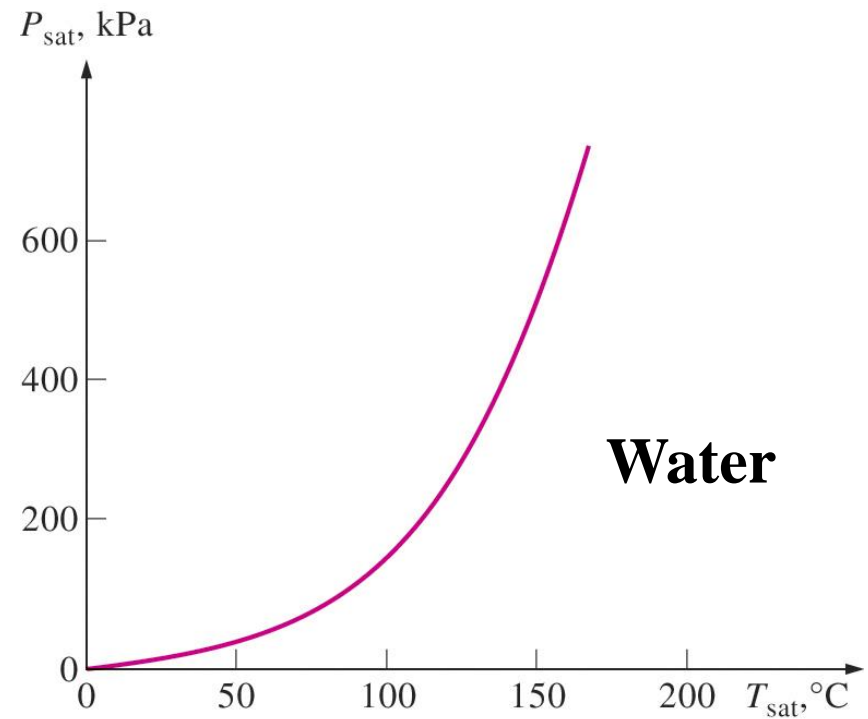
The T- ν Diagram -- Isobaric Process

- ❑ If the process is reversed by cooling the superheated vapor (state 5), the water will go back to state 1 along the same path
- ❑ The water will release the same amount of heat it gained during the heating process from state 1 to state 5.



Boiling Temperature versus Boiling Pressure

- ❑ The temperature at which a pure substance starts boiling depends on the pressure
- ❑ For a given pure substance, the boiling temperature depends only on pressure.
- ❑ Water boils at 100°C at 1 atm; it boils at 159°C at 6 atm.



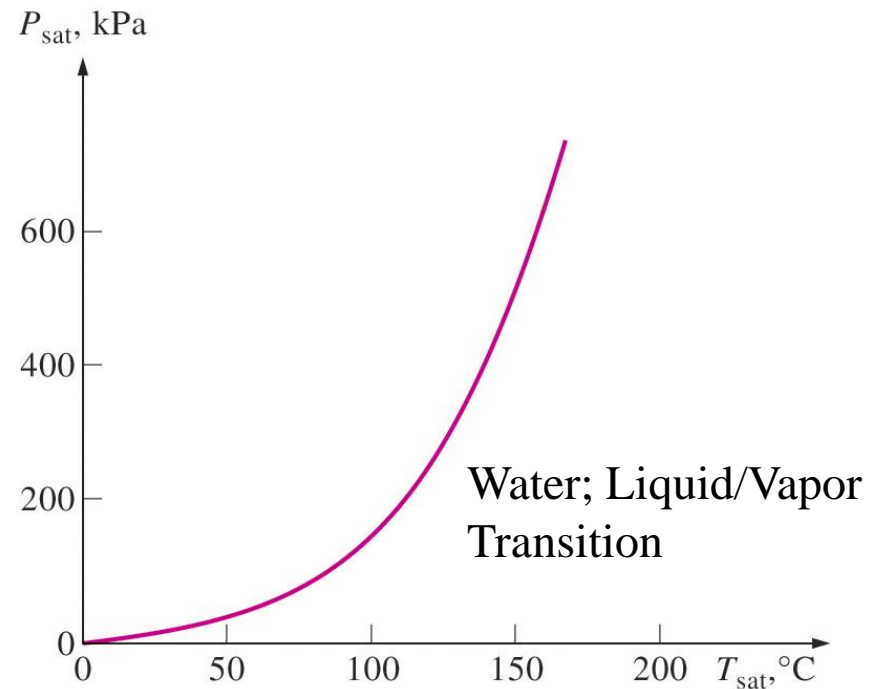
Saturation Temperature & Saturation Pressure

□ Saturation temperature

T_{sat} : The temperature at which a pure substance changes phase at a given pressure (boiling point for liquid/vapor transition).

□ Saturation pressure

P_{sat} : The pressure at which a pure substance changes phase at a given temperature.



Saturation Temperature & Saturation Pressure

TABLE 3–1

Saturation (boiling) pressure of water at various temperatures

Temperature, $T, ^\circ\text{C}$	Saturation pressure, $P_{\text{sat}}, \text{kPa}$
–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 tempera- ture, $^\circ\text{C}$
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

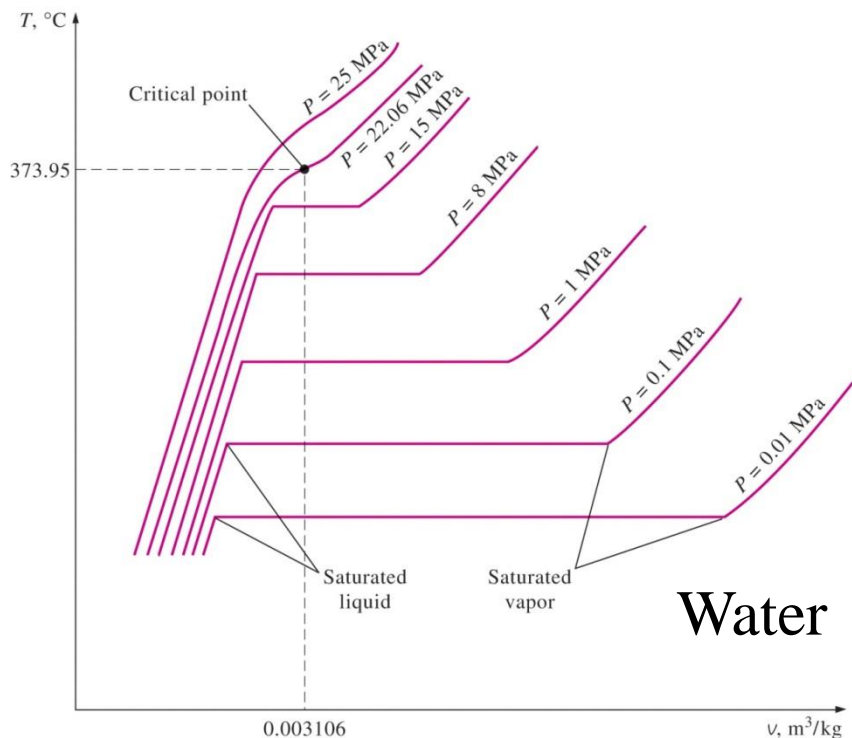


- ❑ **Latent heat:** The amount of energy absorbed or released during a phase-change process.
- ❑ **Latent heat of vaporization:** The amount of energy absorbed during vaporization and it is equal to the energy released during condensation.
- ❑ **Latent heat of fusion:** The amount of energy absorbed during melting. It is equal to the amount of energy released during freezing.
- ❑ The magnitudes of the latent heats depend on the temperature (i.e. pressure) at which the phase change occurs.
- ❑ At 1 atm pressure, the latent heat of vaporization of water is 2256.5 kJ/kg and the latent heat of fusion is 333.7 kJ/kg.

Property Diagrams for Phase Change Processes

- ❑ Variations of properties during phase-change processes for pure substances are best studied and understood with the help of property diagrams such as the T - v , P - v , and P - T diagrams.

➤ T - v diagram shows isobaric phase-change processes of a pure substance at different pressures.



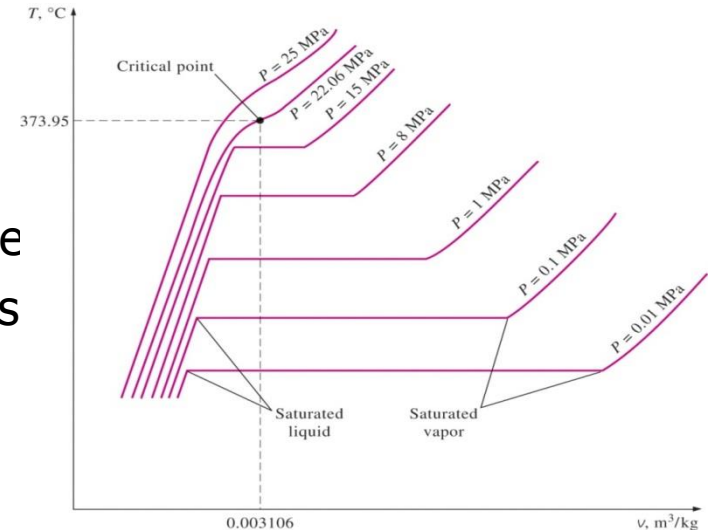
The T- ν Diagram -- Isobaric Processes

● As pressure increases:

- Saturation temperature increases
- Specific volume of saturated liquid increase
- Specific volume of saturated vapor decreases
- Latent heat of vaporization decreases

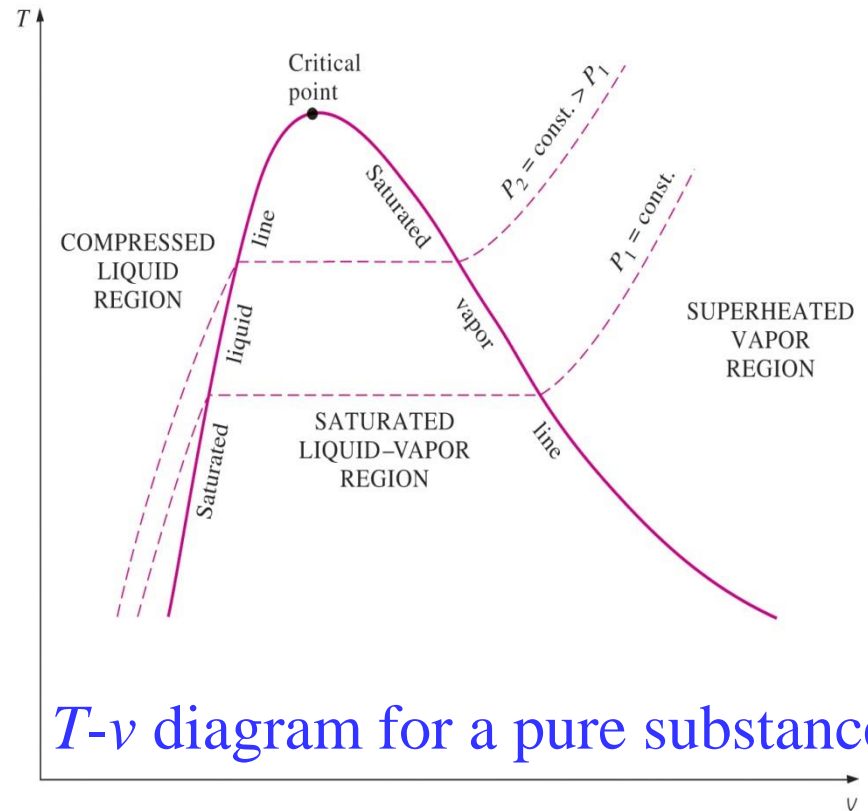
● At the Critical Point:

- **For water:** 22.06 MPa and 373.95 °C ($\nu = 0.003106 \text{ m}^3/\text{kg}$)
- No distinction between liquid and vapor phases
- Latent heat of vaporization = zero



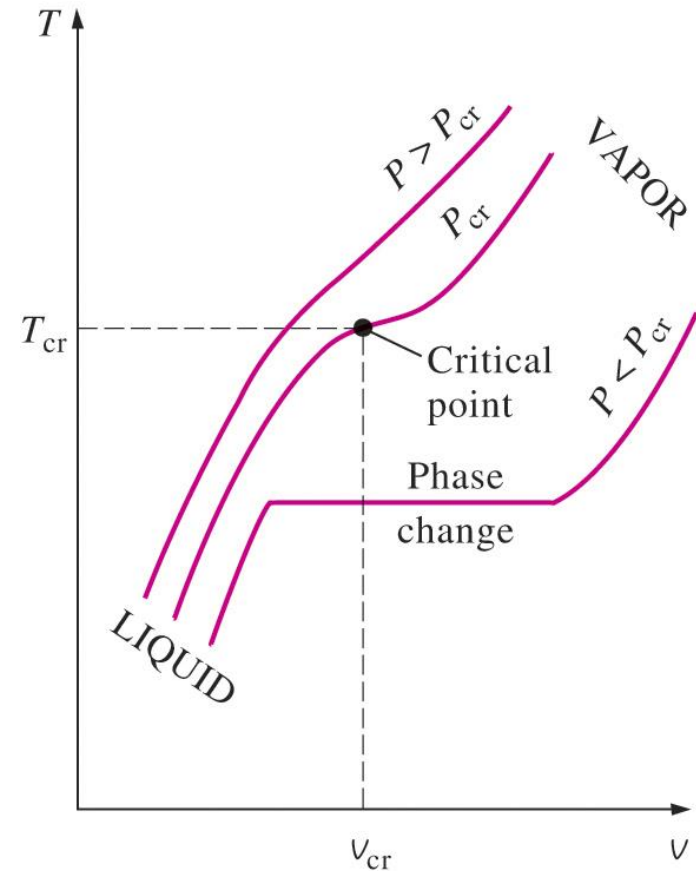
The T- ν Diagram – Key Features

- ☐ Saturated Liquid Line
- ☐ Saturated Vapor Line
- ☐ Critical Point (P_c, T_c)
 - Point at which saturated liquid and saturated vapor states are identical
 - Table A-1 (p. 908) lists P_c and T_c for various substances
- ☐ Compressed (“subcooled”) liquid region
- ☐ Saturated liquid-vapor mixture region (“wet region”)
- ☐ Superheated vapor region



The T- ν Diagram (Supercritical Pressures)

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



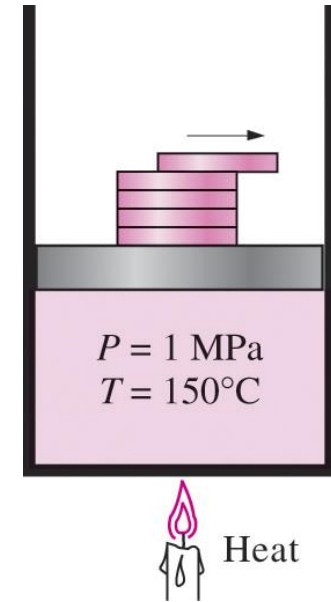
LECTURE # 7



Chapter 3 (Session #2): **Properties of Pure Substances**

The P- v Diagram -- Isothermal Process

- **Experiment:** Isothermal depressurization of liquid
 - Water initially at 1 MPa and 150 °C
 - Pressure is to be gradually decreased while the temperature is kept constant
 - Heat exchange with the surroundings is allowed to maintain constant temperature

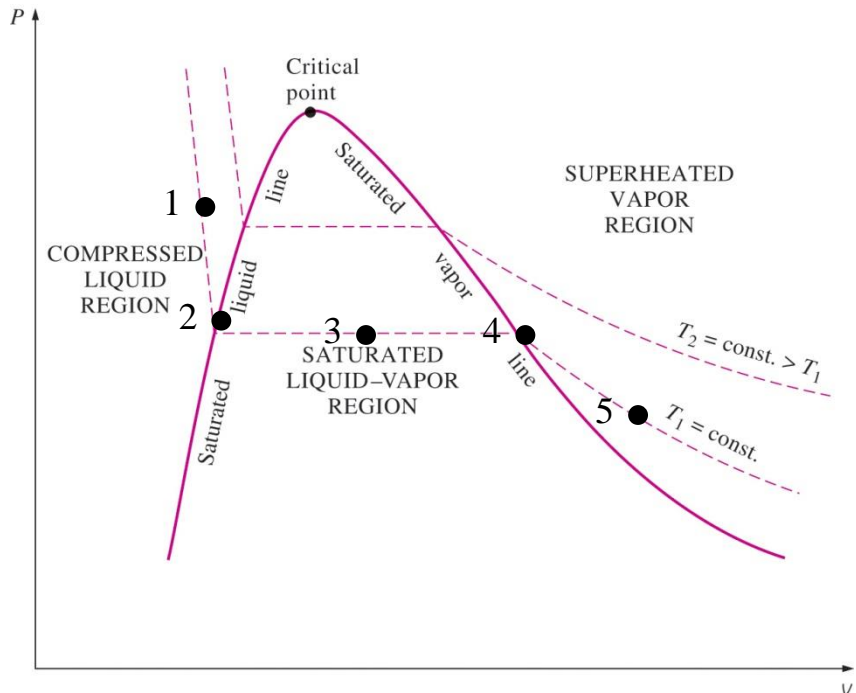


The pressure in a piston–cylinder device can be reduced by reducing the weight of the piston.

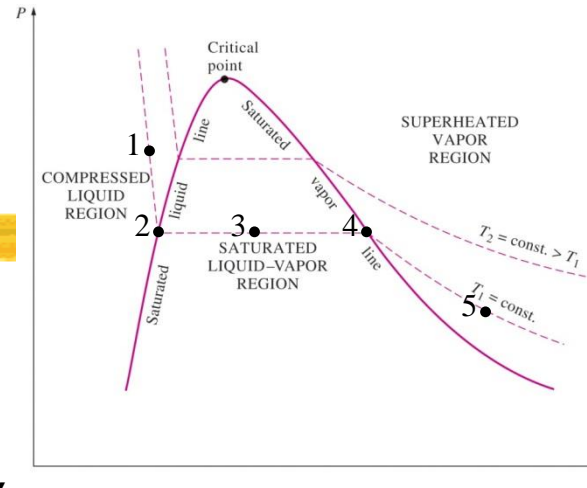
The P- v Diagram -- Isothermal Process

□ At 1 Mpa , T_{sat} for water = 179.9°C

- At 1 Mpa and 150°C , Water is compressed liquid (State 1)
- When pressure reaches 476.2 kPa, water becomes saturated liquid (State 2)
- Pressure remains constant at 476.2 kPa - heat is added until liquid is fully converted to saturated vapor (State 4)
- As pressure is decreased below 476.2 kPa, vapor becomes superheated since $T_{\text{sat}} < 150^{\circ}\text{C}$ (State 5).
- **Reverse process -- start from state 5 and increase pressure until state 1 is reached follows same path**



The P- ν Diagram -- Isothermal Process

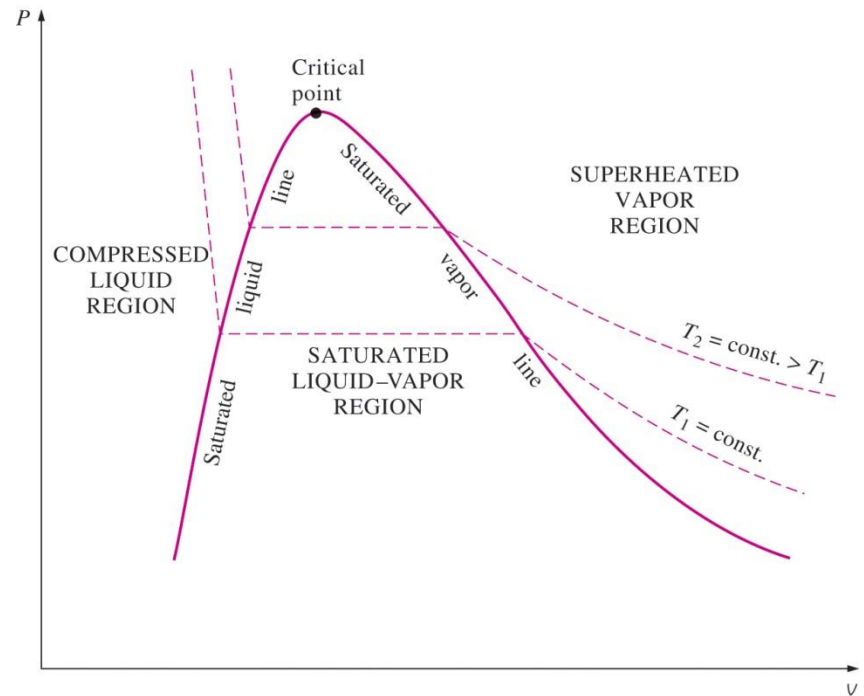


- 1 → 2: Compressed Liquid
 - As P decreases, ν increases while T is kept constant
 - Pressure can be decreased until liquid becomes "saturated"
 - P_2 is the "saturation pressure" corresponding to temperature T
- 2 → 4: Saturated (liquid-vapor) mixture
 - P & T remain constant while ν increases with heat addition
 - Add latent heat of vaporization to completely convert "saturated liquid" to "saturated vapor" (point 4)
 - Point "3" is a "saturated mixture" of liquid and vapor
- 4 → 5: Superheated Vapor
 - P decreases and ν increases while T is kept constant

Same path is followed if process is reversed 5 to 4 to 3 to 2 to 1

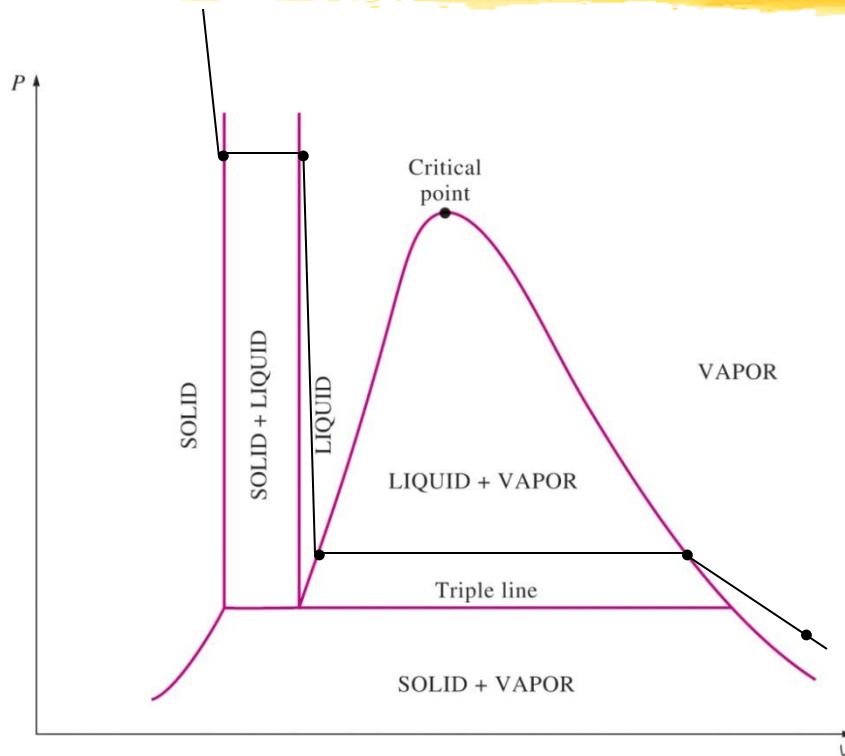
The P- v Diagram – Key Features

- ❑ Saturated Liquid Line
- ❑ Saturated Vapor Line
- ❑ Critical Point (P_c, v_c)
- ❑ Compressed (subcooled) liquid region
- ❑ Saturated liquid-vapor mixture region (wet region)
- ❑ Superheated vapor region
- ✓ Note difference between “**Isothermal**” processes on P- v Diagram and “**Isobaric**” processes on T- v Diagram

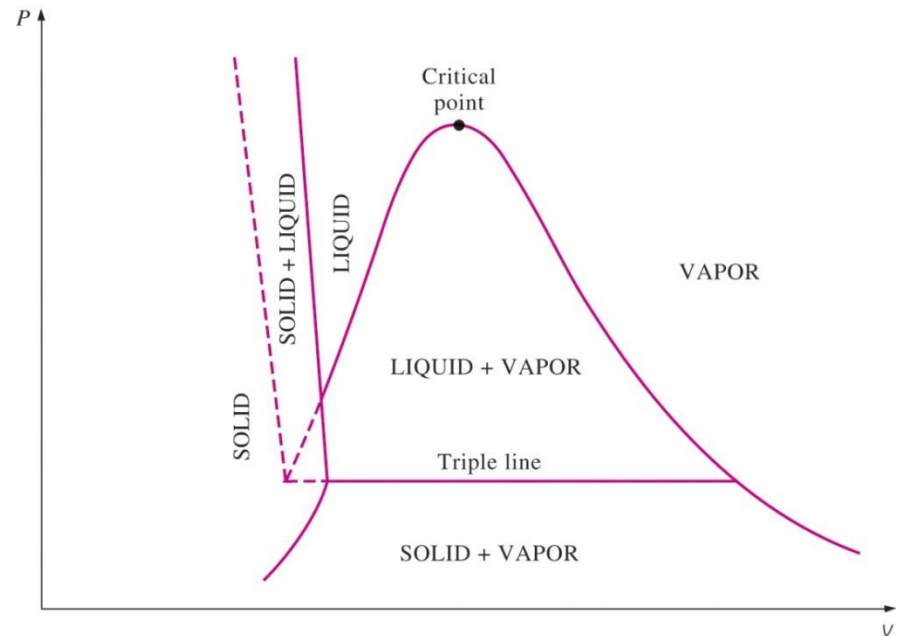


P- v Diagram for a pure substance

Extending the P - v Diagram to include the Solid Phase



P - v diagram of a substance that contracts on freezing (most substances).



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

The Triple Line (Triple Point)

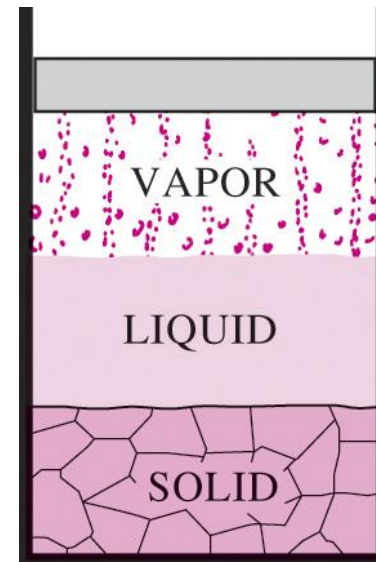
❑ All three phases exist in equilibrium along the “**Triple Line**”

- Same Pressure and Temperature but different specific volumes (depending on mass fractions of phases)
- Triple Line appears as a point on P-T Diagram (**The Triple Point**)

For water:

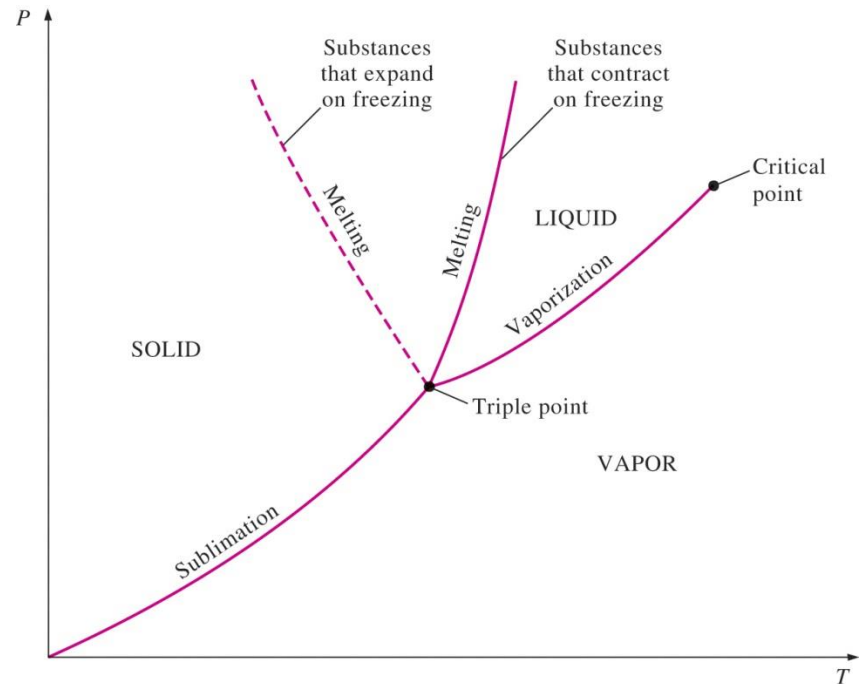
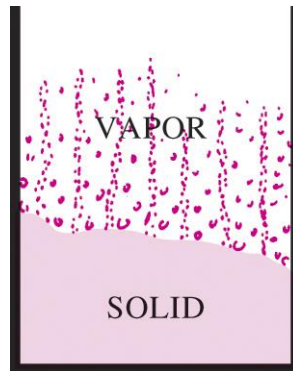
$$T_{tp} = 0.01^{\circ}\text{C}$$

$$P_{tp} = 0.6117 \text{ kPa}$$



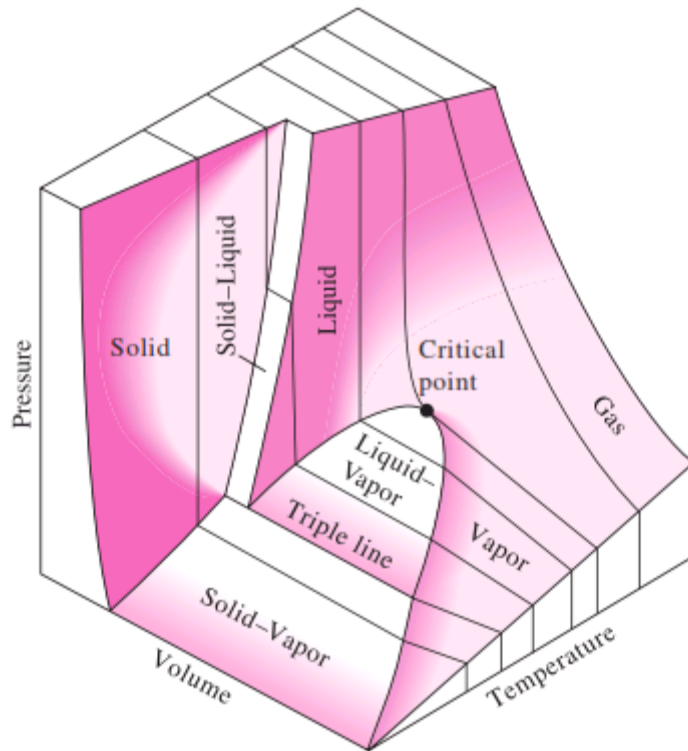
The P-T Diagram

- ❑ At low pressures (below the triple-point value), solids evaporate (sublime) without melting first
- ❑ **Sublimation**: transition from the solid phase directly to the vapor phase.

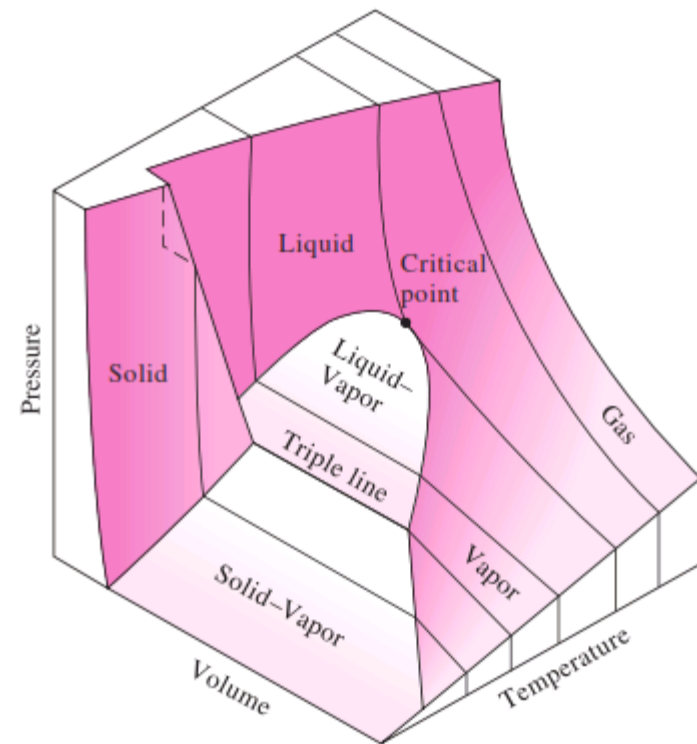


P-T diagram of pure substances.

The P- v -T Surface



Substance that contracts on freezing
(most substances)



Substance that expands on freezing
(like water)

Evaluation of Thermodynamic Properties

- Thermodynamic analysis of systems requires quantitative knowledge of their properties

➤ Example: Application of the First Law of Thermodynamics

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

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

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

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

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

Evaluation of Thermodynamic Properties

- **Recall -- The State Postulate:** “The properties of matter are functionally related -- **Do not need to specify all properties to fix a state**”
- The equilibrium state of a simple system is completely specified **by any two independent intensive properties**
 - “Simple” = no electrical, magnetic, motion, gravitational, or surface tension effects

Examples -- Suitable Properties?

- Mass & Pressure [**No**; mass is extensive]
- Density & specific volume [**No**; $v = 1/\rho$; not independent]
- Pressure & specific volume [**yes**]
- Temperature & specific volume [**yes**]
- Pressure & temperature [**yes** for single phase; **No** during phase change $T = T(P)$]

Question



- If we know two independent intensive properties (for a given state), how do we determine the rest of the properties?
- **“Equation of state”** A relationship between three independent intensive properties
 - Example “ideal Gas”: $P v = R T$
- How about water, refrigerants, etc. ?
 - Pure substances

Property Tables



- ❑ For most substances, the relationships among thermodynamic properties (the equations of state) 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.

Enthalpy

- The combination $[u + P v]$ often appears in thermodynamic analyses of control volumes (open systems)
 - Since u , P , and v are all properties, then $[u + P v]$ must also be a property -- called **“specific enthalpy”**
 - Units: (kJ/kg) -- Intensive property
 - **Total enthalpy** $H = m h = U + P V$ (kJ)

PROPERTY TABLES

● Saturated Liquid and Saturated Vapor

- Known T_{sat} [Tables A-4 (water); A-11 (R134a)]
- Known P_{sat} [Tables A-5 (water); A-12 (R134a)]
- How to use for saturated Liquid-Vapor Mixture?

● Superheated Vapor

- Tables A-6 (water); A-13 (R134a)

● Compressed (subcooled) Liquid

- Table A-7 (water)
- Approximations using saturated liquid values

PROPERTY TABLES --

Saturated Liquid & Saturated Vapor

- Provide Properties of Saturated liquid (subscript "f") and Saturated Vapor (Subscript "g")
 - Since T_{sat} and P_{sat} are uniquely related, one needs to specify only one or the other
- Table A-4 (water); A-11 (Refrigerant 134a)
 - **Given T_{sat} :** Table gives $P_{\text{sat}}, v_f, v_g, u_f, u_g, u_{fg}, h_f, h_g, h_{fg}, s_f, s_g, s_{fg}$
- Table A-5 (water); A-12 (Refrigerant 134a)
 - **Given P_{sat} :** Table gives $T_{\text{sat}}, v_f, v_g, u_f, u_g, u_{fg}, h_f, h_g, h_{fg}, s_f, s_g, s_{fg}$

PROPERTY TABLES --

Saturated Liquid & Saturated Vapor

□ $v_{fg} \equiv$ difference between
 v_g and v_f

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

➤ **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)
 $h_{fg} = h_g - h_f$

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

Specified
Temp

Specific
Volume of
Saturated
Liquid

Corresponding
Saturation
Pressure

Specific
Volume of
Saturated
Vapor

LECTURE # 8



Chapter 3 (Session #3): **Properties of Pure Substances**

PROPERTY TABLES --

Saturated Liquid & Saturated Vapor

- Table A-4 (Water) -- **Examples:**

- **For $T_{\text{sat}} = 50^{\circ}\text{C}$:**

- $P_{\text{sat}} = 12.352 \text{ kPa}$; $v_f = 0.001012 \text{ m}^3/\text{kg}$; $v_g = 12.026 \text{ m}^3/\text{kg}$;
 $u_f = 209.33 \text{ kJ/kg}$; $u_g = 2442.7 \text{ kJ/kg}$; $u_{fg} = 2233.4 \text{ kJ/kg}$; etc.

- **For $T_{\text{sat}} = 100^{\circ}\text{C}$:**

- $P_{\text{sat}} = 101.42 \text{ kPa}$; $v_f = 0.001043 \text{ m}^3/\text{kg}$; $v_g = 1.6720 \text{ m}^3/\text{kg}$;
 $u_f = 419.06 \text{ kJ/kg}$; $u_g = 2506.0 \text{ kJ/kg}$; $u_{fg} = 2087.0 \text{ kJ/kg}$; etc.

- **For $T_{\text{sat}} = 373.95^{\circ}\text{C}$:**

- $P_{\text{sat}} = 22.064 \text{ MPa}$; $v_f = 0.003106 \text{ m}^3/\text{kg}$; $v_g = 0.003106 \text{ m}^3/\text{kg}$;
 $u_f = 2015.7 \text{ kJ/kg}$; $u_g = 2015.7 \text{ kJ/kg}$; **$u_{fg} = 0 \text{ kJ/kg}$** ; etc.

PROPERTY TABLES --

Saturated Liquid & Saturated Vapor

- Table A-5 (Water) -- **Examples:**

- **For $P_{\text{sat}} = 75 \text{ kPa}$:**

- $T_{\text{sat}} = 91.76 \text{ }^{\circ}\text{C}$; $v_f = 0.001037 \text{ m}^3/\text{kg}$; $v_g = 2.2172 \text{ m}^3/\text{kg}$;
 $u_f = 384.36 \text{ kJ/kg}$; $u_g = 2496.1 \text{ kJ/kg}$; $u_{fg} = 2111.8 \text{ kJ/kg}$; etc.

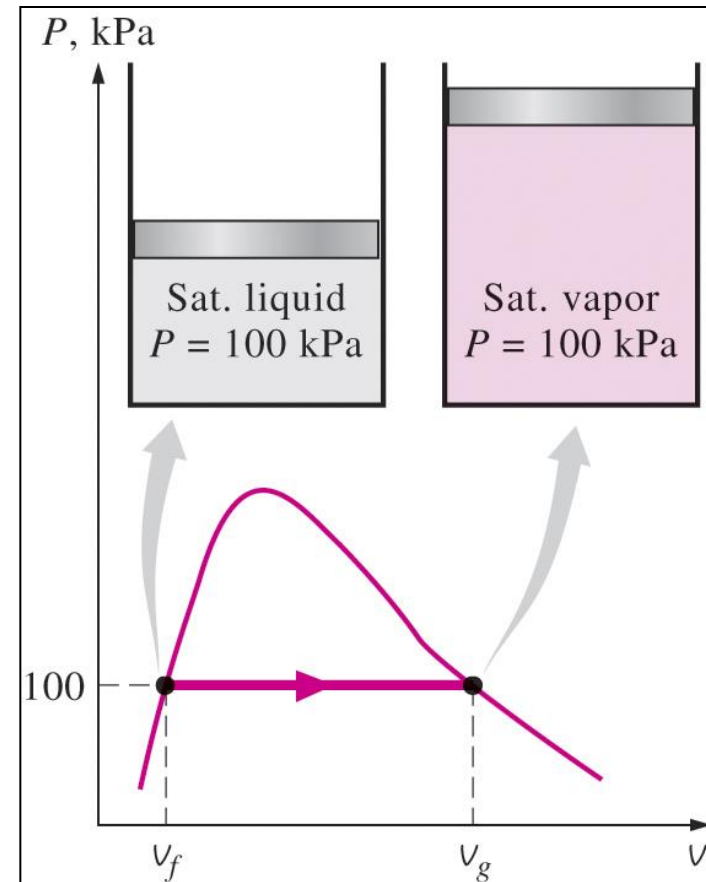
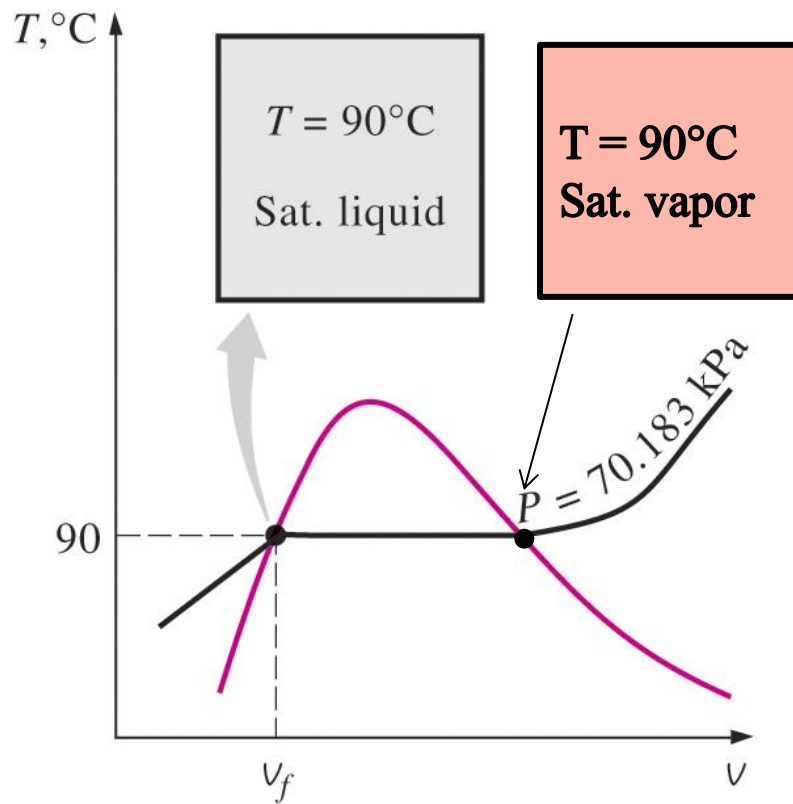
- **For $P_{\text{sat}} = 2.00 \text{ MPa}$:**

- $T_{\text{sat}} = 212.38 \text{ }^{\circ}\text{C}$; $v_f = 0.001177 \text{ m}^3/\text{kg}$; $v_g = 0.099587 \text{ m}^3/\text{kg}$;
 $u_f = 906.12 \text{ kJ/kg}$; $u_g = 2599.1 \text{ kJ/kg}$; $u_{fg} = 1693.0 \text{ kJ/kg}$; etc.

- **For $P_{\text{sat}} = 22.064 \text{ MPa}$:**

- $T_{\text{sat}} = 373.95 \text{ }^{\circ}\text{C}$; $v_f = 0.003106 \text{ m}^3/\text{kg}$; $v_g = 0.003106 \text{ m}^3/\text{kg}$;
 $u_f = 2015.7 \text{ kJ/kg}$; $u_g = 2015.7 \text{ kJ/kg}$; $u_{fg} = 0 \text{ kJ/kg}$; etc.

Saturated Liquid & Saturated Vapor States



Saturated Liquid-Vapor Mixture



- ❑ During boiling, at a given pressure, the temperature of a pure substance remains the same.
- ❑ This means that pressure and temperature are not independent during this period.
- ❑ Therefore, pressure and temperature cannot be used to specify the state in this case.
- ❑ Another independent property (in addition to T or P) is needed to specify the state, e.g. v , u , or h
- ❑ How do we find v , u , or h ?

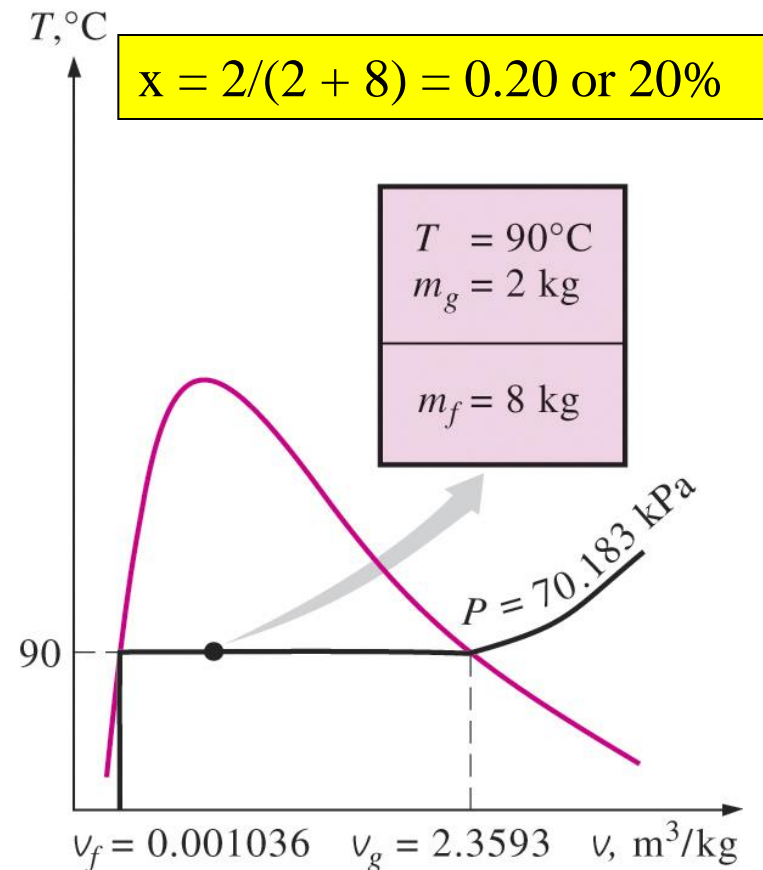
Saturated Liquid-Vapor Mixture

Definition: “Mixture Quality”

- **Quality:** Mass fraction of vapor present in a saturated liquid/vapor mixture

$$\begin{aligned} \text{➤ } x &\equiv m_g / m_{\text{mixture}} \\ &= m_g / (m_g + m_f) \end{aligned}$$

- For saturated liquid $x = 0$
- For saturated vapor $x = 1.0$ (100%)
- For saturated liquid-vapor mixture $0 < x < 1.0$



Saturated Liquid-Vapor Mixture – Evaluation of Properties

- Specified Temperature (T_{sat}) **and Quality (x)**
 - Use Saturated Tables [Table A-4 (water); A-11 (Refrigerant 134a)] to determine properties of saturated liquid and saturated vapor
 - Use quality + properties of saturated liquid and saturated vapor to determine “**average**” properties of the mixture
- Specified Pressure (P_{sat}) **and Quality (x)**
 - Same as above using saturated pressure tables [Table A-5 (water); A-12 (Refrigerant 134a)]

Saturated Liquid-Vapor Mixture -- “Average” Properties

- Consider a saturated liquid-vapor mixture

m_f = mass of saturated liquid in the mixture

m_g = mass of saturated vapor in the mixture

m_t = total mass of the mixture = $m_f + m_g$

- **Quality:**

$$x \equiv (m_g/m_t) = [m_g/(m_f + m_g)]$$

$$1 - x = (m_f/m_t) = [m_f/(m_f + m_g)]$$

- Let “Y” be any **extensive** property of the mixture (e.g. V, U, H)

Saturated Liquid-Vapor Mixture -- “Average” Properties

- Extensive property of the mixture is the sum of extensive properties of saturated liquid and saturated vapor in the mixture

$$Y = Y_f + Y_g$$

$$m_t y = m_f y_f + m_g y_g$$

[y , y_f , and y_g are corresponding specific properties]

$$y = (m_f/m_t) y_f + (m_g/m_t) y_g$$

$$y = (1-x) y_f + x y_g$$

- Knowing “ y_f ” & “ y_g ” from saturated tables & quality “ x ”, calculate the average specific mixture property “ y ”

Saturated Liquid-Vapor Mixture

Example: Evaluation of Average Specific Volume

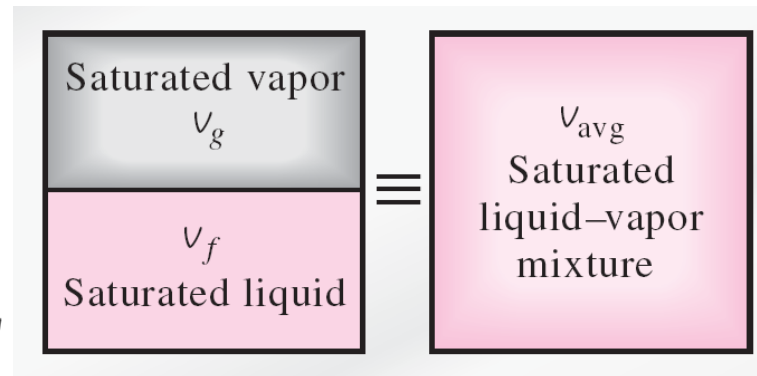
$$m_{\text{total}} = m_{\text{liquid}} + m_{\text{vapor}}$$

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

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

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

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



Saturated Liquid-Vapor Mixture

Example: Evaluation of Average Specific Volume

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

$$v_{avg} = (1 - x) v_f + x v_g = v_f + x \underbrace{(v_g - v_f)}_{\equiv v_{fg}}$$

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

Saturated Liquid-Vapor Mixture – Evaluation of Properties

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

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

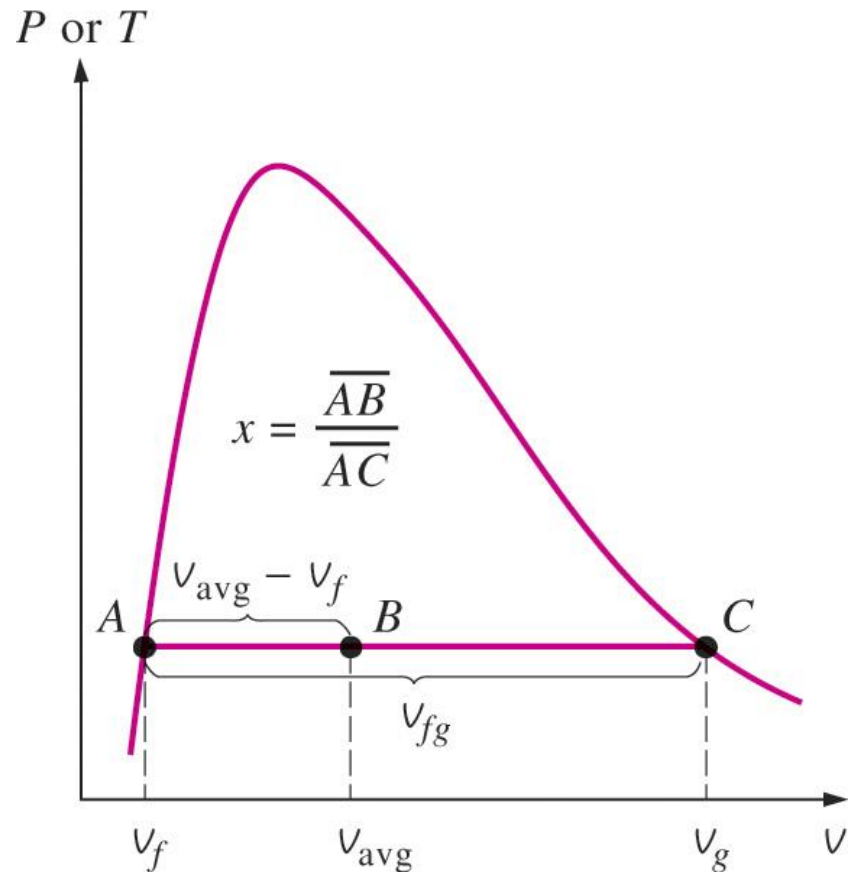
$$h_{avg} = h_f + x h_{fg}$$

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

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

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

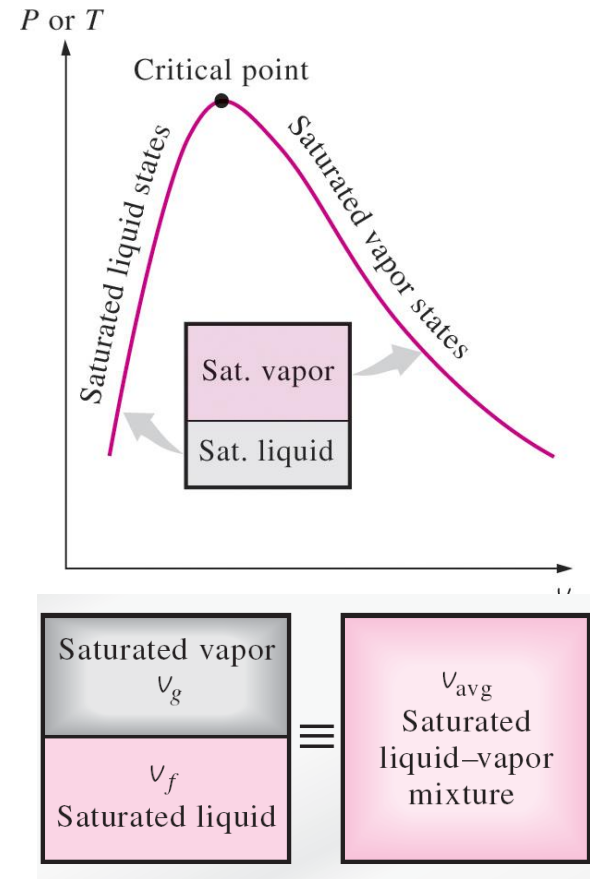
$$x = \frac{h_{avg} - h_f}{h_{fg}}$$



Saturated Liquid-Vapor Mixture – Evaluation of Properties

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.



Average Saturated Mixture Properties -- Examples

- Example: Saturated water liquid-vapor mixture
 - Known: $T = 150\text{ }^{\circ}\text{C}$ and $x = 0.70$ (70%)
 - Determine v , and u
- Table A-4 for $T_{\text{sat}} = 150\text{ }^{\circ}\text{C}$:
 - $v_f = 0.001091\text{ m}^3/\text{kg}$; $v_g = 0.39248\text{ m}^3/\text{kg}$
 $v = v_f + x v_{fg} = 0.001091 + 0.70 (0.39248 - 0.001091)$
 $= \mathbf{0.2751\text{ m}^3/\text{kg}}$
 - $u_f = 631.66\text{ kJ/kg}$; $u_{fg} = 1927.4\text{ kJ/kg}$
 $u = u_f + x u_{fg} = 631.66 + 0.70 (1927.4) = \mathbf{1980.8\text{ kJ/kg}}$

LECTURE # 9



Chapter 3 (Session #4): **Properties of Pure Substances**

QUESTION



- ❑ **Recall the State Postulate:** “The equilibrium state of a simple system is completely specified **by any two independent intensive properties**”
- ❑ What are the two independent intensive properties used to evaluate the properties of the saturated liquid-vapor mixture in the above example?
- ❑ The **quality** of a saturated liquid-vapor mixture in equilibrium is an **intensive thermodynamic property**

PROPERTY TABLES --

Superheated vapor



- State is fixed by specifying any two **independent** intensive properties
- For superheated vapor, Temperature and Pressure are independent
- Tables A-6 (water) and A-13 (R134a):
 - Properties (v , u , h and s) are given as functions of (T&P)

PROPERTY TABLES --

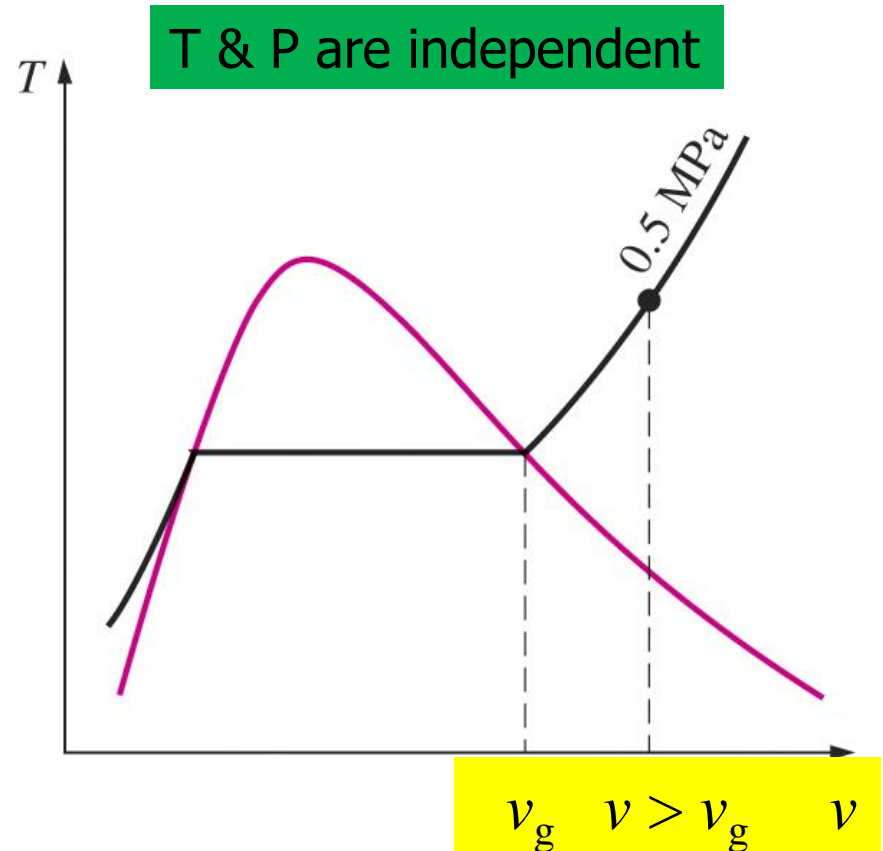
Superheated vapor (Table A-6)

	v	u	h
$T, ^\circ\text{C}$	m^3/kg	kJ/kg	kJ/kg
<hr/> $P = 0.1 \text{ MPa } (99.61^\circ\text{C})$ <hr/>			
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
<hr/> $P = 0.5 \text{ MPa } (151.83^\circ\text{C})$ <hr/>			
Sat.	0.37483	2560.7	2748.1
200	0.42503	2643.3	2855.8
250	0.47443	2723.8	2961.0

Superheated Vapor

❑ The superheated region is characterized by:

- Higher temperatures ($T > T_{\text{sat}}$ 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)



PROPERTY TABLES --

Superheated vapor



- Example: Water (superheated vapor) at 200 °C and 0.1 MPa

- **Table A-6:**

$$v = 2.1724 \text{ m}^3/\text{kg}$$

$$u = 2658.2 \text{ kJ/kg}$$

$$h = 2875.5 \text{ kJ/kg}$$

$$s = 7.8356 \text{ kJ/kg K}$$

PROPERTY TABLES --

Superheated vapor

● How do we know that H₂O is superheated vapor at 200 °C and 0.1 MPa?

- $P < P_{\text{sat}}$ at a given T [@ 200 °C, $P_{\text{sat}} = 1.5549 \text{ MPa}$]
- $T > T_{\text{sat}}$ at a given P [@ 0.1 MPa, $T_{\text{sat}} = 99.61 \text{ °C}$]
- $v > v_g$ at a given P or T [@ 200 °C, $v_g = 0.12721 \text{ m}^3/\text{kg}$;
@ 0.1 MPa, $v_g = 1.6941 \text{ m}^3/\text{kg}$]
- $u > u_g$ at a given P or T [@ 200 °C, $u_g = 2594.2 \text{ kJ/kg}$;
@ 0.1 MPa, $u_g = 2505.6 \text{ kJ/kg}$]
- $h > h_g$ at a given P or T [@ 200 °C, $h_g = 2792.0 \text{ kJ/kg}$;
@ 0.1 MPa, $h_g = 2675.0 \text{ kJ/kg}$]

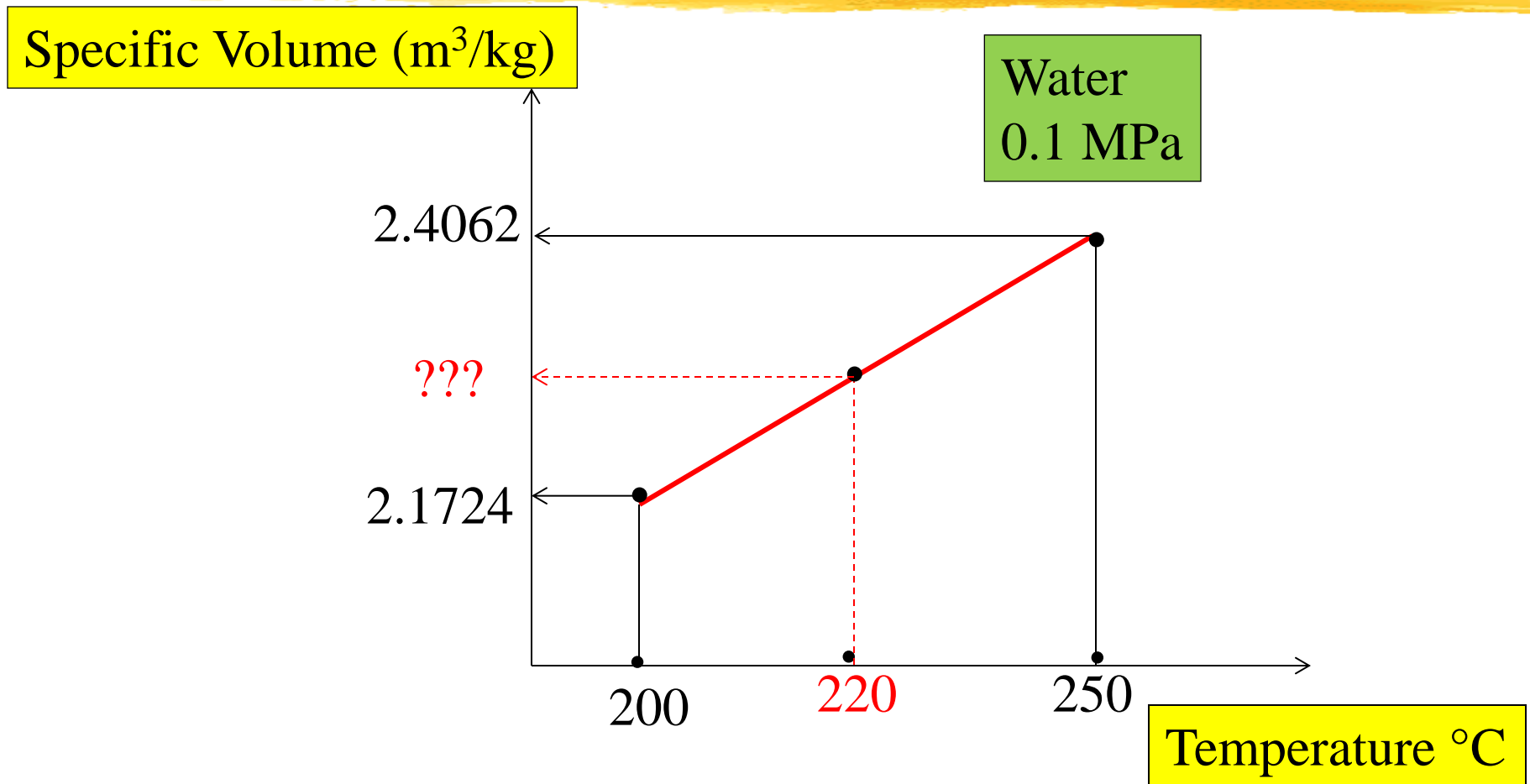
PROPERTY TABLES -- Superheated vapor

- What if P and/or T values are not directly given in Table A-6 (or A-13 for R134a)?
 - Use linear interpolation between table values
- Example: Water at **220 °C** and **0.1 MPa**

P = 0.1 MPa

T	v	u	h	s
200	2.1724	2658.2	2875.5	7.8356
220	?	?	?	?
250	2.4062	2733.9	2974.5	8.0346

PROPERTY TABLES -- Superheated Vapor



PROPERTY TABLES -- Superheated vapor

- Linear interpolation between table values
- $v(220\text{ }^{\circ}\text{C}, 0.1\text{ MPa}) = 2.1724 + [(220-200)/(250-200)]$
 $\times [2.4062 - 2.1724]$
 $= 2.2659\text{ m}^3/\text{kg}$
- $u(220\text{ }^{\circ}\text{C}, 0.1\text{ MPa}) = 2658.2 + [(220-200)/(250-200)]$
 $\times [2733.9 - 2658.2]$
 $= 2688.5\text{ kJ/kg}$

PROPERTY TABLES -- Superheated vapor

- Example: Water at **200 °C** and **0.15 MPa**

P = 0.1 MPa

T	v	u	h	s
200	2.1724	2658.2	2875.5	7.8356

P = 0.2 MPa

T	v	u	h	s
200	1.08049	2654.6	2870.7	7.5081

- $$u(200\text{ °C}, 0.15\text{ MPa}) = 2658.2 + [(0.15-0.1)/(0.2-0.1)] \times [2654.4 - 2658.1]$$
$$= 2656.4\text{ kJ/kg}$$

PROPERTY TABLES --

Superheated vapor

- What if we know two properties other than T & P?

➤ Use linear interpolation between table values

- Example: Water; $P = 0.1 \text{ MPa}$ & $v = 2.30 \text{ m}^3/\text{kg}$
 $P = 0.1 \text{ MPa}$

T	v	u	h	s
200	2.1724	2658.2	2875.5	7.8356
?	2.30	?	?	?
250	2.4062	2733.9	2974.5	8.0346

PROPERTY TABLES -- Superheated vapor



- **Linear interpolation between table values**
- $$T(0.1 \text{ MPa}, 2.30 \text{ m}^3/\text{kg}) = 200 + [(2.30 - 2.1724)/(2.4062 - 2.1724)] \times [250 - 200]$$
$$= 227.3 \text{ }^\circ\text{C}$$
- $$U(0.1 \text{ MPa}, 2.30 \text{ m}^3/\text{kg}) = 2658.2 + [(2.30 - 2.1724)/(2.4062 - 2.1724)] \times [2733.9 - 2658.2]$$
$$= 2699.5 \text{ kJ/kg}$$

PROPERTY TABLES --

Compressed Liquid

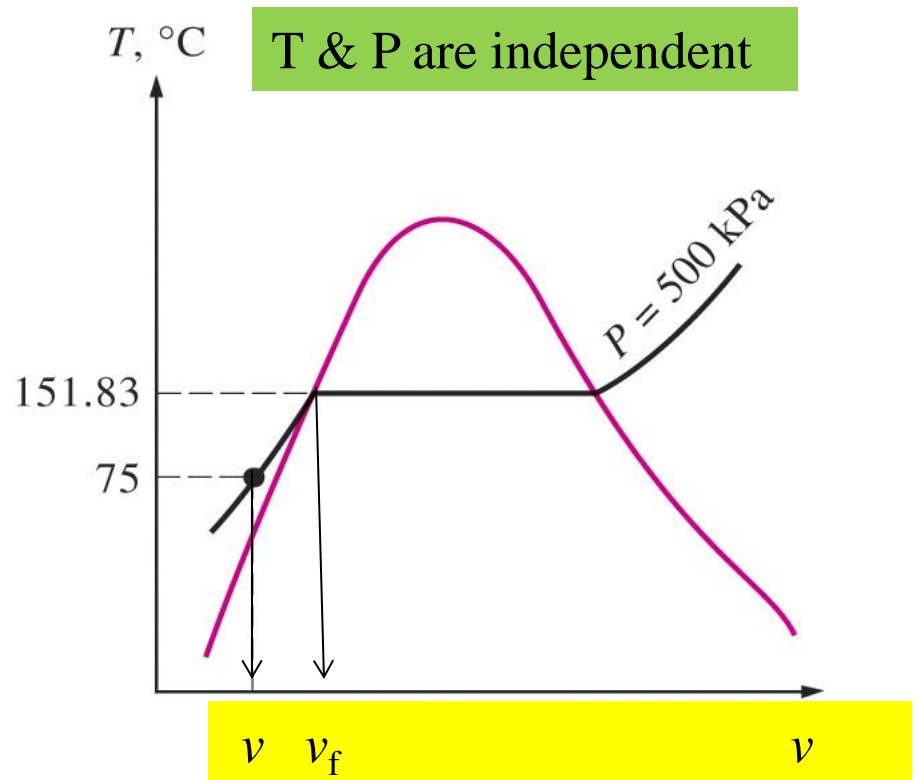


- State is fixed by specifying any two **independent** intensive properties
- For compressed (“subcooled”) liquid, Temperature & Pressure are independent
- Tables A-7 (water):
 - Properties (v , u , h and s) are given as functions of (T&P)

Compressed Liquid

❑ The compressed liquid region is characterized by:

- 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)



PROPERTY TABLES --

Compressed Liquid



- Example: Compressed Liquid Water at 200 °C and 10 MPa

- **Table A-7:**

$$v = 0.0011482 \text{ m}^3/\text{kg}$$

$$u = 844.32 \text{ kJ/kg}$$

$$h = 855.80 \text{ kJ/kg}$$

$$s = 2.3174 \text{ kJ/kg K}$$

PROPERTY TABLES --

Compressed Liquid

● How do we know that H₂O is compressed liquid at 200 °C and 10 MPa?

- $P > P_{\text{sat}}$ at a given T [@ 200 °C, $P_{\text{sat}} = 1.5549 \text{ MPa}$]
- $T < T_{\text{sat}}$ at a given P [@ 10 MPa, $T_{\text{sat}} = 311.00 \text{ °C}$]
- $v < v_f$ at a given P or T [@ 200 °C, $v_f = 0.001157 \text{ m}^3/\text{kg}$;
@ 10 MPa, $v_f = 0.001452 \text{ m}^3/\text{kg}$]
- $u < u_f$ at a given P or T [@ 200 °C, $u_f = 850.46 \text{ kJ/kg}$;
@ 10 MPa, $u_f = 1393.3 \text{ kJ/kg}$]
- $h < h_f$ at a given P [@ 10 MPa, $h_f = 1407.8 \text{ kJ/kg}$]

Note: @ 200 °C, $h_f = 852.26 \text{ kJ/kg}$ vs. 855.80 kJ/kg for compressed liquid at $P \gg P_{\text{sat}}$

APPROXIMATE PROPERTIES -- Compressed Liquid

- Properties of compressed liquids can be well approximated using saturated liquid values **at the same temperature**
 - $v(T, P) \cong v_f@T$
 - $u(T, P) \cong u_f@T$
 - $h(T, P) \cong h_f@T + v_f (P - P_{\text{sat}})$ or $h(T, P) \cong h_f@T$
- Percent error in v , u , and h values for previous example (200 °C and 10 MPa) < 1%

Compressed Liquid Properties

- **Compressed Liquid Water at 200 °C and 10 MPa**

<u>Property</u>	<u>Table A-7</u>	<u>Approx. value</u>	<u>% Error</u>
ν (m ³ /kg)	0.0011482	0.001157	0.77
u (kJ/kg)	844.32	850.46	0.73
h (kJ/kg)	855.80	862.03	0.73

or $h \approx h_f = 852.26$ - 0.41

EXAMPLE



- 2.0 kg of water in a piston-cylinder assembly
- Initial state: $P_1 = 300 \text{ kPa}$; $T_1 = 200 \text{ }^\circ\text{C}$
- Heat is added at constant pressure until temperature reaches $400 \text{ }^\circ\text{C}$
- Determine ΔV , ΔU , ΔH
- Sketch process on P - v and T - v Diagrams

Example

● Problem statement:

- Initial state: $P_1 = 300 \text{ kPa}$; $T_1 = 200 \text{ }^\circ\text{C}$
- Process: Constant pressure heat addition
- Final state: $P_2 = 300 \text{ kPa}$; $T_2 = 400 \text{ }^\circ\text{C}$

● Solution: First step is to determine the phase(s) at states "1" and "2"

- For water at $P = 300 \text{ kPa}$, Table A-5 gives:

$$T_{\text{sat}} = 133.52 \text{ }^\circ\text{C}$$

- Both states "1" & "2" must be superheated vapor

Solution - Continued

- Table A-6 (Superheated water vapor)

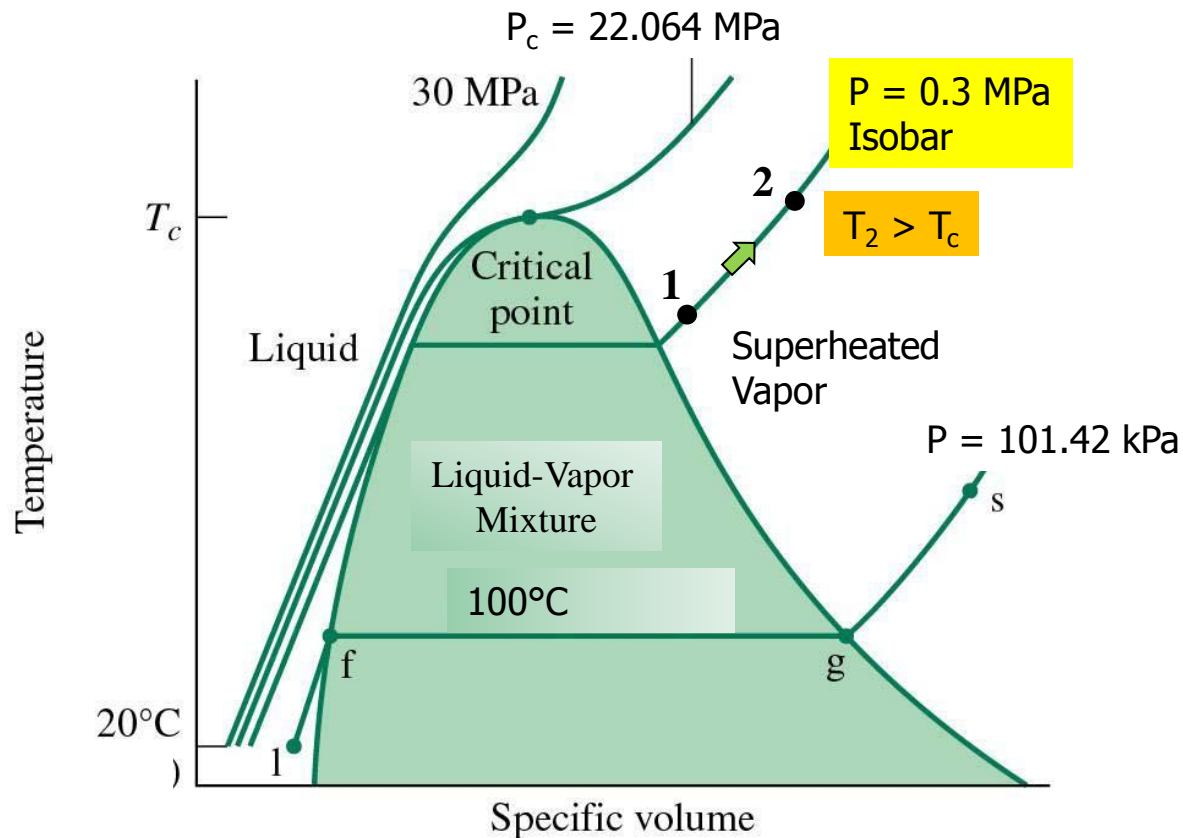
P = 0.30 MPa (133.52°C)

T(°C)	v (m ³ /kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)
200	0.71643	2651.0	2865.9	7.3132
400	1.03155	2966.0	3275.5	8.0347

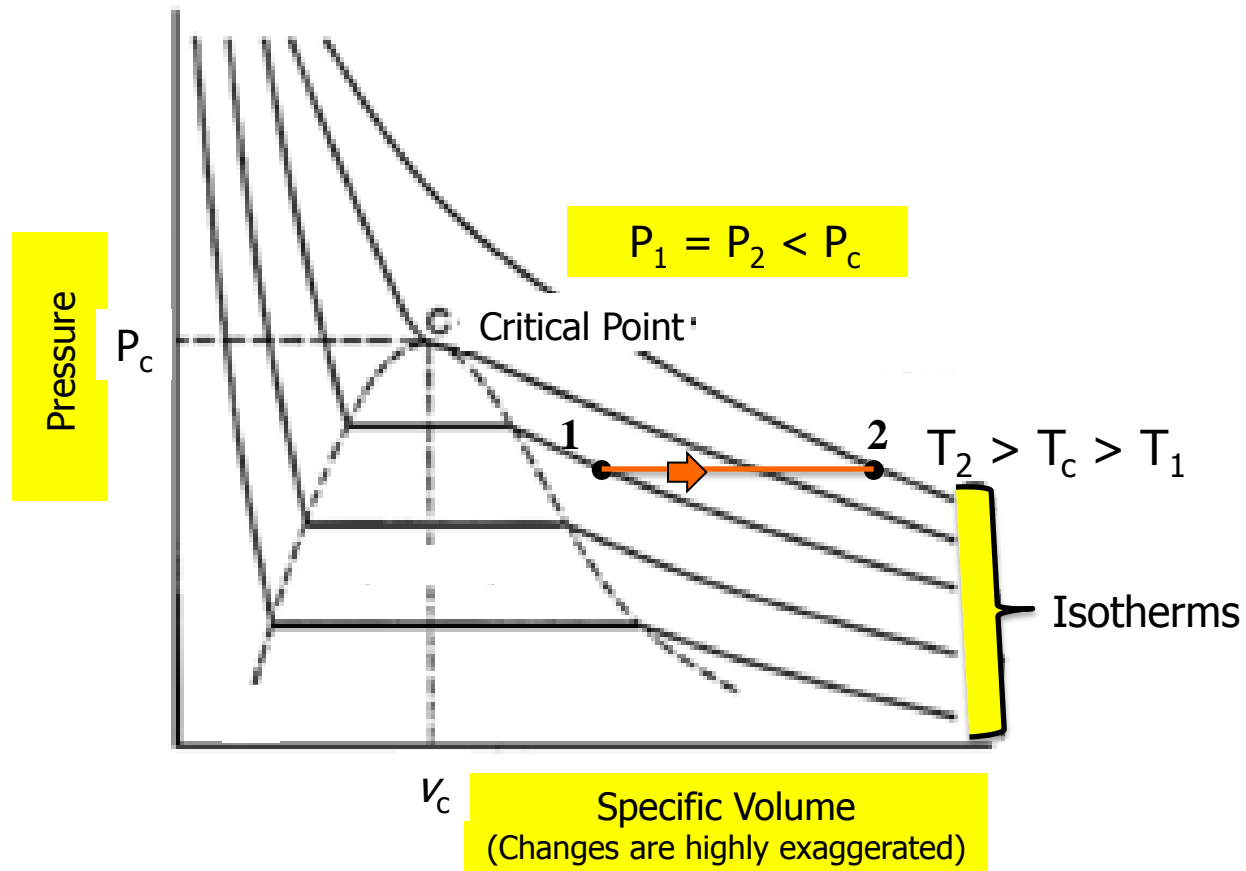
Solution -- Continued

- $\Delta V = V_2 - V_1 = m (v_2 - v_1)$
 $= 2 \text{ (kg)} [1.03155 - 0.71643] \text{ (m}^3\text{/kg)} = 0.63024 \text{ m}^3$
- $\Delta U = U_2 - U_1 = m (u_2 - u_1)$
 $= 2 \text{ (kg)} [2966.0 - 2651.0] \text{ (kJ/kg)} = 630.0 \text{ kJ}$
- $\Delta H = H_2 - H_1 = m (h_2 - h_1)$
 $= 2 \text{ (kg)} [3275.5 - 2865.9] \text{ (kJ/kg)} = 819.2 \text{ kJ}$

Solution -- Process T-v Diagram



Solution -- Process P-v Diagram



LECTURE # 10



Chapter 3 (Session #5): **Properties of Pure Substances**

Identification of Phase

If P and T are given

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

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

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

EXAMPLE

□ Fill in the missing information for water

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

EXAMPLE

□ Fill in the missing information for water

P , kPa	T , °C	v , m ³ /kg	h , kJ/kg	Condition description and quality (if applicable)
200	120.21	0.88578	2706.3	Saturated Vapor
270.28	130	0.43463	1959.3	0.650
200	400	1.54934	3277.0	Superheated Vapor
800	30	0.001004	125.74	Compressed Liquid
450	147.90	??	??	Need to specify mixture quality

Property Tables for Other Pure Substances



- ❑ There are property tables for substances other than water (e.g. Mercury, Ammonia, and R-134a).
- ❑ R-134a is a common refrigerant in many commercial air conditioners.
- ❑ Tables for refrigerant 134a (R-134a) are given in the text (Tables A-11, 12 & 13); tables for other substances can be found in the literature.

Reference State and Reference Values

- ❑ Values of u , h (and s) at a given state cannot be measured directly
- ❑ They are calculated from measurable quantities using the relations between thermodynamic properties.
- ❑ These relations give the **changes** in properties rather than the values at a specific state.
- ❑ Therefore, a reference state is needed where **some** properties are arbitrarily assigned a value of zero. **(Why only some??)**
 - For Water, reference state is saturated liquid at the triple point (0.01°C), where u_f and s_f are set equal to zero
 - For R-134a, reference state is saturated liquid at -40°C , where h_f and s_f are set equal to zero.

The “*Ideal Gas*” Equation of State

● What is an “Equation of State”?

- **Equation of state**: Any equation that relates the pressure, temperature, and specific volume of a substance in an equilibrium state.
- **In general** – any relation between three independent intensive properties at equilibrium states is referred to as an Equation of State (e.g. $f(P, \nu, u) = 0$)
- The simplest and best-known equation of state for substances in the gas phase is the **ideal-gas equation of state**.

The “*Ideal Gas*” Equation of State



- What is an “ideal gas”?
 - An “imaginary” substance that obeys the relation $P v = R T$
 - Ideal gas relation closely approximates P- v -T behavior of **real gases at low density**

The “*Ideal Gas*” Equation of State

● $P v = R T$

- P = Absolute pressure (kPa)
- v = Specific volume (m^3/kg)
- T = Absolute temperature (K)
- R = Gas constant ($\text{kPa m}^3/\text{kg K}$) or (kJ/kg K)

● **Gas Constant: $R = R_u/M$**

- R_u = Universal gas constant
= $8.314 \text{ kPa m}^3/\text{kmole K}$ = 8.314 kJ/kmole K
- M = molar mass (molecular weight) (kg/kmole)
= mass of 1 kmole in kg or 1 mole in g

The “*Ideal Gas*” Equation of State

- Values of “M” and “R” for different gases are given in Table A-1

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

- Avogadro’s number

$$\begin{aligned}\text{➤ } Av &= 6.02252 \times 10^{23} \text{ molecules/g-mole} \\ &= 6.02252 \times 10^{26} \text{ molecules /kg-mole} \\ &= 2.73177 \times 10^{26} \text{ molecules /lb-mole}\end{aligned}$$

Other Expressions for the Ideal Gas EOS

$$V = m\upsilon \longrightarrow PV = mRT$$

Mass = Molar mass \times number of Moles

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

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

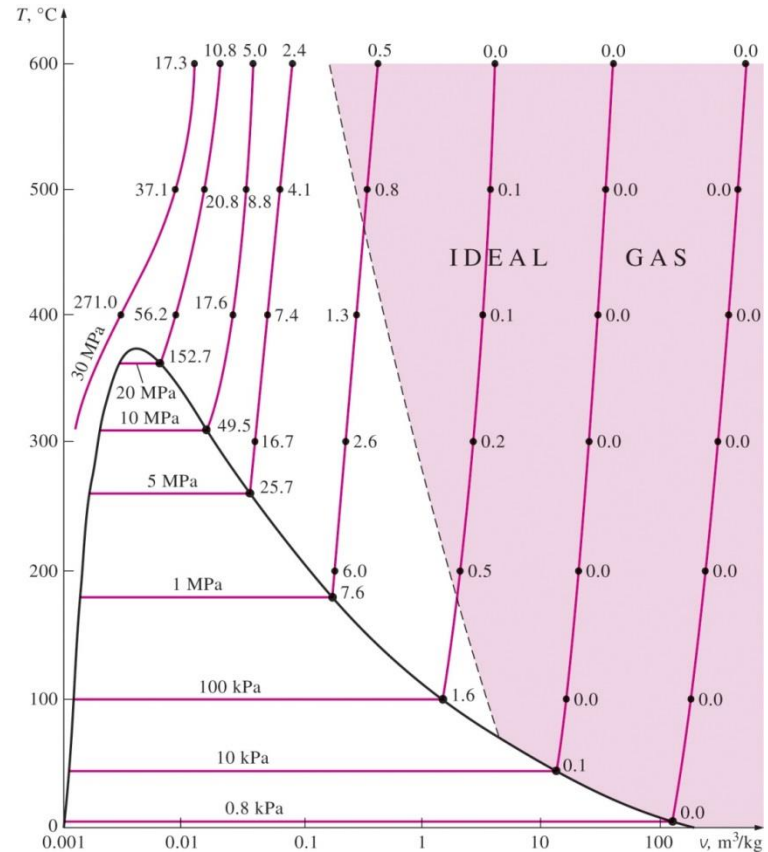
Applicability of the Ideal Gas Equation of State

□ Is the ideal gas EOS always applicable for gases?

- Real gases behave as an ideal gas at low densities (i.e., low pressure, high temperature).
- At low densities, collisions among molecules are insignificant (zero density limit)
- Often, the ideal-gas relation is **NOT** applicable to real gases
- Care should be taken when using it.

Is Superheated Water Vapor an Ideal Gas?

- ❑ At pressures below 10 kPa, superheated 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.



$$\% \text{ error} = \left(\left| \frac{v_{\text{table}} - v_{\text{ideal}}}{v_{\text{table}}} \right| \times 100 \right)$$

Actual Gases

- Ideal gas P - v - T relation is very simple and convenient to use; however,
 - Gases deviate significantly from ideal gas behavior at states near the saturation region and critical point.
 - Deviation can be accounted for by introducing a correction factor – the compressibility factor, Z
- $P v = Z R T$
 - $Z = 1$ for ideal gas

Actual Gases -- Compressibility Factor

- $P v = Z R T$

- $Z = v_{\text{actual}} / v_{\text{ideal}}$

- Deviation of Z from unity is a measure of deviation from ideal gas behavior

- Experimental data shows that for different substances, Z is a unique function of “reduced pressure” & “reduced temperature”

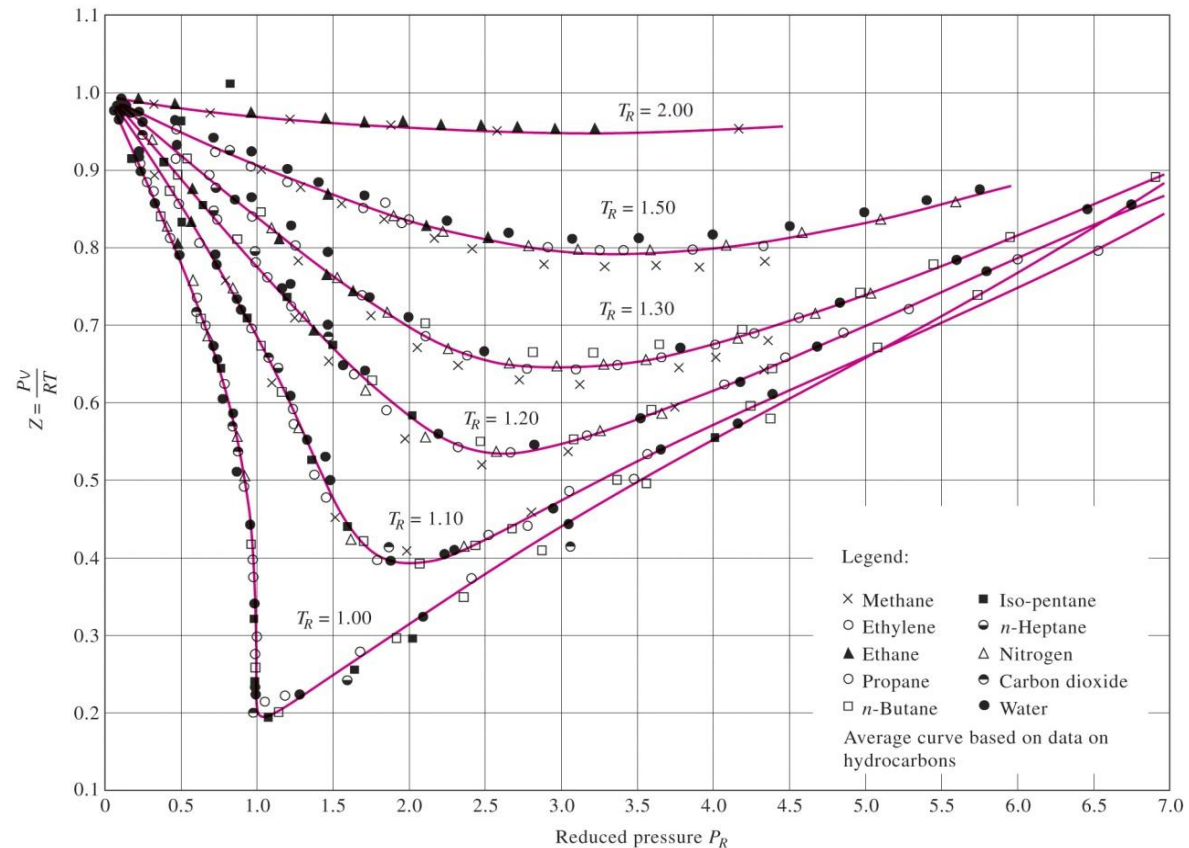
- $Z = f(P_R, T_R)$; $P_R = P/P_C$ & $T_R = T/T_C$

- **“Principle of corresponding states”**

Generalized Compressibility Chart

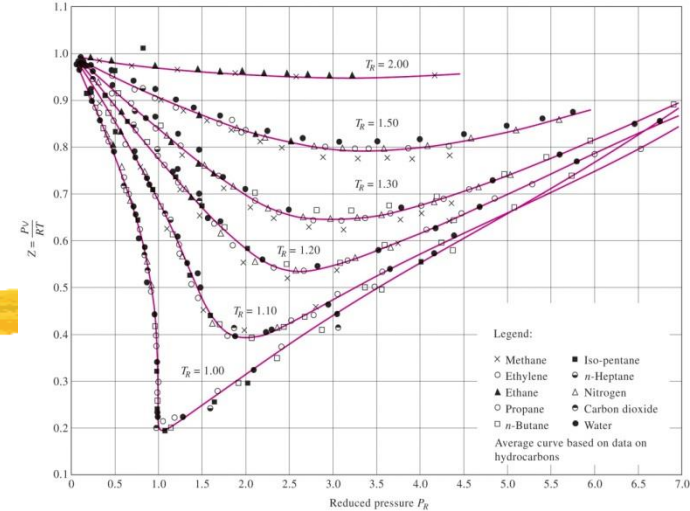
- Generalized compressibility chart obtained by fitting experimental data for a wide variety of gases.
- For Different Gases, Z depends only on the reduced Pressure P_R and reduced temperature T_R
- Principle of Corresponding States
- Figure A-15 shows Z as a function of P_R and ν_R

$$\nu_R \equiv \nu / (R T_{cr} / P_{cr})$$



Ideal Gas Criteria

- $P_R \ll 1$ (for any T_R)
- $T_R > 2$ (for any P_R , except $P_R \gg 1$)
- Deviation from ideal gas behavior is greatest near critical point (P_R & $T_R = 1$)
- Should never use ideal gas approximation except for “highly superheated vapors” at low pressures; use property tables instead



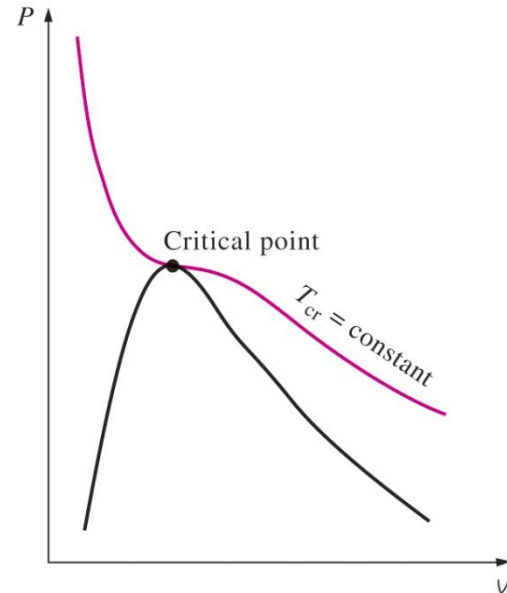
Other Equations of State

□ Van der Waals EOS

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

- Accounts for Intermolecular attraction forces (a/v^2) and volume occupied by molecules (b)
- Constants (a) and (b) determined from critical properties (Table A-1)
- Model accuracy is often inadequate

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



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

Relations describing critical temperature isotherm used to determine "a" and "b"

Other Equations of State (Contd.)

□ Beattie-Bridgeman EOS

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

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

- Constants A_0 , a , B_0 , and b are given in Table 3-4
- Equation is reasonably accurate for densities up to $0.8 \rho_{cr}$

Other Equations of State (Contd.)

□ Benedict-Webb-Rubin EOS

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

- Eight Constants are given in Table 3-4
- Equation is reasonably accurate for densities up to $2.5 \rho_{cr}$
- Equation further extended by Strohbridge (16 constants)

Other Equations of State (Contd.)

□ Virial Equation of State

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

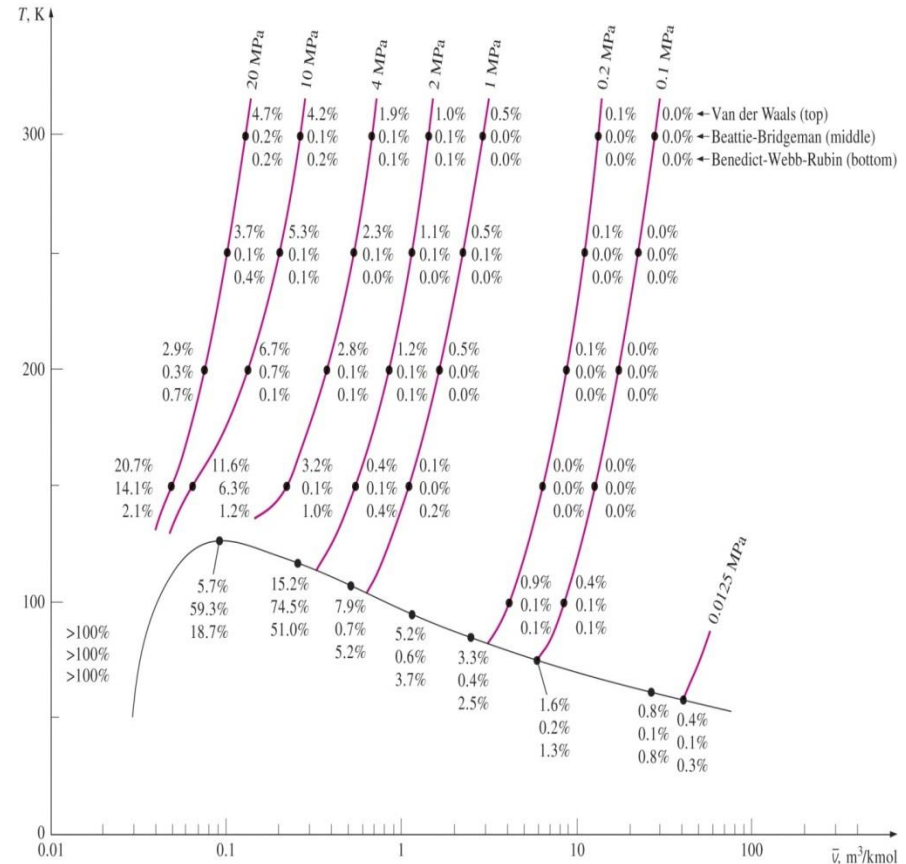
- “Virial Coefficients” $a(T)$, $b(T)$, $c(T)$, etc. are functions of temperature alone
- Determined either experimentally or from Statistical Mechanics
- All virial coefficients vanish as pressure approaches zero

Accuracy of Alternate Equations of State

- ❑ As EOS complexity increases (i.e. number of constants increases), the $P-v-T$ behavior of gases is more accurately represented over a wider range.

- Graph shows percentage of error for various EOS for nitrogen

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



CHAPTER 3

PROPERTIES OF PURE SUBSTANCES



OUTCOMES:

- ✓ Understand the physics of phase change processes for a pure substance
- ✓ Be able to plot the T - v , P - v , and P - T property diagrams for a pure substance
- ✓ Be able to evaluate the properties of a pure substance using tables of property data
- ✓ Understand the concept of an ideal gas and use the ideal gas Equation of State in solving problems