

# **CHAPTER THREE**

# **PROPERTIES OF PURE SUBSTANCES**

### Pure Substance (Section 3.1)

- A substance that has a fixed chemical composition throughout
- A pure substance does not have to be of a single chemical element or compound
- A mixture of various chemical elements or compounds is considered a pure substance if the mixture is homogeneous

#### Examples:

- ⇒ Water, nitrogen, and helium are all pure substances because they have the same chemical composition throughout even if they exist in two different phases (e.g. vapor and liquid)
- ⇒ Air (in the gaseous form) is considered a pure substance because the mixture of nitrogen, oxygen, ...etc is homogeneous

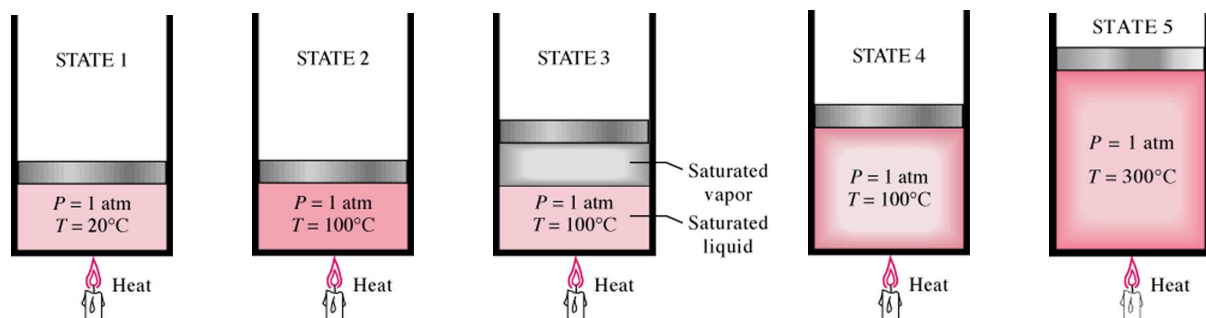
### Phases of a Pure Substance (Section 3.2)

Solid: Molecules are at relatively fixed positions

Liquid: Groups of molecules move about each other

Gas: Molecules move about at random in the gas phase

### Phase-Change Processes of Pure Substances (Section 3.3)



#### **State 1 (compressed liquid or subcooled liquid):**

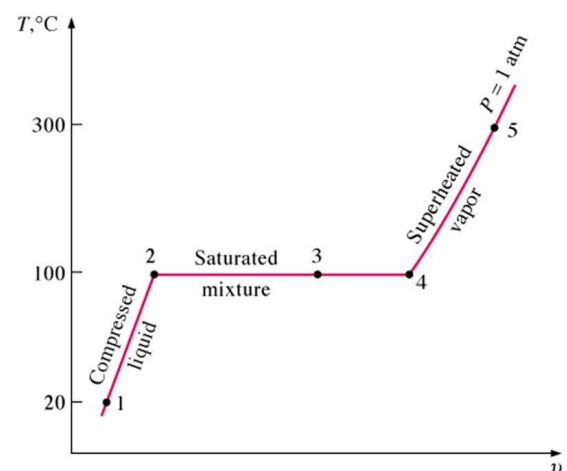
Water exists in the liquid phase, and it is called a compressed liquid or a subcooled liquid, meaning that it is not about to vaporize

#### **State 2 (saturated liquid):**

- Water is about to start vaporizing ⇒ saturated liquid
- The volume is slightly higher than the compressed liquid case because water is still a liquid.

#### **State 3 (saturated liquid-vapor mixture):**

- Boiling starts
- The temperature will stop rising until the liquid is completely vaporized
- Part of the water is in the liquid phase and part of it is in the gas phase



**State 4 (saturated vapor):**

- As we continue transferring heat, the vaporization process will continue until the last drop of liquid is vaporized
- At this point, the entire cylinder is filled with vapor.

**State 5 (superheated vapor)**

- Water goes to a single phase region again
- Further transfer of heat will result in an increase in both temperature and specific volume

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

Latent Heat

The amount of energy absorbed or released during a phase-change process

Latent Heat of Fusion

The amount of energy absorbed during melting

Latent Heat of Vaporization

The amount of energy absorbed during vaporization

**Saturation (boiling) temperature of water at various pressures**

Pressure P, kPa	Saturation Temperature $T_{sat}$ , °C
1	6.98
10	45.81
100	99.63
800	170.43
8000	295.06

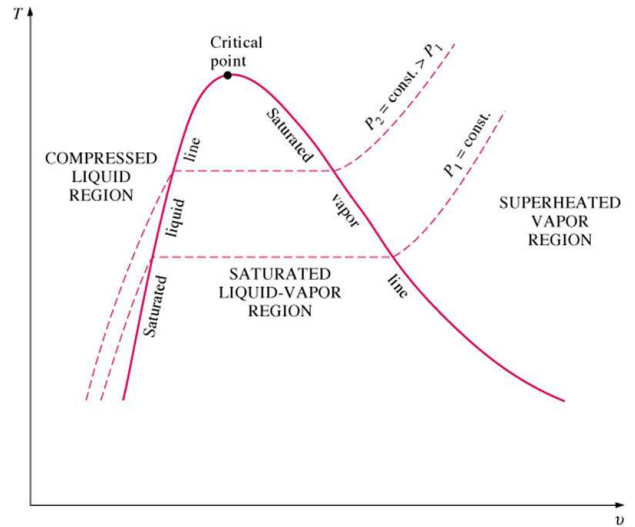
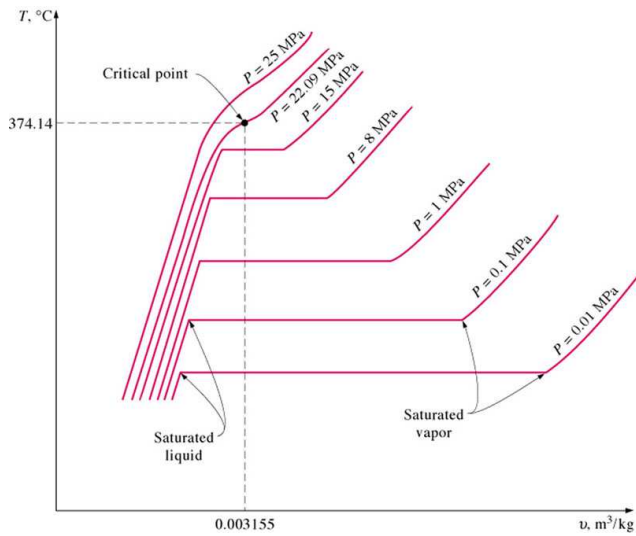
**Saturation (boiling) pressure of water at various temperatures**

Temperature $T$ , °C	Saturation Pressure $P_{sat}$ , kPa
-10	0.26
0	0.61
20	2.34
100	101.3
300	8581

**Property Diagrams for Phase-Change Processes (Section 3.4)**

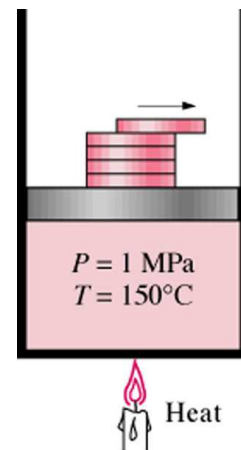
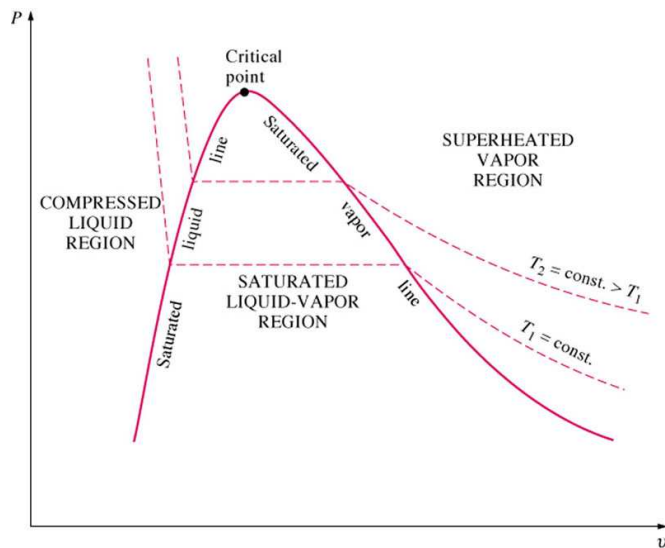
The T-v Diagram

- If the pressure is increased from  $P_{atm}$  to 1 MPa, water will boil at a higher temperature
- The saturation line will get shorter
- If the pressure is further increased, we will reach a point at which the saturation line disappears. This point is called the **critical point**
- Beyond the critical point, there is no distinct phase change process
- Connecting all the saturated liquid points results in a **saturated liquid line**
- Connecting all the saturated vapor points results in a **saturated vapor line**
- The two lines meet at the critical point and form a “dome”
- The region to the left of the dome is the **compressed liquid region**
- The region to the right of the dome is the **superheated vapor region**
- The region inside the dome is the **saturated liquid-vapor mixture region**



The P-v Diagram

The general shape of the P-v diagram is similar to the T-v diagram, but the T=constant lines have a downward trend

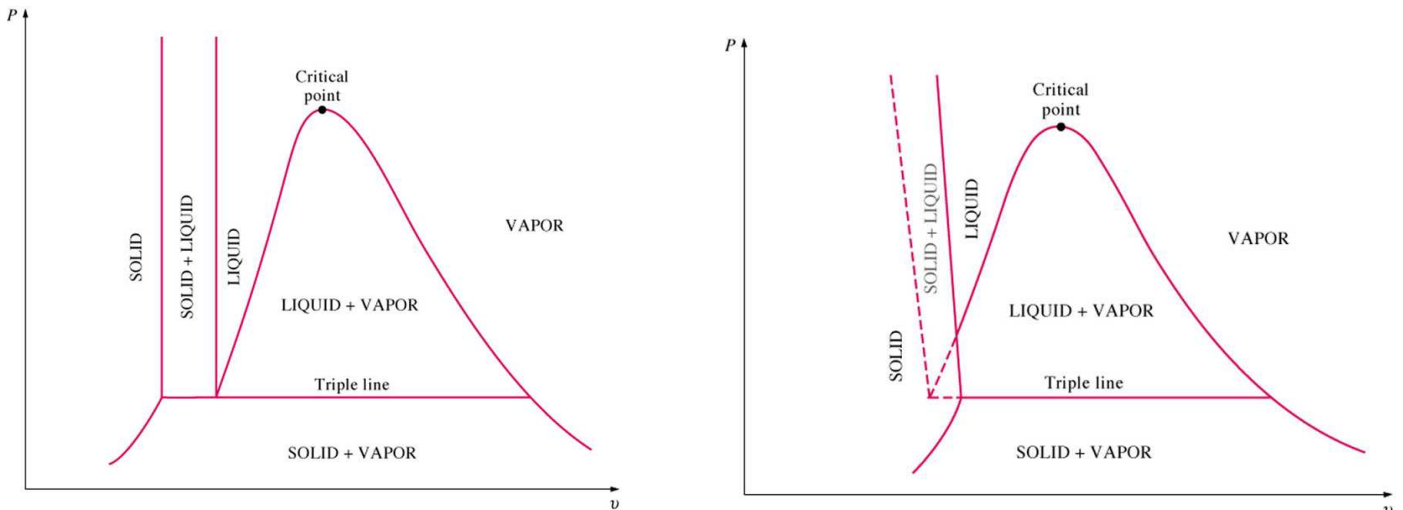


Following a T=constant line

- Initially, the system contains liquid water at 1 MPa and 150°C.
- The weights on top are removed one by one so that the pressure decreases
- The system exchanges heat with the surroundings to keep temperature constant
- When the pressure reaches saturation pressure, the water will start to boil
- After the vaporization process is complete, the specific volume of water starts to increase considerably because it is now vapor

Extending the Diagrams to Include the Solid Phase

- The diagrams presented so far involve only the liquid and vapor phases
- However, these diagrams can be extended to include the solid phase
- Most substances contract during a freezing process (left figure)
- A few substances, like water, expand during a freezing process (right figure)
- At the triple line, also called the **triple point**, all three phases exist in equilibrium
- For water, this situation exists at 0.01°C and 0.6113 kPa
- At pressures below the triple point pressure, a substance changes phase from solid to vapor directly. This process is called **sublimation**



Enthalpy ( $H$ )

- $H = U + PV$
- Since  $U$ ,  $P$ , and  $V$  are all properties,  $H$  is also a property

Specific Enthalpy ( $h$ )

$h = u + Pv$

**Property Tables (Section 3.5)**

Part (1a): Saturated Liquid and Saturated Vapor States

- The properties of saturated liquid and saturated vapor for water are listed in Tables A-4 and A-5 of the textbook
- It is more convenient to use Table A-4 when temperature is given
- It is more convenient to use Table A-5 when pressure is given
- The subscript  $f$  is used to denote the saturated liquid case
- The subscript  $g$  is used to denote the saturated vapor case
- The subscript  $fg$  is used to denote the difference between the saturated vapor and saturated liquid values of the same property

Temp. °C $T$	Sat. press. kPa $P_{sat}$	Specific volume $m^3/kg$	
		Sat. liquid $v_f$	Sat. vapor $v_g$
85	57.83	0.001 033	2.828
90	70.14	0.001 036	2.361
95	84.55	0.001 040	1.982

↑ Specific temperature      ↑ Specific volume of saturated liquid      ↑ Specific volume of saturated vapor  
 Corresponding saturation pressure

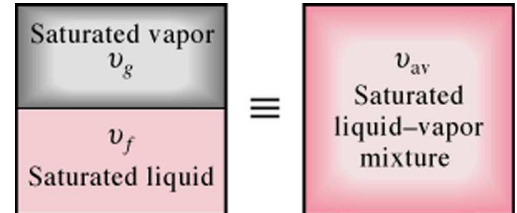
**Example**

$v_f$  = specific volume of saturated liquid  
 $v_g$  = specific volume of saturated vapor  
 $v_{fg}$  = difference between  $v_g$  and  $v_f$  (that is,  $v_{fg} = v_g - v_f$ )

Part (1b): Saturated Liquid-Vapor Mixture

**Quality:** The ratio of the mass of vapor to the total mass of the mixture

$$x = \frac{m_{\text{vapor}}}{m_{\text{total}}}, \text{ where } m_{\text{total}} = m_{\text{liquid}} + m_{\text{vapor}} = m_f + m_g$$



At saturated liquid point,  $x = 0$ . At saturated vapor point,  $x = 1$

$$V = V_f + V_g$$

$$\Rightarrow m_t v = m_f v_f + m_g v_g$$

$$\Rightarrow m_t v = (m_t - m_g) v_f + m_g v_g$$

Dividing by  $m_t$ :

$$v = (1 - x) v_f + x v_g$$

$$\Rightarrow v_{\text{av}} = v_f + x v_{fg}$$

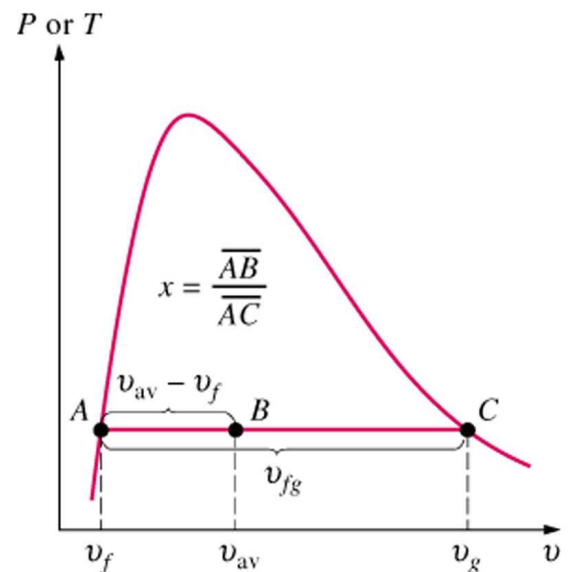
$$\Rightarrow x = \frac{v - v_f}{v_{fg}}$$

The analysis above can be repeated for internal energy and enthalpy with the following results:

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

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

For any general property,  $y$ :

$$y = y_f + x y_{fg}$$


Part (2): Superheated Vapor

The superheated region is a single-phase region  $\Rightarrow$  pressure and temperature are no longer dependent

Part (3): Compressed Liquid

- Variation of properties of compressed liquid with pressure is very small
- Compressed liquid data is very limited. Therefore, a general approximation is to *treat compressed liquid as saturated liquid at the given temperature*:  
 $y = y_{f@T}$

$T, ^\circ\text{C}$	$v, \text{m}^3/\text{kg}$	$u, \text{kJ/kg}$	$h, \text{kJ/kg}$
$P = 0.1 \text{ MPa (99.63}^\circ\text{C)}$			
Sat.	1.6940	2506.1	2675.5
100	1.6958	2506.7	2676.2
150	1.9364	2582.8	2776.4
$\vdots$	$\vdots$	$\vdots$	$\vdots$
1300	7.260	4683.5	5409.5
$P = 0.5 \text{ MPa (151.86}^\circ\text{C)}$			
Sat.	0.3749	2561.2	2748.7
200	0.4249	2642.9	2855.4
250	0.4744	2723.5	2960.7

**The Ideal-Gas Equation of State (Section 3.6)**Equation of State

An equation that relates the pressure, temperature, and specific volume of a substance

The Ideal-Gas Equation of State

$$Pv = RT \quad \text{OR} \quad PV = mRT$$

where  $R$  is called the **gas constant**

- This equation is based on the experiments of Boyle, Charles, and Gay-Lussac
- It is based on the assumptions that:
  - there are no attraction forces between molecules
  - molecules have zero volume.

**Specific Heat (Section 3.9)**

The energy required to raise the temperature of a unit mass of a substance by one degree

Specific Heat at Constant Volume ( $C_v$ )

The energy required to raise the temperature of a unit mass of a substance by one degree as the volume is maintained constant

Specific Heat at Constant Pressure ( $C_p$ )

The energy required to raise the temperature of a unit mass of a substance by one degree as the pressure is maintained constant

$$C_v = \left( \frac{\partial u}{\partial T} \right)_v, \quad C_p = \left( \frac{\partial h}{\partial T} \right)_p$$

Observations on  $C_v$  and  $C_p$ 

- $C_v$  and  $C_p$  are properties because they are expressed in terms of properties
- They can be used for any process (not just constant-volume and constant-pressure processes)
- $C_p$  is always larger than  $C_v$

**Internal Energy, Enthalpy, and Specific Heats of Ideal Gases (Section 3.10)**

- It has been proven that, for an ideal gas, the internal energy ( $u$ ) is a function of temperature only, i.e.:

$$u = u(T)$$

- Using the definition of enthalpy and the equation of state of an ideal gas, we have:

$$\left. \begin{array}{l} h = u + Pv \\ Pv = RT \end{array} \right\} h = u + RT$$

- This means that, for an ideal gas, enthalpy is also a function of temperature only, i.e.:  
 $h = h(T)$

- Therefore, for ideal gases,  $C_v$  and  $C_p$  can be expressed as follows:

$$C_v = \left( \frac{du}{dT} \right)_v \quad \text{OR} \quad C_v dT = du \quad (\text{at constant volume})$$

$$C_p = \left( \frac{dh}{dT} \right)_p \quad \text{OR} \quad C_p dT = dh \quad (\text{at constant pressure})$$

### How to Calculate Changes in Internal Energy and Enthalpy for Ideal Gases

- For some gases,  $C_v$  and  $C_p$  change significantly with temperature
- However, for small temperature ranges, it may be appropriate to use constant average specific heat values ( $C_{v,av}$  and  $C_{p,av}$ )
- In this case,  $\Delta u$  and  $\Delta h$  can be expressed as:  
 $\Delta u = u_2 - u_1 = C_{v,av} (T_2 - T_1)$   
 $\Delta h = h_2 - h_1 = C_{p,av} (T_2 - T_1)$
- The average specific heat should be evaluated at the average temperature:  $(T_1 + T_2)/2$
- Another option is to find  $C_v$  and  $C_p$  at  $T_1$  and  $T_2$  (from Table A-2b) and take the average value of  $C_v$  and  $C_p$

### Relationship Between $C_p$ and $C_v$

- We have already seen that:  $h = u + RT$   
 $\Rightarrow dh = du + R dT \quad \Rightarrow \quad C_p dT = C_v dT + R dT \quad \Rightarrow \quad C_p = C_v + R$

### Specific Heat Ratio ( $k$ )

The specific heat ratio is an ideal-gas property defined as:  $k = \frac{C_p}{C_v}$

### **Internal Energy, Enthalpy, and Specific Heats of Solids and Liquids (Section 3.11)**

- Solids and liquids are approximated as incompressible substances (changes in density and specific volume are very small)
- It can be shown that for incompressible substances:  
 $C_p \approx C_v = C$

### Internal Energy Changes

$$du = C_v dT = C(T) dT \quad \rightarrow \quad \Delta u = u_2 - u_1 = \int_1^2 C(T) dT$$

If we are considering a small temperature range (where changes in  $C$  are small), we can use an average value of  $C$ :

$$\Delta u \cong C_{av} (T_2 - T_1)$$



Enthalpy Changes

$$h = u + Pv \quad \Leftrightarrow \quad dh = du + v dP + P dv$$

For incompressible substances, changes in volume are very small  $\Leftrightarrow dv \approx 0$ :

$$dh = du + v dP$$

Integrating:

$$\Delta h = \Delta u + v \Delta P \cong C_{av} \Delta T + v \Delta P$$

Special Case I (Solid)

The term  $v \Delta P$  is insignificant:

$$\Delta h = \Delta u = C_{av} \Delta T$$

Special Case II (Liquid with constant pressure process)

$$\Delta h = \Delta u = C_{av} \Delta T$$

Special Case III (Liquid with constant temperature process)

$$\Delta h = v \Delta P$$