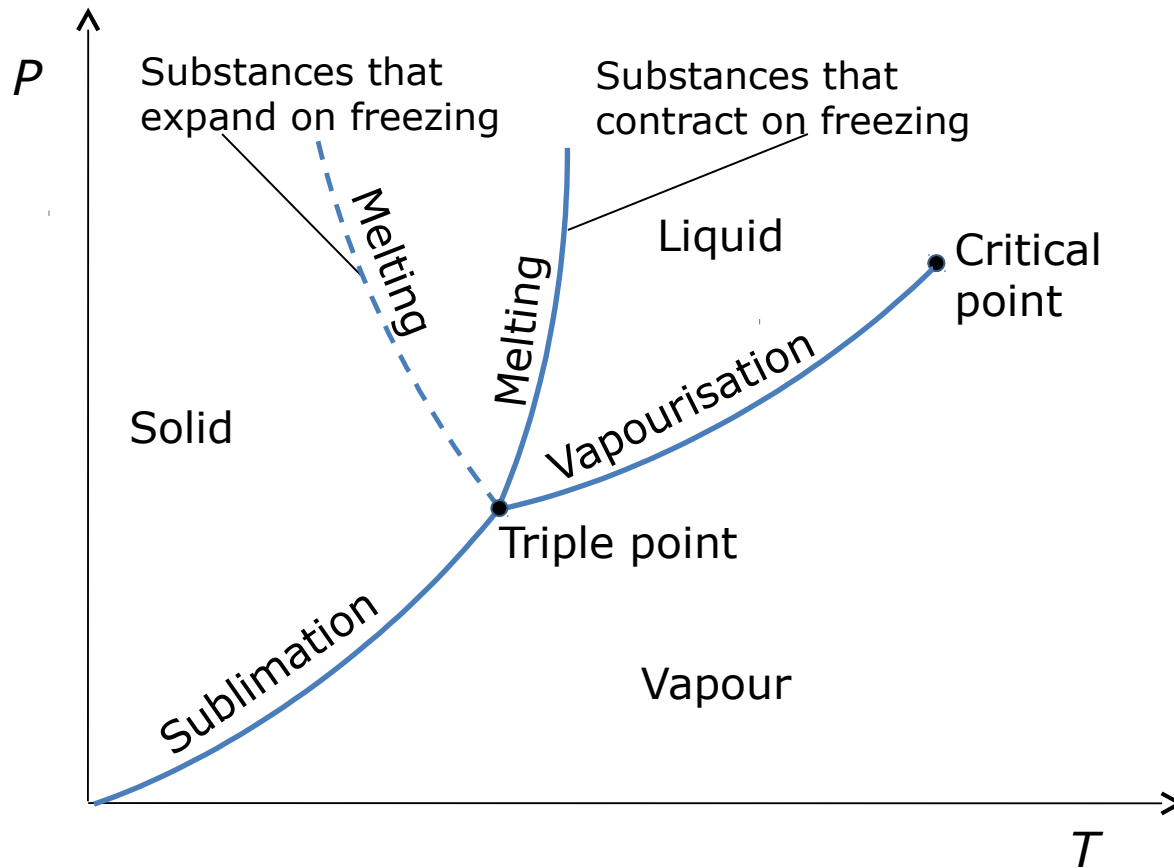


- Recap: Lecture 22: 04th March 2014, 0830-0930 hrs.
  - Helmholtz and Gibbs functions
  - The Maxwell relations
  - Ideal gas equation of state and other equations of state
  - Compressibility factor
  - Joule-Thomson coefficient and effect

# Properties of pure substances



P-T diagram of pure substances

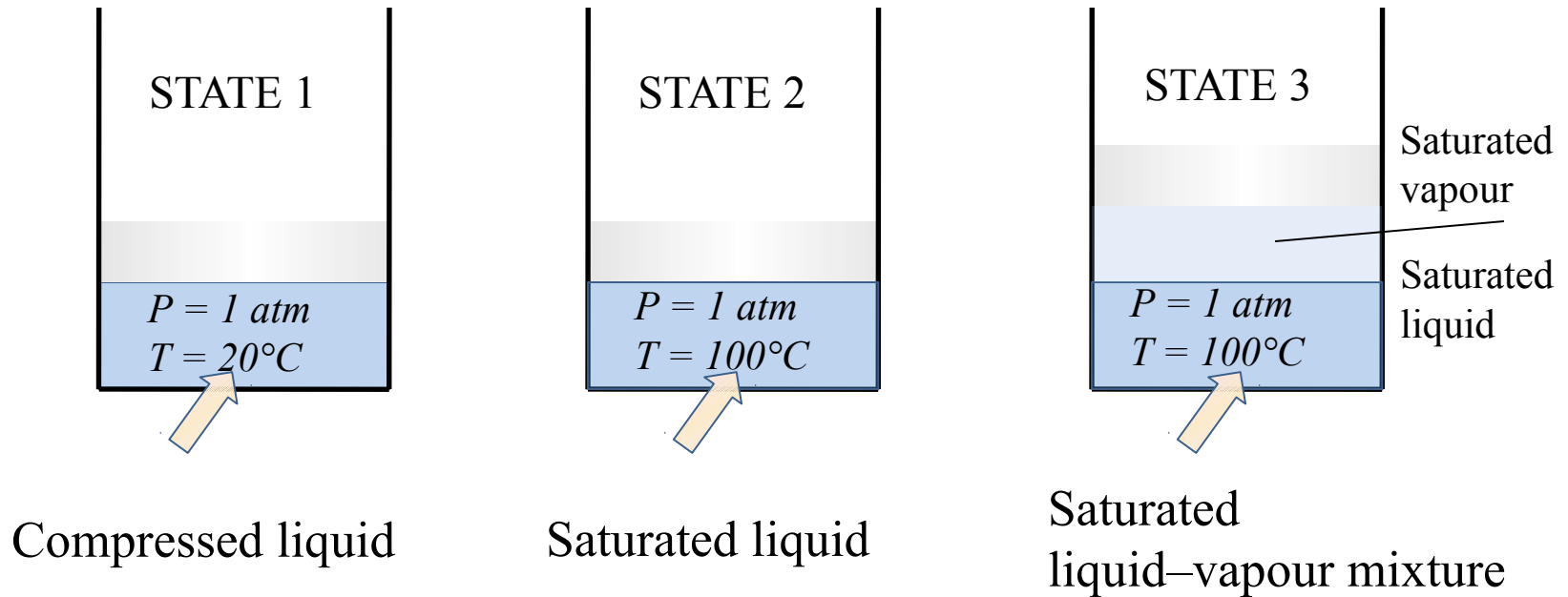
## **Properties of pure substances**

- A substance that has a fixed chemical composition throughout is called a pure substance. Eg. Water, nitrogen, helium etc.
- A mixture of two or more phases of a pure substance is still a pure substance as long as the chemical composition of all phases is the same. Eg. Mixture of ice and water.
- Properties of water (and its different phases) important part of analysis.

# Properties of pure substances

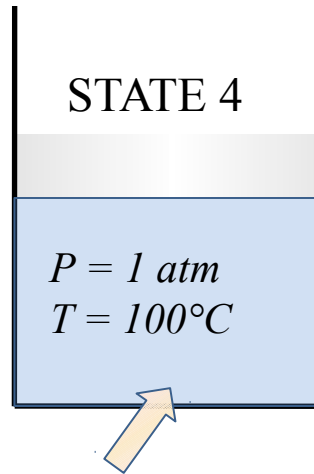
- When water (or any other liquid) exists in a state when it is not about to vapourize: **compressed liquid or subcooled liquid**. Eg. water at 20oC, 1atm.
- A liquid that is about to vaporize is called a **saturated liquid**.
- A vapour that is about to condense is called a **saturated vapour**.
- A vapour that is not about to condense (i.e., not a saturated vapour) is called a **superheated vapour**.

# Properties of pure substances

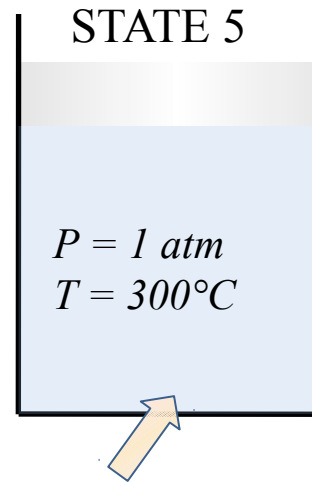


Different states of water

# Properties of pure substances



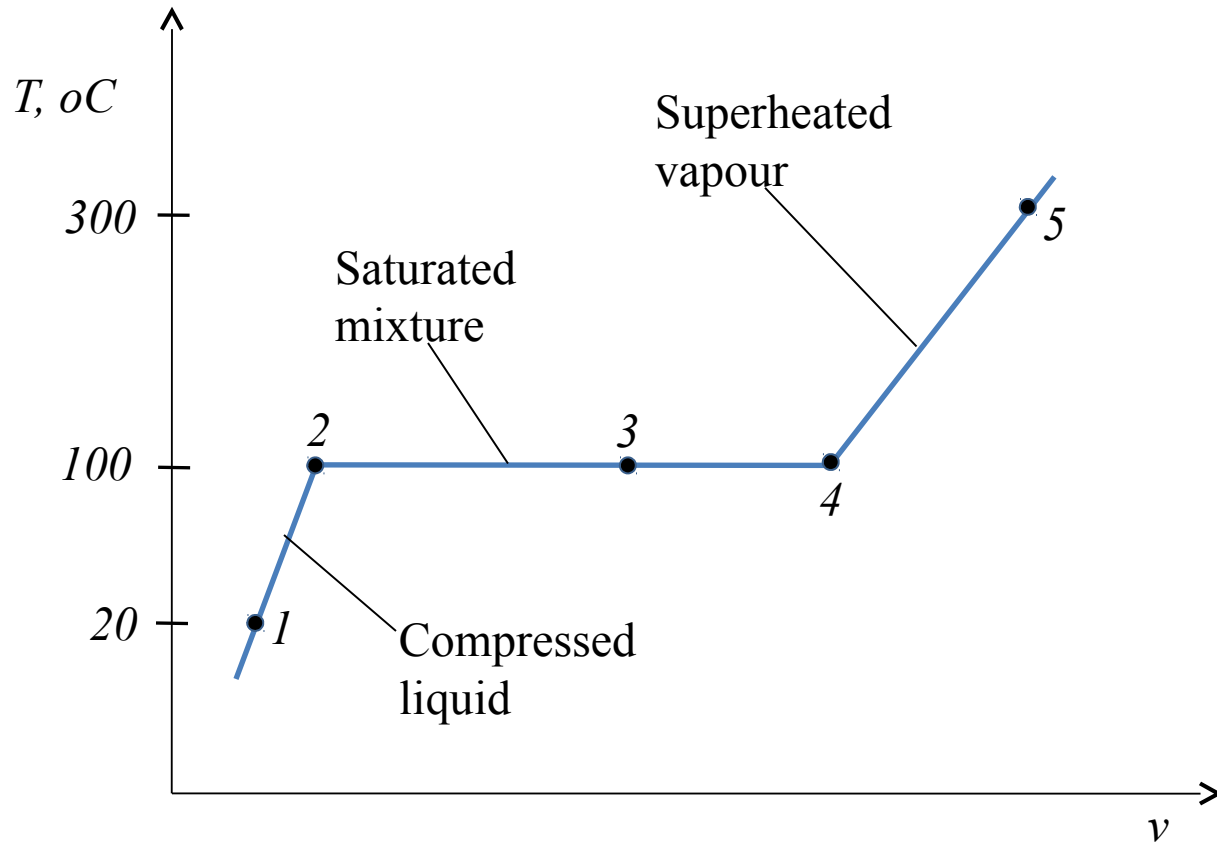
Saturated vapour



Superheated vapour

Different states of water

# Properties of pure substances



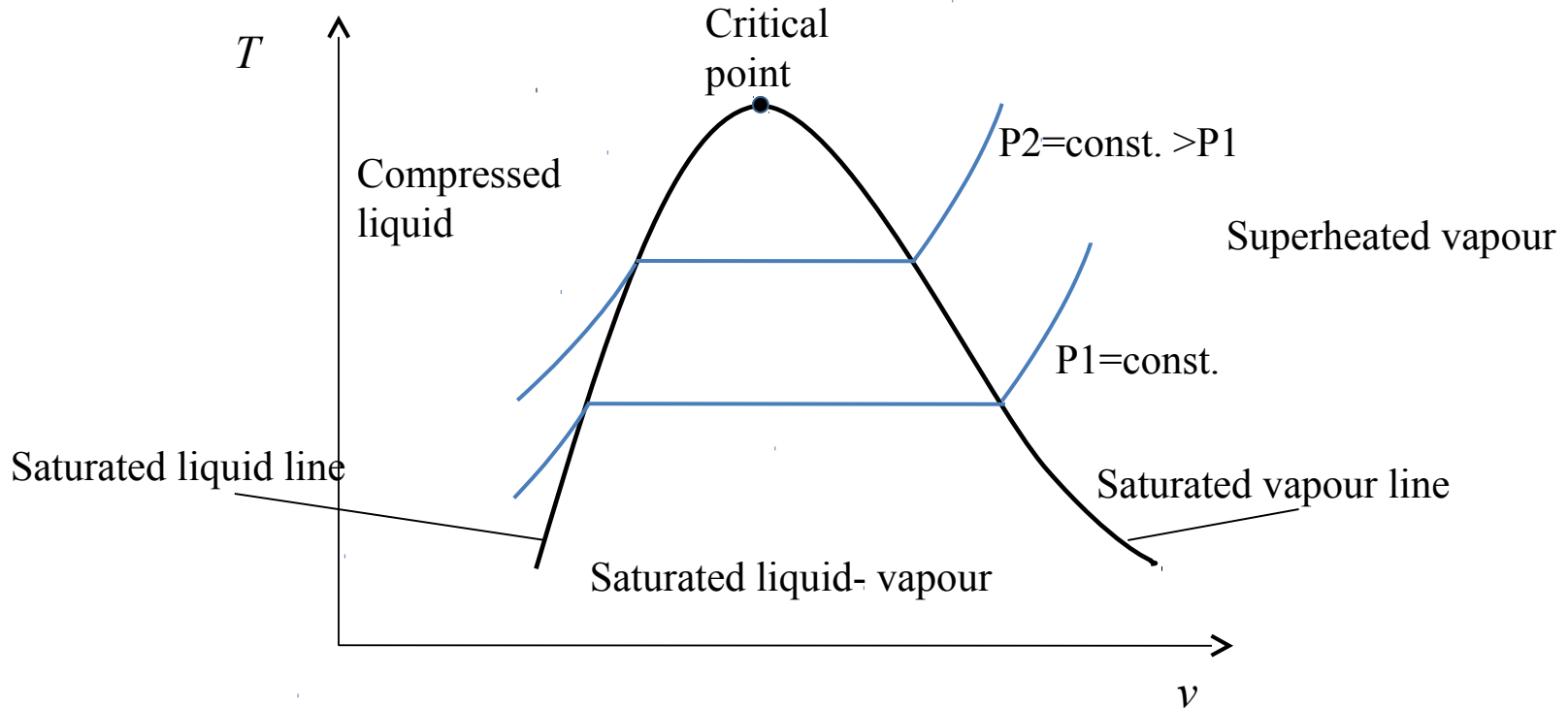
T-v diagram for the heating process of water at constant pressure ( $P=1\text{ atm.}$ )

## Properties of pure substances

- The temperature at which water starts boiling depends on the pressure; therefore, if the pressure is fixed, so is the boiling temperature.
- At a given pressure, the temperature at which a pure substance changes phase is called the **saturation temperature,  $T_{sat}$** .
- Likewise, at a given temperature, the pressure at which a pure substance changes phase is called the **saturation pressure,  $P_{sat}$** .

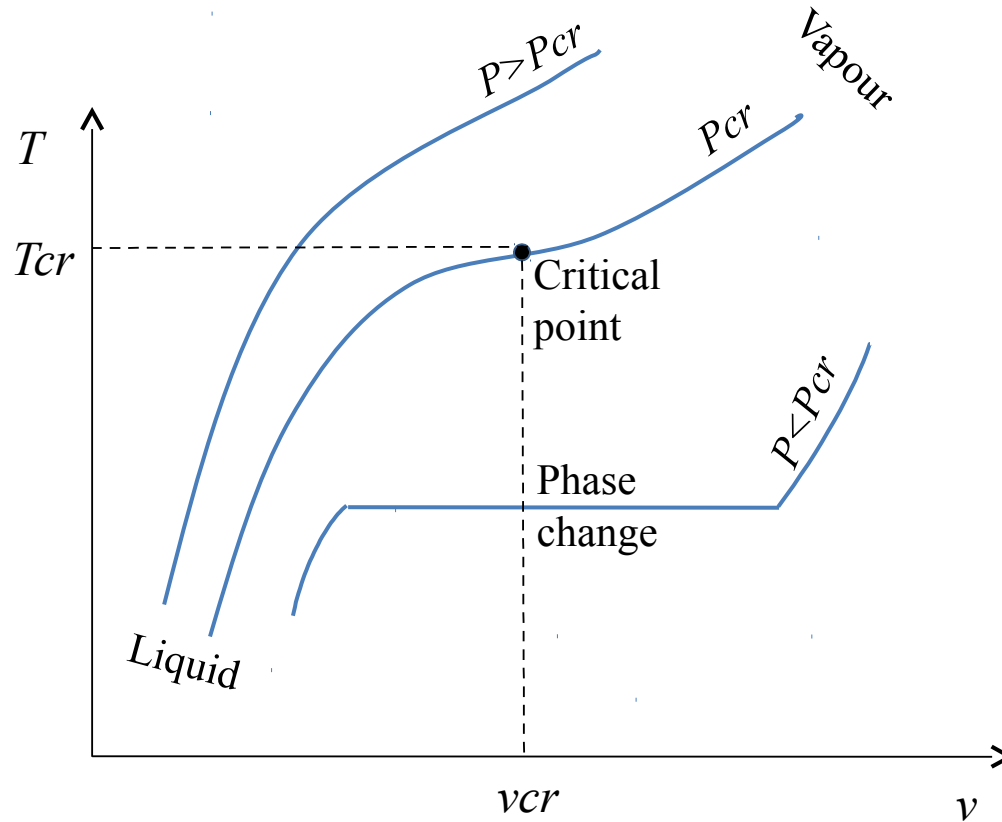


# Properties of pure substances



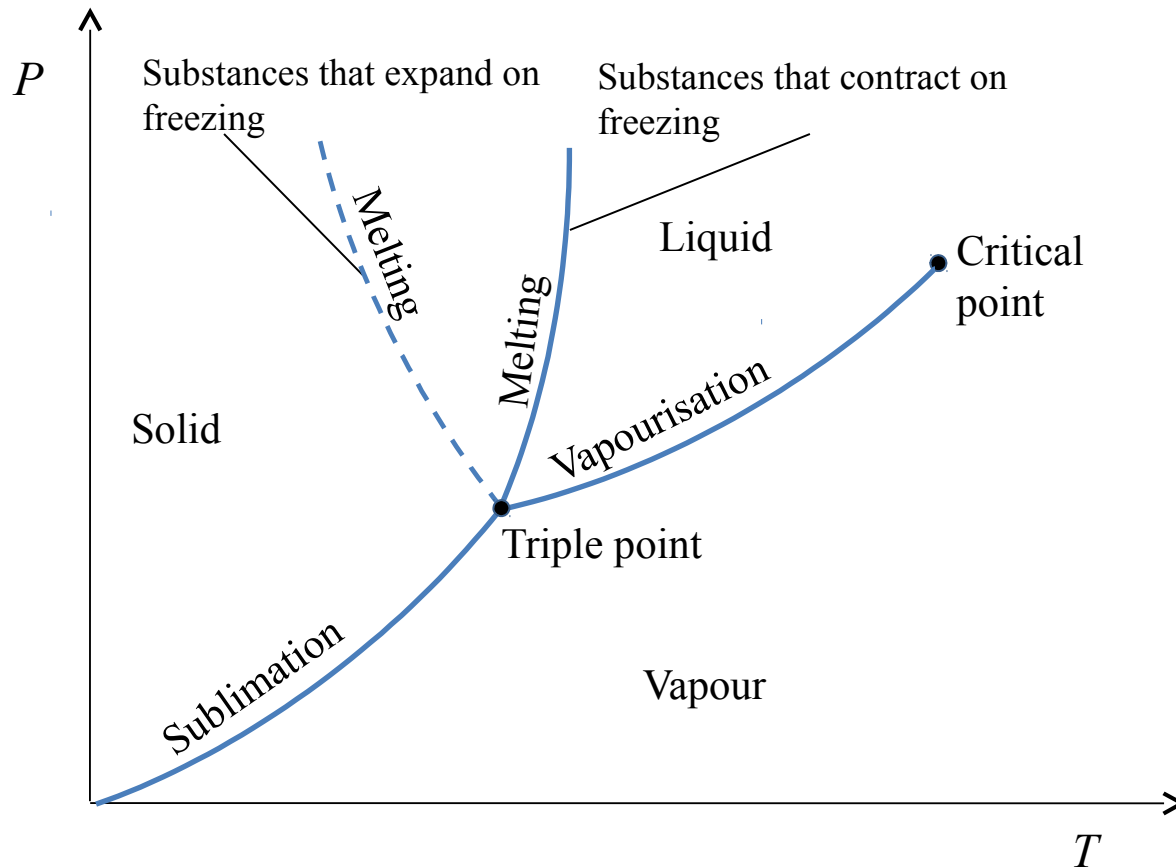
$T$ - $v$  diagram of a pure substance

# Properties of pure substances



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

# Properties of pure substances



P-T diagram of pure substances

# Property tables

- The relationships among thermodynamic properties are too complex to be expressed by simple equations.
- Properties are frequently presented in the form of tables.
- The subscript,  $f$ , denotes properties of a saturated liquid, and the subscript,  $g$ , denotes the properties of saturated vapour.
- $fg$ , denotes the difference between the saturated vapour and saturated liquid values of the same property.

# Property tables

- For eg.:
  - $h_f$  = specific enthalpy of saturated liquid
  - $h_g$  = specific enthalpy of saturated vapour
  - $h_{fg} = h_g - h_f$  Enthalpy of vapourisation or latent heat of vapourisation
- Quality,  $x$ , is defined as the ratio of the mass of vapour to the mass of liquid.
- Quality has a value ranging between 0 and 1.

# Property tables

- $x=0$   $\Rightarrow$  saturated liquid,  $x=1$   $\Rightarrow$  saturated vapour
- It can be shown that in general,

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

where,  $y$  can be:  $v$ ,  $u$ ,  $s$  or  $h$

- For eg:  $h_{avg} = h_f + x h_{fg}$
- Usually, the subscript  $avg$  is dropped for simplicity.
- Also,  $y_f \leq y_{avg} \leq y_g$

|                                    |   | Specific volume<br>$\text{m}^3/\text{kg}$ |                       |
|------------------------------------|---|---|-----------------------|
| Temp.<br>$^{\circ}\text{C}$<br>$T$ | Sat. press.<br>$\text{kPa}$<br>$P_{\text{sat}}$ | Sat. liquid<br>$\nu_f$                    | Sat. vapor<br>$\nu_g$ |
| 85                                 | 57.868  | 0.001032                                  | 2.8261                |
| 90                                 | 70.183  | 0.001036                                  | 2.3593                |
| 95                                 | 84.609  | 0.001040                                  | 1.9808                |

Specific temperature

Corresponding saturation pressure

Specific volume of saturated liquid

Specific volume of saturated vapor

Steam tables: saturation tables

# Superheated vapour

- Region to the right of the saturated vapour line and at temperatures above the critical point temperature.
- In the superheated region (single phase), pressure and temperature are no longer dependant properties.
- Compared to saturated vapour, superheated vapour is characterised by:
  - Lower pressures ( $P < P_{sat}$  at a given  $T$ )
  - Higher temperatures ( $T > T_{sat}$  at a given  $P$ )
  - Higher specific volume/enthalpy/internal energy ( $v > v_g$ ,  $h > h_g$ ,  $u > u_g$  at a given  $P$  or  $T$ )



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

Steam tables: superheated vapour

# Composition of a gas mixture

- Consider a gas mixture of  $k$  components.
- Let  $m_m$  is the mass of the mixture and  $N_m$  is sum of the mole numbers.

$$m_m = \sum_{i=1}^k m_i \quad \text{and} \quad N_m = \sum_{i=1}^k N_i$$

- Mass fraction,  $mf$ , is the ratio of the mass of a component to the mass of the mixture
- Mole fraction,  $Y$ , is the ratio of the mole number of a component to the mole number of the mixture.

$$mf_i = m_i / m_m \quad \text{and} \quad y_i = N_i / N_m$$

# Composition of a gas mixture

- The mass of a substance of mole number  $N$  and molar mass  $M$  is  $m = NM$
- The average molar mass and gas constant:

$$M_m = \frac{m_m}{N_m} = \frac{\sum m_i}{N_m} = \frac{\sum N_i M_i}{N_m} = \sum_{i=1}^k y_i M_i$$

$$R_m = \frac{R_u}{M_m}$$

- Mass and mole fractions of a mixture are related by

$$mf_i = \frac{m_i}{m_m} = \frac{N_i M_i}{N_m M_m} = y_i \frac{M_i}{M_m}$$

# P-v-T behaviour of gas mixtures

- Ideal gas equation of state with compressibility factor for real gases.
- The prediction of the P-v-T behaviour of gas mixtures based on two laws: Dalton's law of additive pressures and the Amagat's law of additive volumes.
- **Dalton's law of additive pressures:** The pressure of a gas mixture is equal to the sum of the pressures each gas would exert if it existed alone at the mixture temperature and volume.

# P-v-T behaviour of gas mixtures

- **Amagat's law of additive volumes:** The volume of a gas mixture is equal to the sum of the volumes each gas would occupy if it existed alone at the mixture temperature and pressure.
- Dalton's and Amagat's laws hold exactly for ideal-gas mixtures, but only approximately for real-gas mixtures.
- For ideal gases, these two laws are identical and give identical results.

# P-v-T behaviour of gas mixtures

- Dalton's and Amagat's laws can be expressed as follows:

Dalton's law : 
$$P_m = \sum_{i=1}^k P_i(T_m, V_m)$$



Amagat's law : 
$$V_m = \sum_{i=1}^k V_i(T_m, V_m)$$

- The above are exact for ideal gases, but approximate for real gases.
- $P_i$  is called the component pressure and  $V_i$  is called the component volume.

# Ideal gas mixtures

- For ideal gases,  $P_i$  and  $V_i$  can be related to the mole fraction  $y_i$  by:

$$\frac{P_i(T_m, V_m)}{P_m} = \frac{N_i R_u T_m / V_m}{N_m R_u T_m / V_m} = \frac{N_i}{N_m} = y_i$$

$$\frac{V_i(T_m, V_m)}{V_m} = \frac{N_i R_u T_m / V_m}{N_m R_u T_m / V_m} = \frac{N_i}{N_m} = y_i$$

$$\text{Therefore, } \frac{P_i}{P_m} = \frac{V_i}{V_m} = \frac{N_i}{N_m} = y_i$$

# Ideal gas mixtures

- The quantity  $y_i P_m$  is called the partial pressure and the quantity  $y_i V_m$  is called the partial volume.
- For an ideal-gas mixture, the mole fraction, the pressure fraction, and the volume fraction of a component are identical.



# Real gas mixtures

- Dalton's law of additive pressures and Amagat's law of additive volumes can also be used for real gases, with some approximations.
- We either use some of the advanced equations of state (like the Beattie–Bridgeman, Benedict–Webb–Rubin etc.)
- The other way is to use the compressibility factor:  
$$PV = ZNR_uT$$

# Real gas mixtures

- The compressibility factor of the mixture,  $Z_m$ , can be expressed in terms of that of the constituents:

$$Z_m = \sum_{i=1}^k y_i Z_i$$

- Here,  $Z_i$  can be determined either at  $T_m$  and  $V_m$  (Dalton's law) or at  $T_m$  and  $P_m$  (Amagat's law) for each individual gas.
- It is however not necessary that both these methods give the same result

# Properties of gas mixtures

- To evaluate the extensive properties of a non-reacting ideal or real gas mixture, we add the contributions of each component.
- The internal energy, enthalpy and entropy can be expressed as:

$$\begin{aligned}U_m &= \sum_{i=1}^k U_i = \sum_{i=1}^k m_i u_i \\H_m &= \sum_{i=1}^k H_i = \sum_{i=1}^k m_i h_i \\S_m &= \sum_{i=1}^k S_i = \sum_{i=1}^k m_i s_i\end{aligned}$$

# Properties of gas mixtures

- The internal energy, enthalpy, and entropy of a mixture *per unit mass of the mixture can be determined by dividing the equations above by the mass of the mixture:*

$$u_m = \sum_{i=1}^k mf_i u_i \quad \text{and} \quad h_m = \sum_{i=1}^k mf_i h_i \quad \text{in (kJ/kg)}$$

$$s_m = \sum_{i=1}^k mf_i s_i \quad (\text{kJ/kg.K})$$



$$\text{Also, } c_{v,m} = \sum_{i=1}^k mf_i c_{v,i} \quad (\text{kJ/kg.K}) \quad \text{and} \quad c_{p,m} = \sum_{i=1}^k mf_i c_{p,i}$$