

Properties of Pure Substances & Equations of State

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ME 203: Engineering Thermodynamics



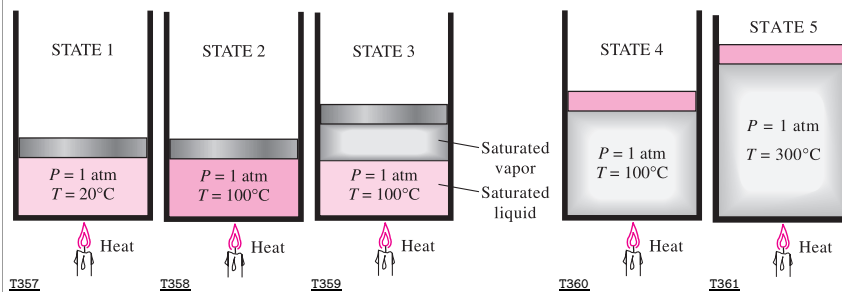
Pure Substance

- A **pure substance** is one that has a homogeneous and invariable chemical composition. It may exist in more than one phase, but the chemical composition is the same in all phases.
 - Liquid water, a mixture of liquid water and water vapour (steam), and a mixture of ice and liquid water are all pure substances; every phase has the same chemical composition.
 - A mixture of liquid air and gaseous air is not a pure substance as the composition of the liquid phase is different from that of the vapour phase.
- Sometimes a mixture of gases, such as air, is considered a pure substance as long as there is no change of phase. Strictly speaking, this is not true.



Phase Equilibrium in a Pure Substance

Vapour-Liquid-Solid Phase Equilibrium



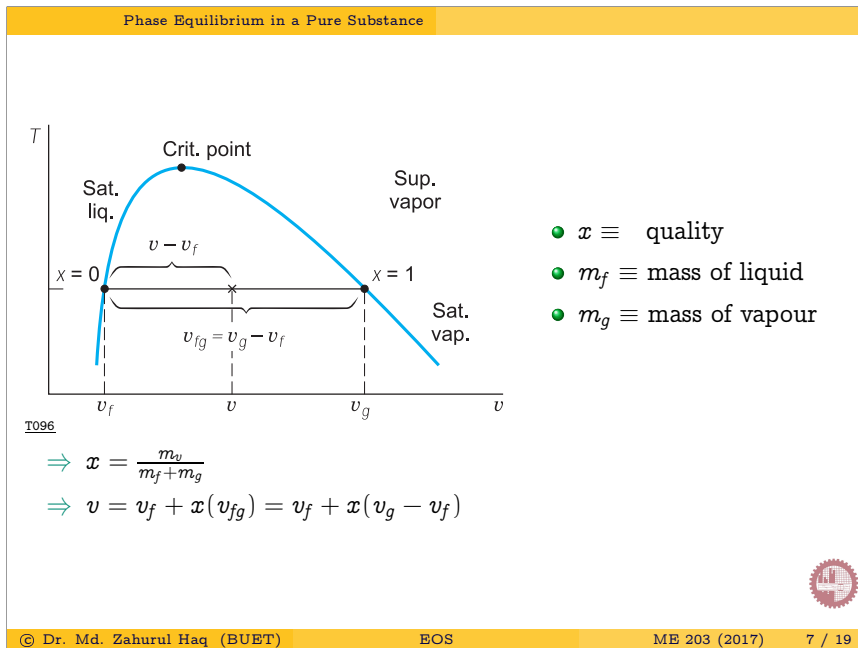
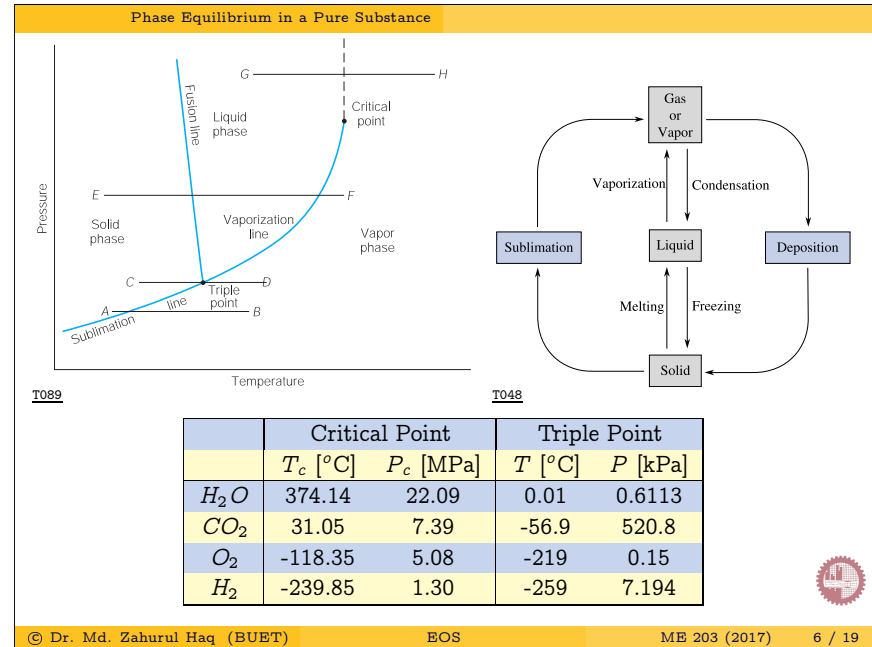
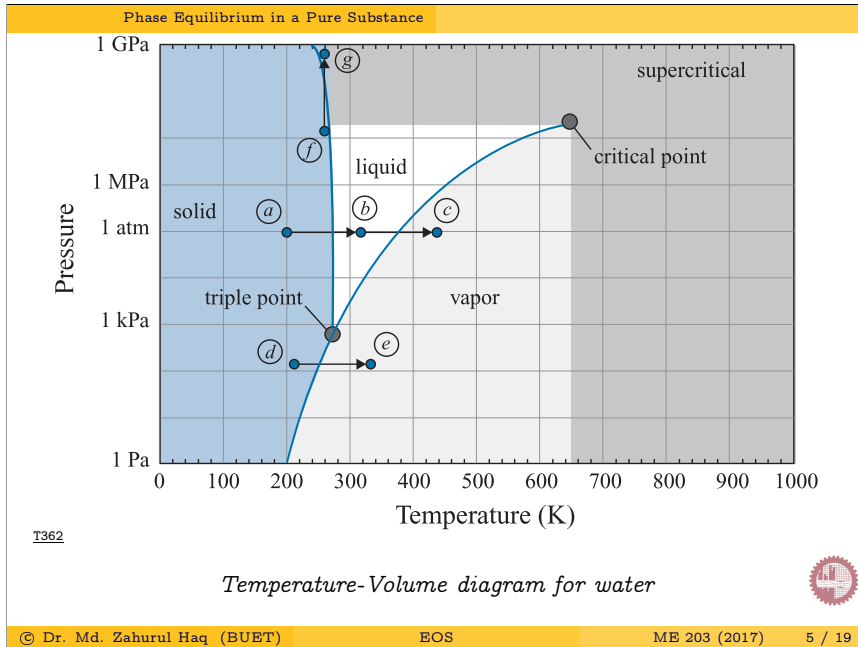
- 1 Compressed ($P > P_{sat}(T)$) or subcooled liquid ($T < T_{sat}(P)$).
- 2 Saturated liquid ($T = T_{sat}(P)$).
- 3 Saturated liquid-vapour mixture ($T = T_{sat}(P)$).
- 4 Saturated vapour ($T = T_{sat}(P)$).
- 5 Superheated vapour ($T > T_{sat}(P)$).



Phase Equilibrium in a Pure Substance

- **Saturation temperature**, T_{sat} is the temperature at which vaporization takes place at a given pressure. This pressure is called the **saturation pressure**, P_{sat} for the given temperature.
- If a substance exists as liquid at T_{sat} and P_{sat} is called a **saturated liquid**.
- If the temperature of the liquid is lower than the saturation temperature for the existing pressure, it is called either a **sub-cooled liquid** (implying $T < T_{sat}(P)$) or a **compressed liquid** (implying $P > P_{sat}(P)$).
- When a substance exists as part liquid and part vapour at the saturation temperature, its **quality**, x is defined as the ratio of the mass of vapour to the total mass.
- If a substance exists as vapour at T_{sat} , it is called **saturated vapour**. When the vapour is at $T > T_{sat}$, it is said to exist as **superheated vapour**.





Phase Equilibrium in a Pure Substance

Phase Equilibrium: Gibb's Phase Rule

Gibb's Phase Rule

The number of degrees of freedom within a heterogeneous mixture of pure substances is given by Gibb's phase rule as

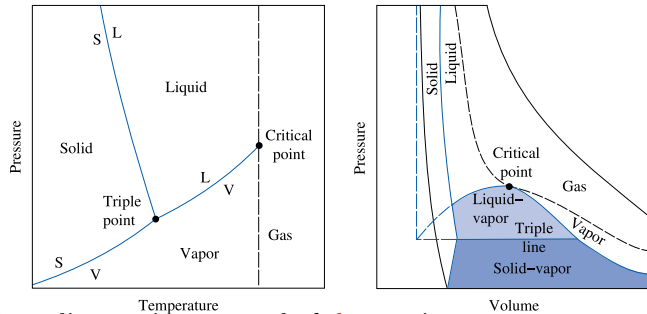
$$f = C - P + 2$$

$f \equiv$ number of degrees of freedom
 $C \equiv$ number of components (pure substances) in the mixture
 $P \equiv$ number of phases

- A homogeneous ($P = 1$) pure substance ($C = 1$) requires $f = 1 - 1 + 2 = 2$ intensive properties to fix its state.
- A homogeneous ($P = 1$) mixture of two pure substances ($C = 2$) requires $f = 2 - 1 + 2 = 3$ intensive properties to fix its state.
- A two-phase ($P = 2$) pure substance ($C = 1$) $\Rightarrow f = 1 - 2 + 2 = 1$: Each phase requires one intensive property to fix its state & one intensive property can be varied independently.

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Thermodynamic Surfaces

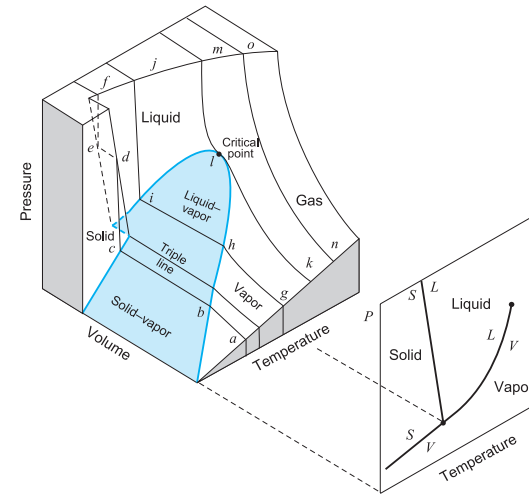


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P-T phase diagram is composed of **three** unique curves:

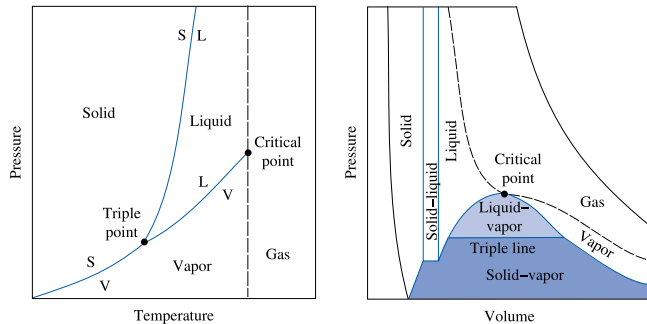
- ➊ **Fusion line** ↔ region of 2-phase solid-liquid equilibrium,
- ➋ **Vaporization line** ↔ region of 2-phase liquid-vapour equilibrium,
- ➌ **Sublimation line** ↔ region of 2-phase solid-vapour equilibrium.

These three lines intersect at one point, called the **triple point**, which is the only point where all three phases can be in equilibrium



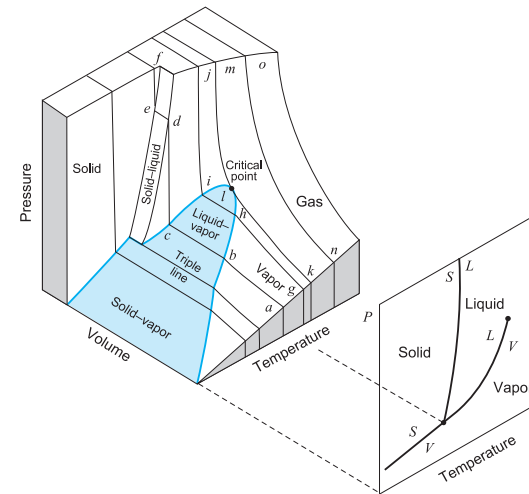
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P-v-T diagram for a substance that expands on freezing (e.g. water)



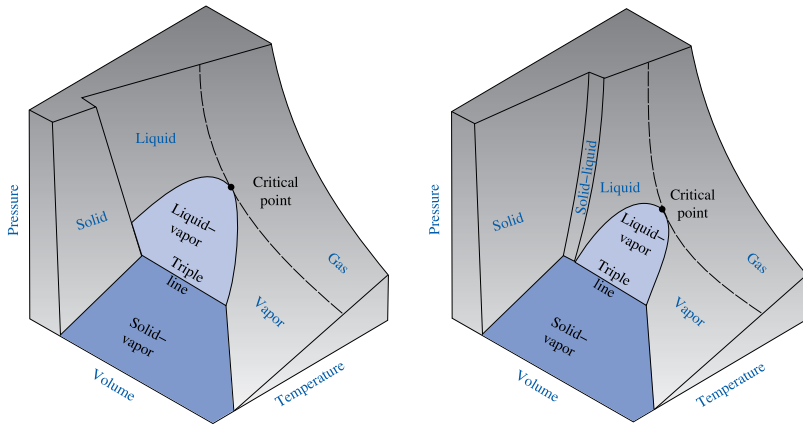
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- At **triple point** of a pure substance, $C = 1$, $P = 3$, and the number of degrees of freedom are $f = 1 - 3 + 2 = 0$; i.e., there is no flexibility in the thermodynamic state & none of the properties can be varied & still keep the system at the triple point.
- At **critical point**, the densities of the liquid & the vapour phases become equal and, consequently, where the physical interface between the liquid & the vapour disappears.



T092

P-v-T diagram for a substance that contracts on freezing (e.g. CO₂)



T046

T047

Expands on freezing (e.g. H₂O)

Contracts on freezing (e.g. CO₂)

Equations of State (EOS)

Equations of State (EOS) have the following form:

$$f(P, v, T) = 0$$

Ideal-gas EOS:

$$PV = nR_u T = \left[\frac{m}{M} \right] R_u T = m \left[\frac{R_u}{M} \right] T = mRT \quad n = \frac{m}{M} \quad R = \frac{R_u}{M}$$

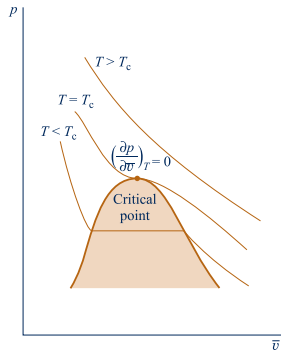
$$PV = nR_u T \leftrightarrow PV = mRT \leftrightarrow P = \rho RT$$

- | | |
|---|---------------------------------------|
| P ≡ pressure [kPa] | T ≡ temperature [K] |
| V ≡ volume [m ³] | v ≡ sp. volume [m ³ /kg] |
| R_u ≡ universal gas constant, 8.314 kJ/kmol.K | ρ ≡ density [kg/m ³] |
| R ≡ specific gas constant, [kJ/kg.K] | n ≡ no. of moles |
| M ≡ molecular weight [kg/kmol] | m ≡ mass [kg] |

van der Waals' Equation

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

- b ⇒ account for the volume occupied by gas molecules
- a ⇒ account for intermolecular forces of attraction.

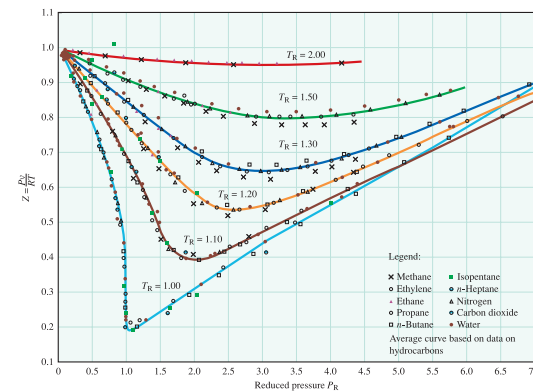


At critical point: $\left(\frac{\partial P}{\partial v} \right)_T = \left(\frac{\partial^2 P}{\partial v^2} \right)_T = 0$
 $\Rightarrow v_c = 3b, a = \frac{27}{64} \frac{R^2 T_c^2}{P_c}, b = \frac{RT_c}{8P_c}$
 $\Rightarrow Z_c = \frac{P_c v_c}{RT_c} = \frac{3}{8} = 0.375$

T097

Generalized Compressibility Chart

- Departure from ideal gas $\rightsquigarrow Z \equiv \frac{Pv}{RT}$, for ideal gas, $Z = 1$
- Reduced properties, $P_R \equiv \frac{P}{P_c}$ & $T_R \equiv \frac{T}{T_c}$



T094

Other Equations of State

● Viral Equation

$$Z = \frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \dots$$

● Redlich-Kwong Equation

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)\sqrt{T}}$$

$$a = 0.42748 \frac{R^2 T_c^{2.5}}{P_c} \quad b = 0.08664 \frac{RT_c}{P_c}$$

● Beattie-Bridgeman Equation

$$P = \frac{RT}{v^2} (1-e)(v+B) - \frac{A}{v^2}$$

$$\text{where, } A = A_0 \left(1 - \frac{a}{v}\right), B = B_0 \left(1 - \frac{b}{v}\right), e = \frac{c}{vT^3}$$



▷ Estimate specific volume of Water at 20.0 MPa & 520°C

- Ideal Gas Law: $R = \frac{R_u}{M} = 8314/18 = 461.89 \text{ J/kg-K}$

$$v_{ideal} = \frac{RT}{P} = \frac{(461.89)(273 + 520)}{20000000} = \underline{0.0183} \text{ m}^3/\text{kg}$$

- Compressibility Chart: $P_R = \frac{20}{22.09} = 0.905$, $T_R = \frac{793}{647.3} = 1.23$
From chart: $Z = 0.83$.

$$v = Zv_{ideal} = (0.83)(0.183) = \underline{0.0152} \text{ m}^3/\text{kg}$$

- Tabulated value, based on experimental data: $\mapsto v = \underline{0.01551} \text{ m}^3/\text{kg}$



▷ Estimate pressure exerted by 3.7 kg CO in a 0.030 m³ container at 215 K

- ① Using ideal gas law:

$$\Rightarrow M = 12 + 16 = 28 \text{ kg/kmol.}$$

$$\Rightarrow R = \frac{R_u}{M} = 8314/28 = 296.92 \text{ J/kg-K}$$

$$\Rightarrow P = \frac{mRT}{V} = \frac{(3\text{kg})(296.92 \frac{\text{J}}{\text{kg}})(215\text{K})}{0.03 \text{ m}^3} \left| \frac{\text{Nm}}{\text{J}} \right| \left| \frac{1\text{bar}}{10^5 \frac{\text{N}}{\text{m}^2}} \right| = \underline{78.7} \text{ bar.}$$

- ② Using van der Waals' Eq.: $P = \underline{66.9}$ bar.
given, $a = 1.463 \text{ bar}\cdot\text{m}^6/\text{kmol}^2$ & $b = 0.0394 \text{ m}^3/\text{kmol}$

- ③ Using Redlich-Kwong Eq.: $P = \underline{69.2}$ bar.
given, $a = 17.26 \text{ bar}\cdot\text{m}^6\cdot\text{K}^{1/2}/\text{kmol}^2$ & $b = 0.02743 \text{ m}^3/\text{kmol}$

- ④ NIST Table $\rightarrow P = \underline{69.13}$ bar.

