Properties of Pure Substances & Equations of State

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ME 6101: Classical Thermodynamics
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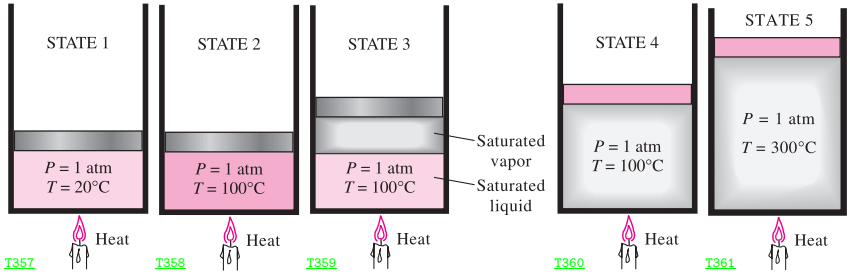
Pure Substance

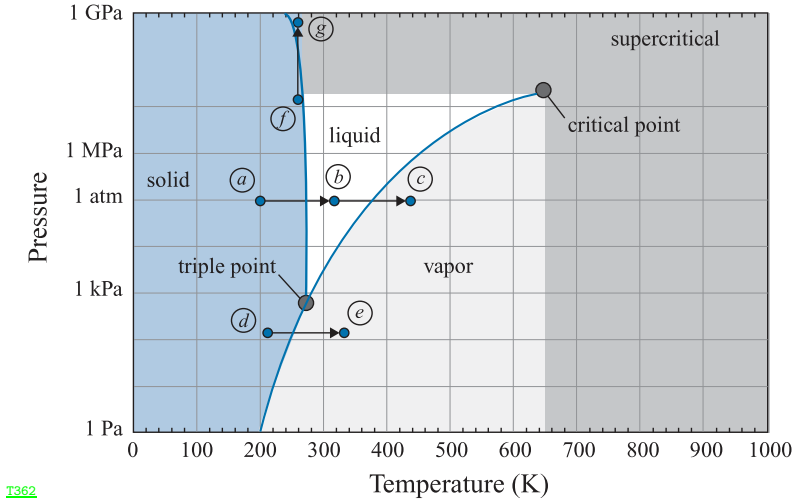
- A **pure substance** is one that has a homogeneous and invariable chemical composition. It may exist in more than one phase, but the chemical composition is the same in all phases.
  - Liquid water, a mixture of liquid water and water vapour (steam), and a mixture of ice and liquid water are all pure 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.

Vapour-Liquid-Solid Phase Equilibrium



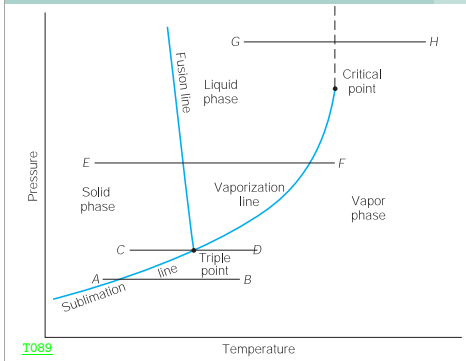
1. Compressed ($P > P_{sat}(T)$) or subcooled liquid ($T < T_{sat}(P)$).
2. Saturated liquid ($T = T_{sat}(P)$).
3. Saturated liquid-vapour mixture ($T = T_{sat}(P)$).
4. Saturated vapour ($T = T_{sat}(P)$).
5. Superheated vapour ($T > T_{sat}(P)$).

- **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**.

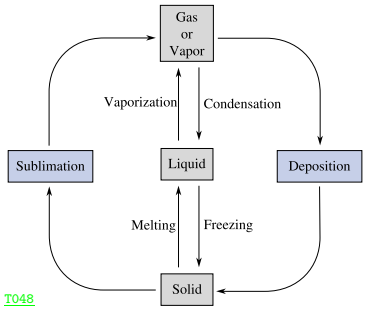


T362

Temperature-Pressure diagram for water

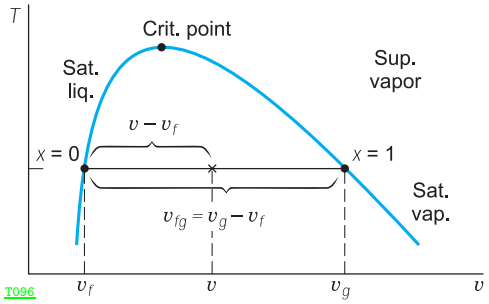


T089



T048

	Critical Point		Triple Point	
	T_c [°C]	P_c [MPa]	T [°C]	P [kPa]
H_2O	374.14	22.09	0.01	0.6113
CO_2	31.05	7.39	-56.9	520.8
O_2	-118.35	5.08	-219	0.15
H_2	-239.85	1.30	-259	7.194



T096

- $x \equiv$ quality
- $m_f \equiv$ mass of liquid
- $m_g \equiv$ mass of vapour

$\Rightarrow x = \frac{m_v}{m_f + m_g}$

$\Rightarrow v = v_f + x(v_{fg}) = v_f + x(v_g - v_f)$

Phase Equilibrium: Gibb's Phase Rule

Gibb's Phase Rule

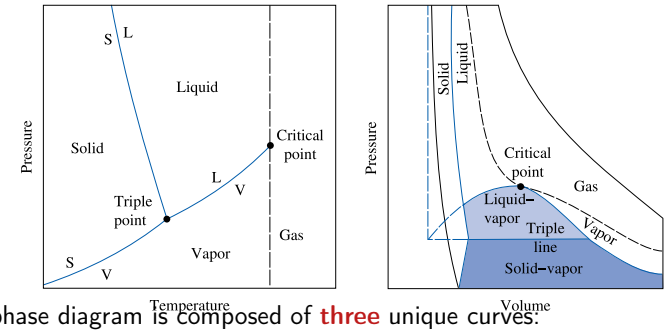
The number of degrees of freedom within a heterogeneous mixture of pure substances is given by Gibb's phase rule as

$$f = C - P + 2$$

$f \equiv$ 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.

Thermodynamic Surfaces

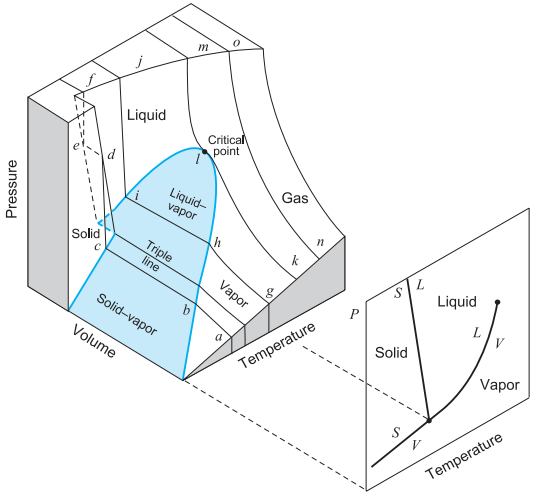


T017

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

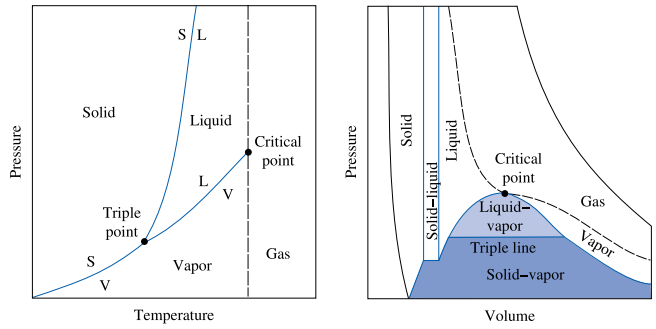
1. **Fusion line** ⇝ region of 2-phase solid-liquid equilibrium,
2. **Vaporization line** ⇝ region of 2-phase liquid-vapour equilibrium,
3. **Sublimation line** ⇝ region of 2-phase solid-vapour equilibrium.

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



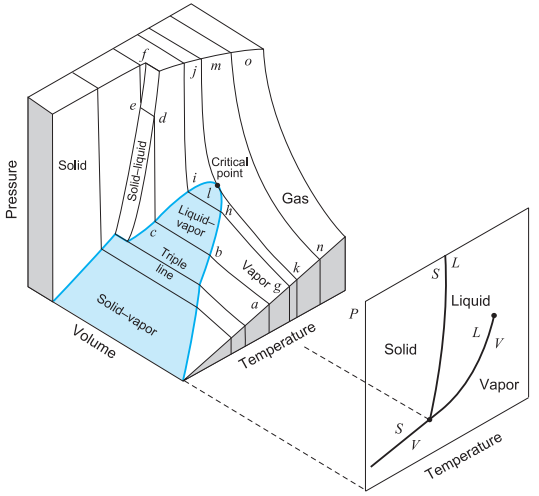
T090

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



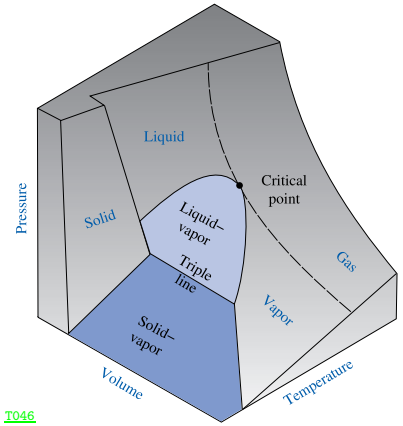
T018

- 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.



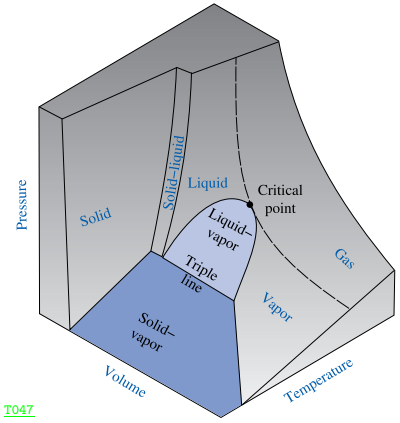
T092

P-v-T diagram for a substance that contracts on freezing (e.g. CO_2)



T046

Expands on freezing (e.g. H_2O)



T047

Contracts on freezing (e.g. CO_2)

Equations of State (EOS)

Equations of State (EOS) have the following form:

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

Ideal-gas EOS:

$$PV = nR_uT = \left[\frac{m}{M}\right]R_uT = m\left[\frac{R_u}{M}\right]T = mRT \qquad n = \frac{m}{M} \qquad R = \frac{R_u}{M}$$

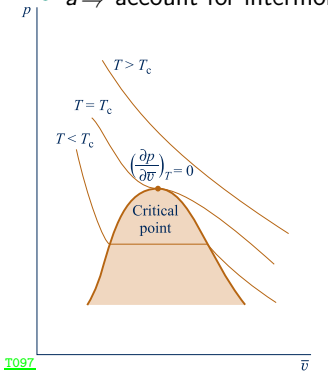
$$PV = nR_uT \longleftrightarrow PV = mRT \longleftrightarrow P = \rho RT$$

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

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

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



T097

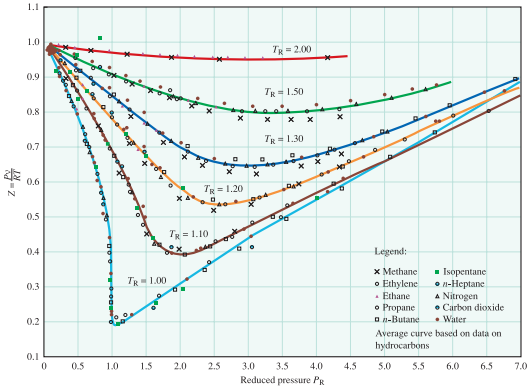
At critical point: $\left(\frac{\partial P}{\partial v}\right)_T = \left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0$

$\Rightarrow v_c = 3b,\ a = \frac{27}{64}\frac{R^2T_c^2}{P_c},\ b = \frac{RT_c}{8P_c}$

$\rightrightarrows Z_c = \frac{P_cv_c}{RT_c} = \frac{3}{8} = 0.375$

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

Wark Ex. 4.6: ▷ Sp. volume of Water at 20.0 MPa & 520°C.

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

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

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

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

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

Other Equations of State

- **Viral Equation**

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

- **Redlich-Kwong Equation**

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

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

- **Beattie-Bridgeman Equation**

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

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

Wark Ex. 11.1: ▷ Estimate pressure exerted by 3.7 kg CO in a 0.030 m^3 container at 215 K.

1. Using ideal gas law:

⇒ $M = 12 + 16 = 28$ kg/kmol.

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

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

2. Using van der Waals' Eq.: $P = \underline{66.9}$ bar.
   given, $a = 1.463\ bar.m^6/kmol^2$ & $b = 0.0394\ m^3/kmol$
3. Using Redlich-Kwong Eq.: $P = \underline{69.2}$ bar.
   given, $a = 17.26\ bar.m^6.K^{1/2}/kmol^2$ & $b = 0.02743\ m^3/kmol$
4. NIST Table ⟶ $P = \underline{69.13}$ bar.