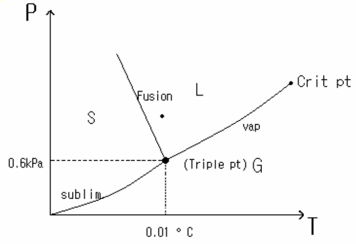
Chapter 3. Properties of Pure Substances and Equations of state

- Properties of Pure Substance 계속...

Phase diagram

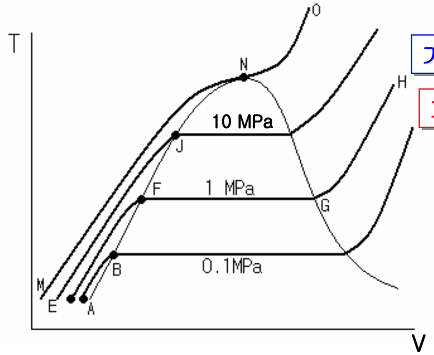
Along these lines, two phases are in equilibrium



p-T diagram for water

- Triple pt at 0.01 °C, 0.6113 kPa (where 10^5 Pa = 1 atm and 0.006 x 10^5 Pa)
  - the state in which all 3 phases may be present in equilibrium.
- Sublimation line.......(both Vapor & Sol exist in equilibrium)
- Vaporization line.... (both Vapor & Liquid exist in equilibrium)
- Fusion line ....(both Solid & Liquid exist in equilibrium)
- Beyond Critical point, no distinct changes from L to V.

- Now consider a process at p = 1 Mpa (10 atm) and T_0.

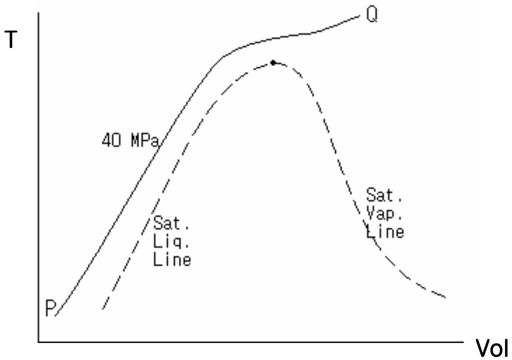


기압의 10배

기압

T_B = 99.6°C
T_F = 179.9°C (Sat. Liquid)
Sat. vapor state (G)
Superheated vapor (G–H)

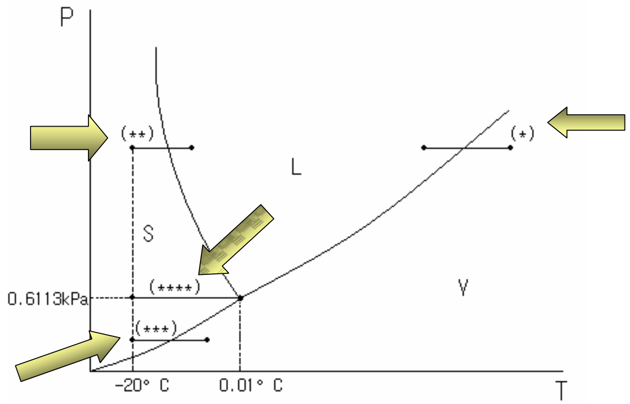
- If p ~ 40 Mpa



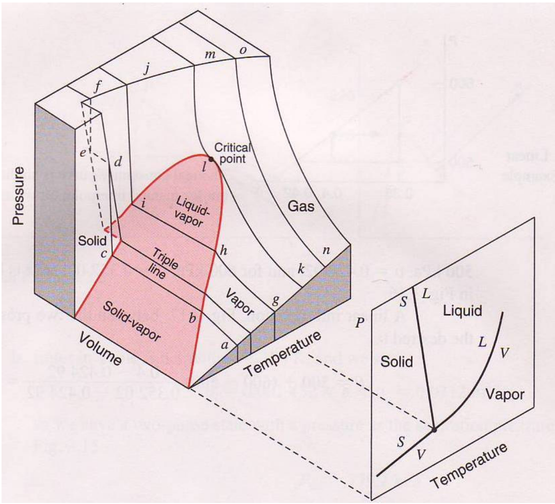
If p > p_{crit}, for water at 40MPa, 20°C is heated in constant p process in a cylinder as shown in (*), there will never be 2 phases present and state (ii) will never exist.

→ only superheated vapor exists at p > p_{crit}.

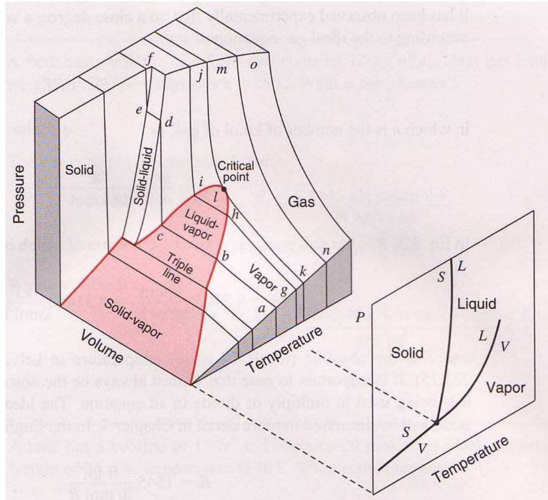
- Describe all 4 processes on P–T curve (Constant–p processes)



These are the lines of phase equilibrium.



P-Vol.-T surface for a substance that expands on freezing
(such as WATER!)



P-Vol.-T surface for a substance that contracts on freezing

- Independent properties of a pure substance

  2-independent properties define the state of a simple compressible pure substance.

- EOS for the vapor phase of a simple compressible substance

  From experiment we find,

$$p\bar{v} = \bar{R}T \quad \text{where} \quad \bar{R} = 8.3144\frac{kJ}{kmol.K} \quad \text{(Univ. Gas Cont.)}$$

Or $R = \dfrac{\bar{R}}{M}$ where M is the molecular weight.

- EOS on a unit mass basis,

$$pv = RT \qquad \text{---------- (i)}$$

R is a constant for a particular gas

- (i) is called Ideal gas EOS.

  At very low density, all gases and vapors approach ideal behavior.

$$\frac{p_1 v_1}{T_1} = \frac{p_2 v_2}{T_2} \qquad \text{---------- (ii)}$$

"Boyle's and Charles law"

- Compressibility Factor, *Z* (압축성인자)

$$Z = \frac{p\bar{v}}{RT} = \frac{pv}{RT}$$

Z → 1 for ideal gas

$$Z = f(p,T)\ and\ f(T,v)\ and\ f(p,v)$$

→ 대단히 복잡한 함수이며 실험에 의하여 알려진다.

- Examples of Real Gas 의 상태 방정식

[1] Virial EOS

$$\frac{pv}{RT} = 1 + \overbrace{\underbrace{\frac{B(T)}{v} + \frac{C(T)}{v^2}}_{0\,if\ ideal}}^{concentration\,terms} + \ldots$$

[2] Van der Waals EOS

$$(p + \frac{a}{\bar{v}^2})(\bar{v} - b) = \bar{R}T$$

a,b 는 기체에 따라 주어지는 상수이다.

eXtreme Combustion Laboratory

[3] Beattie-Bridgeman

$$p = \frac{\bar{R}T(1-\varepsilon)}{\bar{v}^2}(\bar{v} + B) - \frac{A}{\bar{v}^2}$$

with

$$A = A_0(1 - \frac{a}{\bar{v}}),\ B = B_0(1 - \frac{b}{\bar{v}}),\ \varepsilon = \frac{C}{\bar{v}T^3}$$

where A_0, a, B_0, b, C 는 기체 별로 주어짐

eXtreme Combustion Laboratory

- Quality (at saturated state)

$$x = \frac{m_{vap}}{m}$$ where *m* = total mass of a substance

$$V = V_L + V_V$$

Or

$$mv = m_L v_f + m_V v_g$$ where v_f = specific volume of saturated liquid

Divide by *m*,

$$v = \frac{m_L}{m} v_f + \frac{m_v}{m} v_g$$

$$= (1-x)v_f + xv_g$$ ....(a)

eXtreme Combustion Laboratory

- Example 1

  Calculate the specific volume of saturated steam at 200°C having a quality of 70 percent.

Look up table (수증기표, steam table) on p.381, (노승탁 저) and find

$v_f = 0.001157,\ v_g = 0.12736$ at T=200, saturated steam table

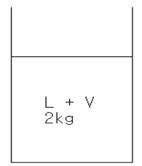
Then use (a) to find,

$$v = (0.3)(0.001157) + 0.7(0.12736)$$
$$= 0.0895\, m^3/kg$$

- Example 2

  Find V_f, V_g, m_f, m_g

V= 0.5 m^3
m= 2 kg
p= 0.5 MPa
In equilibrium.



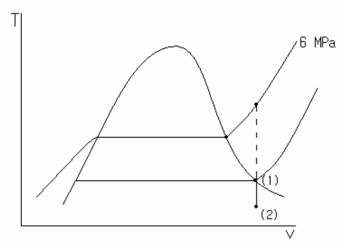
From table, $v_f \sim 0.001093,\ v_g = 0.3749$ at given P

$$v_{total} = \frac{V}{m} = x v_g + (1-x) v_f$$
$$\frac{0.5m^3}{2kg} = 0.3749x + (1-x)0.001093$$
$$0.25 - 0.001093 = 0.373807x$$
$$x = 0.6659 = \frac{m_g}{m} = \frac{m_g}{2kg}$$
$$m_g = 2(0.6658)kg = 1.3318kg$$
$$m_f = m - m_g = 0.6682kg$$
$$V_g = v_g \times m_g = 0.4993m^3$$
$$V_f = v_f \times m_f = 7.3 \times 10^{-4} m^3$$

- Example 3

  Consider super heated vapor contained in a fixed container at p= 6 MPa, T= 300 °C (일정한 용기)

(1) Find P and T at which the steam becomes saturated upon cooling. (i.e. constant volume cooling!)



Answer to 3.1

Look up steam table p. 389, superheated steam (과열증기)

$v_{sat} = 0.03616$

Then find T_{sat} at v_{sat}=0.03616.
i.e. look up saturated table (포화증기표, v_g)

p	T	v_g
5	263.99	0.03944
6	275.64	0.03244

Upon interpolation, (補間)
~P= 5.4 Mpa
~T= 269°C

(2) Determine the state of steam when T becomes 20 C.
(수증기의 상태) Volume remains constant!

As shown in the figure, state (2) is inside the saturation dome.

- When T=20°C, saturated table (p. 380) gives,
- p= 2.339 , v_f= 0.001002 , v_g= 57.79

$$v = x_{(2)} v_g + (1-x) v_f$$
$$= v_f + x_{(2)} v_{fg}$$
$$0.03616 = 0.001002 + x_{(2)}(57.79 - 0.001002)$$
$$or$$
$$\boxed{x_{(2)} = 0.000608}$$

- Homework Set #3 (due 3/23)
- 3-2, 3-4, 3-6, 3-8, 3-10, 3-12, 3-14
- Next we will learn about the First Law of Thermodynamics!!!