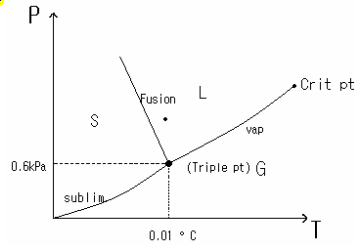


## Chapter 3. Properties of Pure Substances and Equations of state

### • Properties of Pure Substance

#### 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  $10^5 \text{ Pa} = 1 \text{ atm}$  and  $0.006 \times 10^5 \text{ Pa}$ )
  - 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.

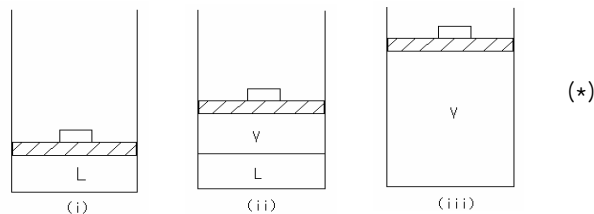
- Pure substance
  - one that has a homogeneous and invariable chemical composition.
  - ex) liquid water + steam  
liquid water + ice  
Air (at room temperature)
- Mixture
  - Air at low temperature (decomposes)
  - ex) liquid nitrogen + liquid oxygen  
(i.e. decomposed composition of Air)

### • Phase equilibrium in a pure substance

Consider a system, 1kg of water contained in the piston-cylinder arrangement:

Water

@p = p<sub>0</sub> = 1 atm = 0.1MPa



Fix p, increase T from 20°C to 100°C  
At (ii), both phases (L+V) co-exist.

### • Saturation (shown in step (ii) in the previous cartoon)

When two phases are in equilibrium, like in (ii).

ex) L + V, S + L, S + V

- Saturation liquid : Liquid that exists at the saturation temperature and pressure
- Sub-cooled liquid : Temperature is lower than the saturation temperature for the given p.
- Compressed liquid : Pressure is greater than the saturation pressure for the given temperature.

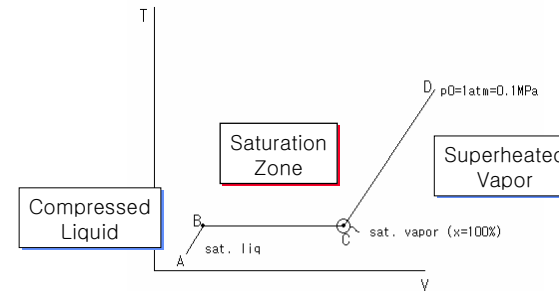
NOTE: Sub-cooled Liquid = Compressed Liquid  
(Shown left of the steam dome on T-Vol Diagram)

- In (ii), if the  $m_{vap} = 0.2kg$  and  $m_{liq} = 0.8kg$ , we define

**Quality (x)**  $\equiv$  Ratio of the mass of vapor to the total mass  
 $= 0.2$  or **20% = x**

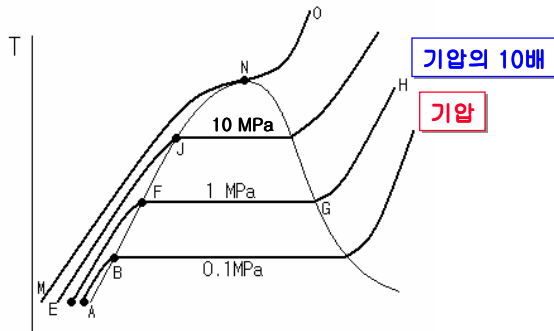
- Saturated vapor = a substance exists as vapor at the saturation temperature
- Superheated vapor = vapor is at a temperature greater than the saturation temperature. (대부분의 기체)  
 (Shown on the right outer end of the steam dome on P-V)

- Let's plot T-V diagram that represents process shown in (\*).



- State (A) Initial state at  $T_0, P_0$   
 (B) Saturated liquid state ( $T_{sat} 99.6^\circ\text{C}$ )  
 (A-B) L is heated to  $T_{sat}$   
 (C) Saturated vapor state  
 (B-C) L, V co-existing at constant T, and p (boiling)  
 (C-D) Steam(Vapor) is superheated at constant p

- Now consider a process at  $p = 1 \text{ Mpa}$  (10 atm) and  $T_0$ .

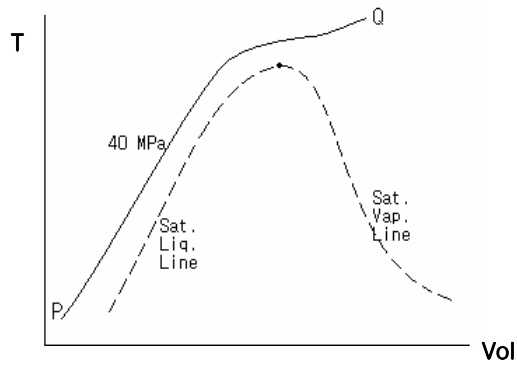


$T_B = 99.6^\circ\text{C}$   
 $T_F = 179.9^\circ\text{C}$  (Sat. Liquid)  
 Sat. vapor state (G)  
 Superheated vapor (G-H)

- Draw  $p = 10 \text{ Mpa}$  case,  $T_J = 311.1^\circ\text{C}$
- At a pressure of 22.09 Mpa (MNO) there is no constant temperature vaporization region or No co-existence region found.
- N is a point of inflection with zero slope.  $\rightarrow$  "Critical point"
- Critical Point  $\equiv$  the saturated-liquid and saturated-vapor states are the same.  $P_{crit}, T_{crit}, V_{crit}$ .
- For some critical point data,

	$T_{crit} (^\circ\text{C})$	$P_{crit} (\text{Mpa})$	$v_{crit} (\text{m}^3/\text{kg})$
Water	374.14	22.09	0.003155
Carbon Dioxide	31.05	7.39	0.002143
Oxygen	-118.35	5.08	0.002438
Hydrogen	-239.85	1.3	0.032192

- If  $p \sim 40 \text{ MPa}$



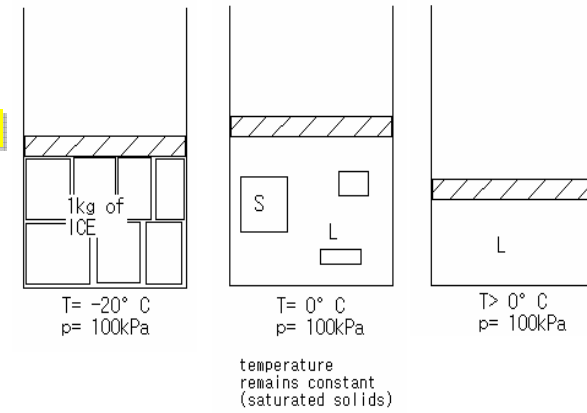
If  $p > p_{\text{crit}}$ , for water at 40MPa, 20°C is heated in constant  $p$  process in a cylinder as shown in (\*), there will never be 2 phases present and state (ii) will never exist.

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

### 3/16

- Another experiment -----(\*\*) for water

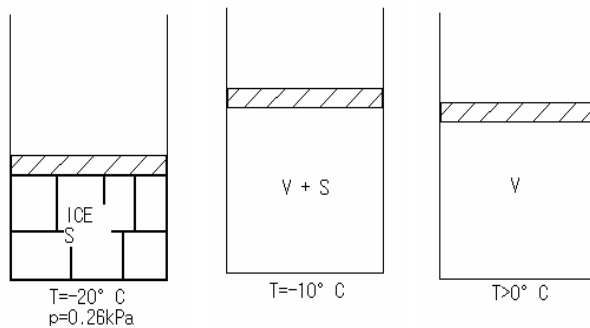
Adding HEAT



- Another example -----(\*\*\*)

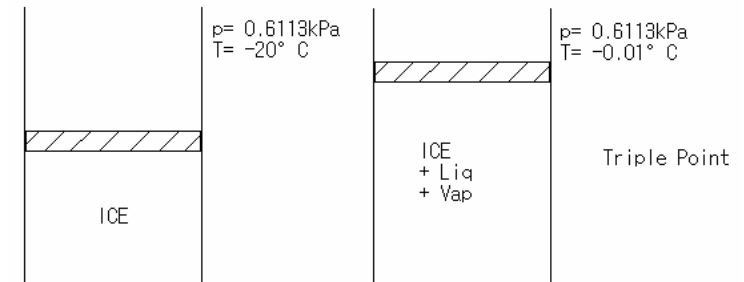
$T = -20^\circ\text{C}$

$P = 0.26\text{kPa}$  (S → Vapor) Sublimation (승화)

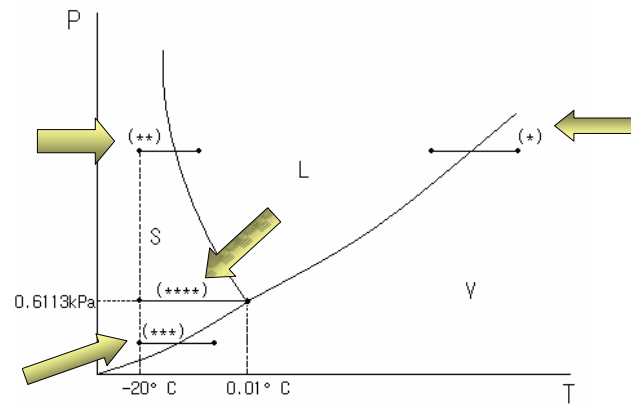


Aside S → L fusion (melt) 용해  
L → V evaporate 증발  
S → V sublimation 승화

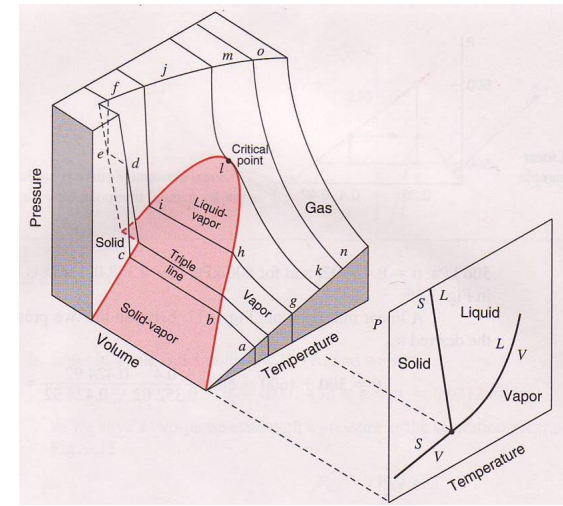
- Another Example -----(\*\*\*\*)



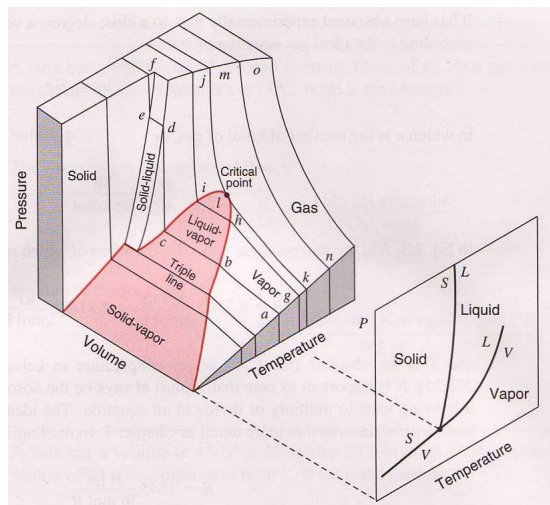
- Describe all 4 processes on P-T curve (Constant-p processes)



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