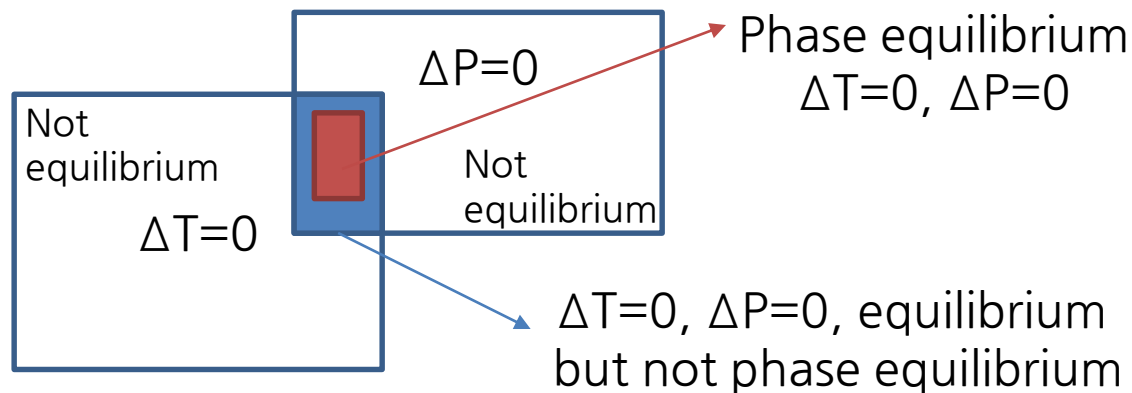


Phase equilibrium basics

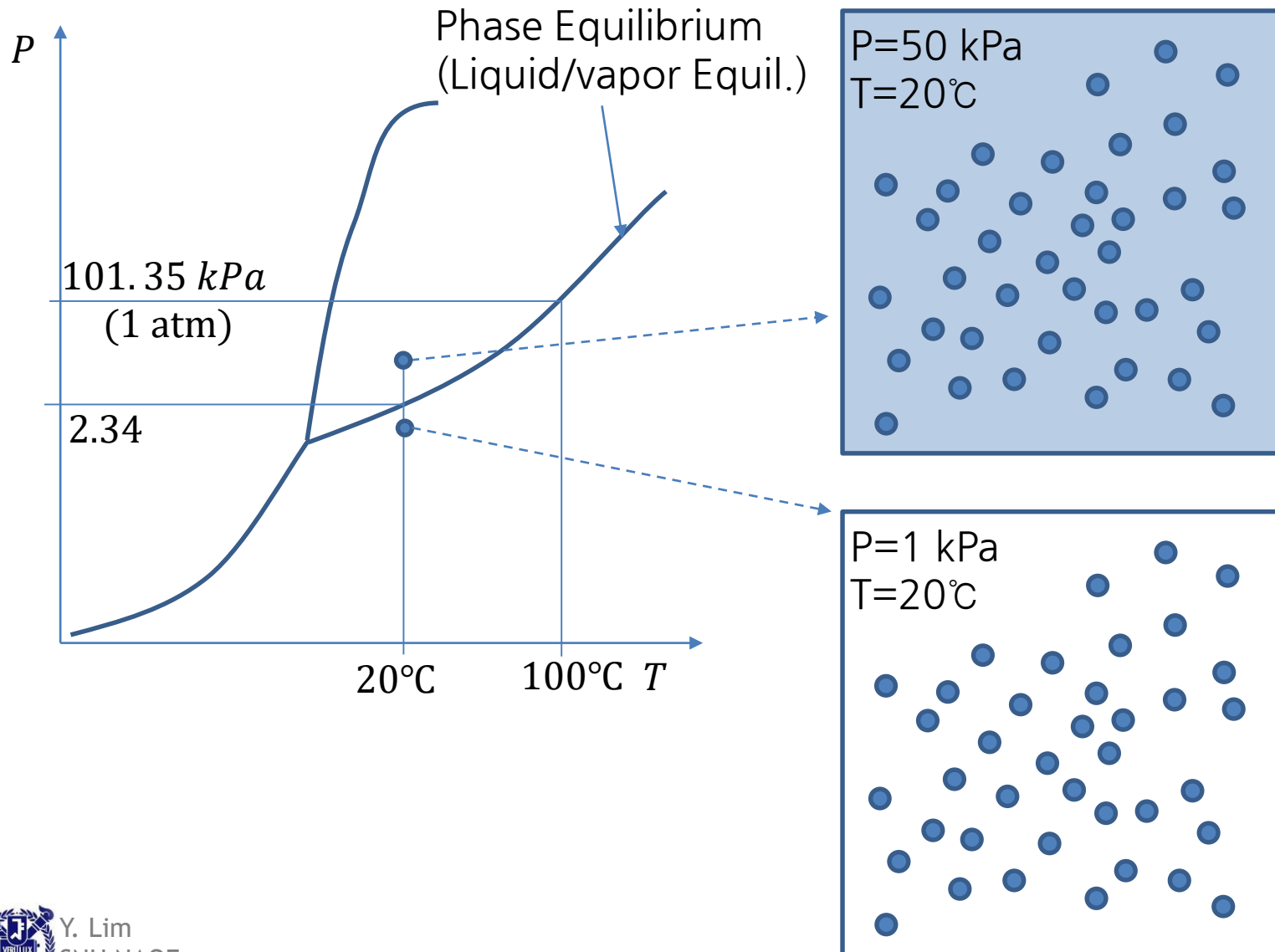


What was the “equilibrium?”

- **Mechanical equilibrium**
 - $F_1 = F_2$
 - Difference in force \rightarrow difference in potential energy \rightarrow movement
- **Mechanical equilibrium**
 - $P_1 = P_2$
 - Difference in pressure \rightarrow difference in potential energy \rightarrow flow
- **Thermal equilibrium**
 - $T_1 = T_2$
 - Difference in temperature \rightarrow difference in thermal energy \rightarrow heat flow
- **Phase equilibrium**
 - Looks like no change from one phase to another phase (ex: liquid \rightarrow vapor)

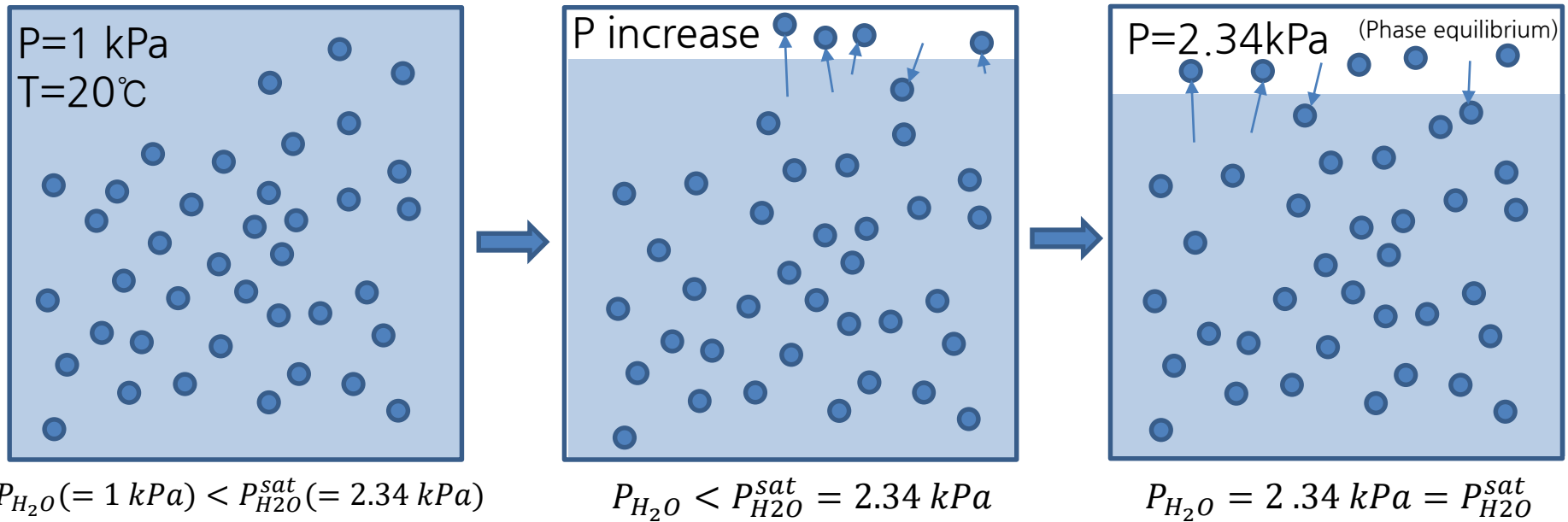


Phase Equilibrium for pure substance



Phase Equilibrium for pure substance

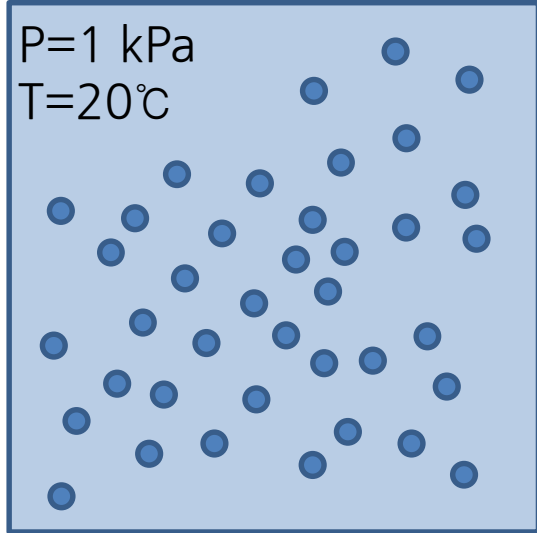
- Let's imagine an unstable state



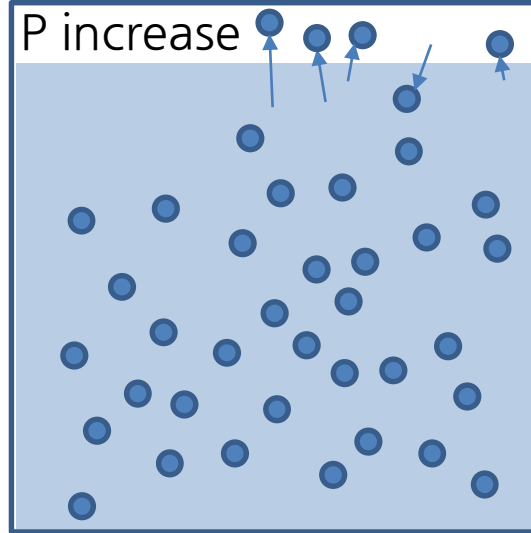
- For pure substance, saturation pressure is**
 - P at which a pure substance boils at a given T .
 - P exerted by the vapor that escapes from the liquid at a given T .
 - P at which vaporization rate is same as condensation rate.
 - P at phase equilibrium

Phase Equilibrium for pure substance

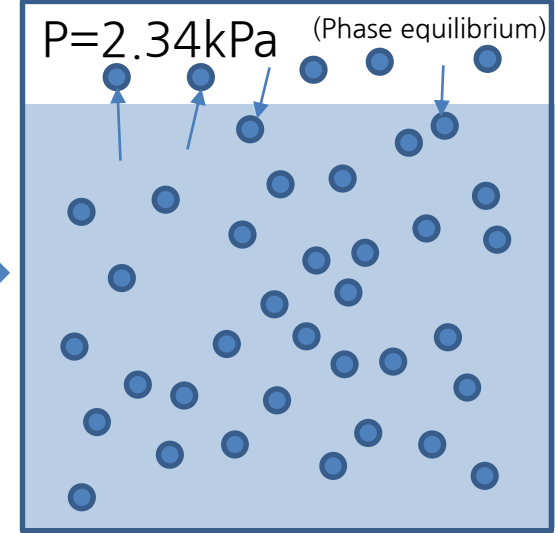
- Let's imagine an unstable state



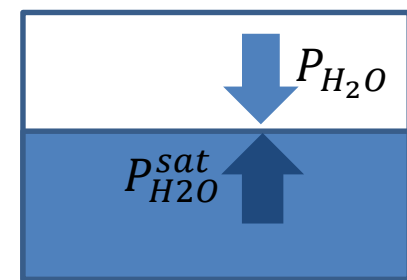
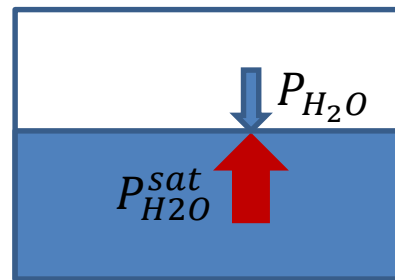
$$P_{H_2O}(= 1 \text{ kPa}) < P_{H_2O}^{sat}(= 2.34 \text{ kPa})$$



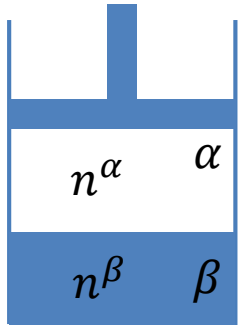
$$P_{H_2O} < P_{H_2O}^{sat} = 2.34 \text{ kPa}$$



$$P_{H_2O} = 2.34 \text{ kPa} = P_{H_2O}^{sat}$$



Gibbs Energy



$$dU = \delta Q + \delta W = \delta Q - PdV$$

$$dH = d(U + PV) = dU + PdV + VdP = \delta Q + VdP$$

With constant P,

$$dH = \delta Q$$

$$0 \geq dH - TdS$$

From 2nd law,

$$dS \geq \frac{\delta Q_{rev}}{T}$$

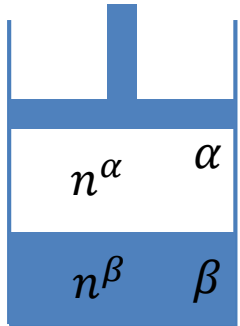
With constant T,

$$0 \geq d(H - TS) = dG$$

- Gibbs Energy must go to decreasing way, to the minimum point.
- Spontaneous change
- For equilibrium, $dG=0$



Gibbs Energy



$$dG = d(g^\alpha n^\alpha + g^\beta n^\beta) \leq 0$$

$$= g^\alpha dn^\alpha + g^\beta dn^\beta \leq 0$$

$$dn^\beta = -dn^\alpha$$

$$dG = (g^\alpha - g^\beta)dn^\alpha \leq 0$$

If $g^\alpha > g^\beta$, $dn^\alpha \leq 0$

$dn^\alpha < 0 \rightarrow$ only β exists

If $g^\alpha < g^\beta$, $dn^\alpha \geq 0$

$dn^\alpha > 0 \rightarrow$ only α exists

\rightarrow Phase equilibrium is possible at $g^\alpha = g^\beta$ only

Chemical potential $\mu = g$



Gibbs Energy

- Ex) $g^\alpha > g^\beta$
 - If $g^\alpha = 2 \text{ J/mol}$, $g^\beta = 1 \text{ J/mol}$, $n^\alpha = 1 \text{ mol}$, $n^\beta = 1 \text{ mol}$

$$G = g^\alpha n^\alpha + g^\beta n^\beta = 2 \cdot 1 + 1 \cdot 1 = 3 \text{ J}$$

- If $(dn^\alpha = 0) \rightarrow G=3$

- If $(dn^\alpha = 0.1)$

$$G = g^\alpha n^\alpha + g^\beta n^\beta = 2 \cdot 1.1 + 1 \cdot 0.9 = 3.1 \text{ J}$$

- If $(dn^\alpha = -0.1)$

$$G = g^\alpha n^\alpha + g^\beta n^\beta = 2 \cdot 0.9 + 1 \cdot 1.1 = 2.9 \text{ J}$$

\rightarrow Condensation to when $G = 2 \cdot 0 + 1 \cdot 2 = 2 \text{ J}$ (minimum)

$$n^\alpha = 1^\alpha$$

$$n^\beta = 1^\beta$$



Gibbs Energy

$$dg = vdP - sdT$$

With constant T,

$$\left(\frac{\partial g}{\partial P}\right)_T = v$$

