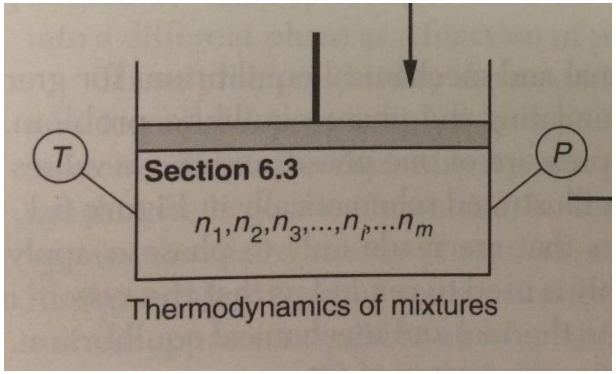
VLE for ideal mixture

Thermodynamic properties of mixture

- At constant T, P,
  - $V = \sum \bar{V}_i n_i \, , \bar{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq i}}$
  - $U = \sum \bar{U}_i n_i \, , \bar{U}_i = \left(\frac{\partial U}{\partial n_i}\right)_{T,P,n_{j\neq i}}$
  - $H = \sum \bar{H}_i n_i \, , \bar{H}_i = \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_{j\neq i}}$
  - $S = \sum \bar{S}_i n_i \, , \bar{S}_i = \left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_{j\neq i}}$
  - $G = \sum \bar{G}_i n_i \, , \bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}}$



Property change of mixing

- $\Delta V_{mix} = V - \sum n_i v_i = \sum \bar{V}_i n_i - \sum n_i v_i = \sum n_i(\bar{V}_i - v_i)$
- $\Delta v_{mix} = v - \sum x_i v_i = \sum x_i(\bar{V}_i - v_i)$

- $\Delta H_{mix} = H - \sum n_i h_i = \sum \bar{H}_i n_i - \sum n_i h_i = \sum n_i(\bar{H}_i - h_i)$
- $\Delta h_{mix} = h - \sum x_i h_i = \sum x_i(\bar{H}_i - h_i)$

Multicomponent phase equilibrium

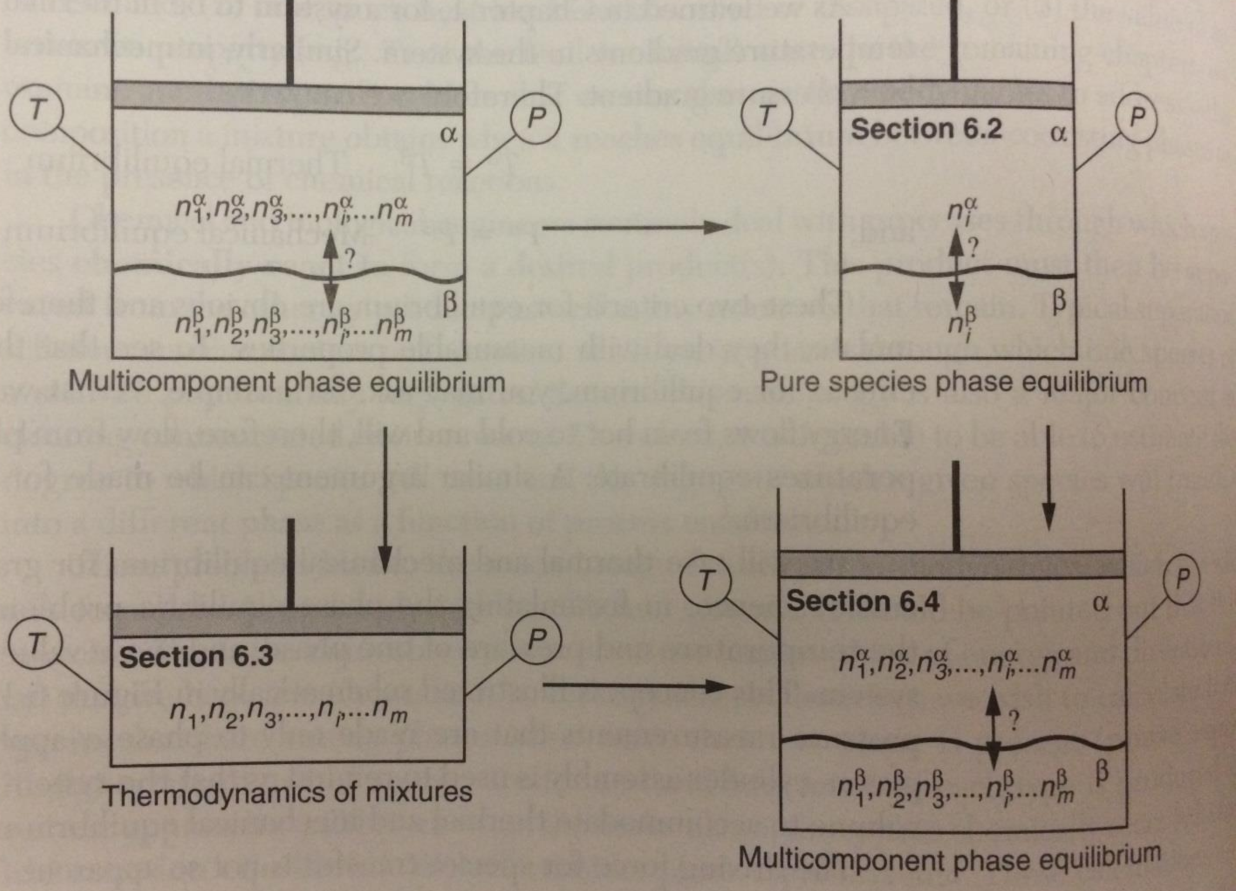


Figure 6.2 Reduction of the multicomponent phase equilibria problem.

Multicomponent phase equilibrium

- **With phase α and β,**

$$0 \geq dG = dG^{\alpha} + dG^{\beta}$$

$$= \left[-SdT + VdP + \sum \bar{G}_i dn_i\right]^{\alpha} + \left[-SdT + VdP + \sum \bar{G}_i dn_i\right]^{\beta}$$

$$= \left[\sum \bar{G}_i dn_i\right]^{\alpha} + \left[\sum \bar{G}_i dn_i\right]^{\beta} = \sum \bar{G}_i^{\alpha} dn_i^{\alpha} + \sum \bar{G}_i^{\beta} dn_i^{\beta}$$

$$0 \geq \sum \left(\bar{G}_i^{\alpha} - \bar{G}_i^{\beta}\right) dn_i^{\alpha}$$

→$\bar{G}_i^{\alpha} = \bar{G}_i^{\beta}$ for the phase equilibrium

∗VLE for mixture $T^{\alpha} = T^{\beta}$

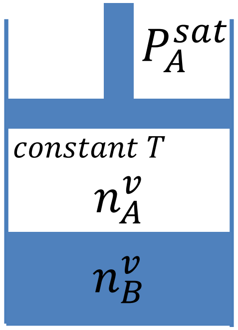
$P^{\alpha} = P^{\beta}$

$\mu_i^{\alpha} = \mu_i^{\beta} \leftrightarrow \bar{G}_i^{\alpha} = \bar{G}_i^{\beta}$ (for each i)

(Chemical potential $\mu_i = \bar{G}_i$)

VLE for ideal mixture

- For pure A in VLE



$$\mu_A^{v*} = \mu_A^o + RT\ln\frac{P_A^{sat}}{P^0}$$

$$\mu_A^{v*} = \mu_A^{l*} = \mu_A^*$$ (* means a pure substance)

$$\mu_A^o = \mu_A^* - RT\ln\frac{P_A^{sat}}{P^0}$$

- For vapor A in ideal gas mixture

At constant T,

$$d\mu_i = d\bar{G}_i = \bar{V}_i dP$$

For an ideal gas,

$$V = \frac{nRT}{P} = \frac{(n_1 + n_2 + \cdots n_i + \cdots + n_m)RT}{P}$$

$$\bar{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{P,T,n_{j\neq i}} = \frac{RT}{P}$$

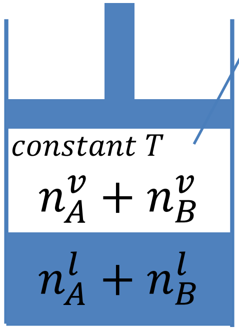
Ideal gas mixture

$$\Delta v_{mix} = 0$$

$$\Delta h_{mix} = 0$$

$$\Delta s_{mix} = -R\sum y_i \ln y_i$$

$$\Delta g_{mix} = RT\sum y_i \ln y_i$$



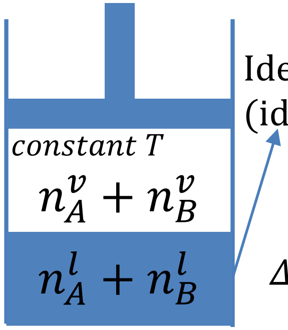
$$d\mu_A^v = \bar{V}_A dP = \frac{RT}{P}dP$$

$$\mu_A^v = \mu_A^o + RT\ln\frac{\mathcal{P}_A}{P^o} = \mu_A^* - RT\ln\frac{P_A^{sat}}{P^0} + RT\ln\frac{\mathcal{P}_A}{P^o}$$

$$= \mu_A^* + RT\ln\frac{\mathcal{P}_A}{P_A^{sat}}$$

VLE for ideal mixture

- For liquid A in ideal solution



Ideal liquid mixture
(ideal solution)

$$\Delta v_{mix} = 0$$
$$\Delta h_{mix} = 0$$
$$\Delta s_{mix} = -R\sum x_i \ln x_i$$
$$\Delta g_{mix} = RT\sum x_i \ln x_i$$

$$\Delta g_{mix} = RT\sum x_i \ln x_i = \sum x_i(\bar{G}_i - g_i)$$

$$\bar{G}_i - g_i = RT\ln x_i$$

$$\downarrow \qquad \downarrow$$

$$\mu_A^l - \mu_A^* = RT\ln x_A$$

- For VLE,

$$\mu_A^v = \mu_A^l$$

$$\mu_A^* + RT\ln\frac{\mathcal{P}_A}{P_A^{sat}} = \mu_A^* + RT\ln x_A$$

$$\frac{\mathcal{P}_A}{P_A^{sat}} = x_A \qquad \mathcal{P}_A = \boxed{y_A P = x_A P_A^{sat}}$$

Raoult's law

Phase equilibrium

- **With ideal gas mixture and ideal liquid mixture**

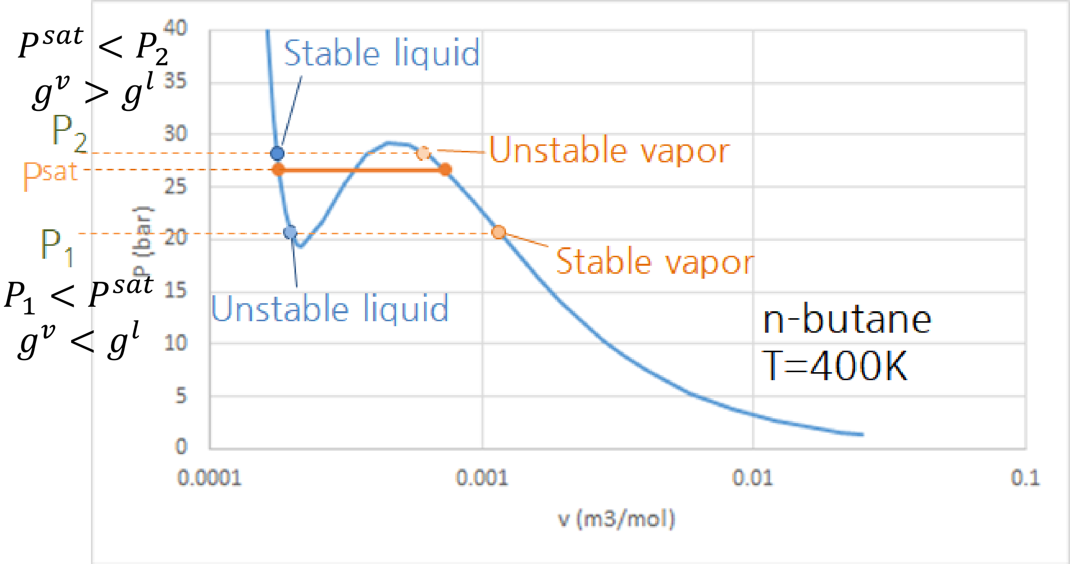
Phase equilibrium:
Partial pressure of i in gas mixture
= Vapor pressure of i in liquid mixture

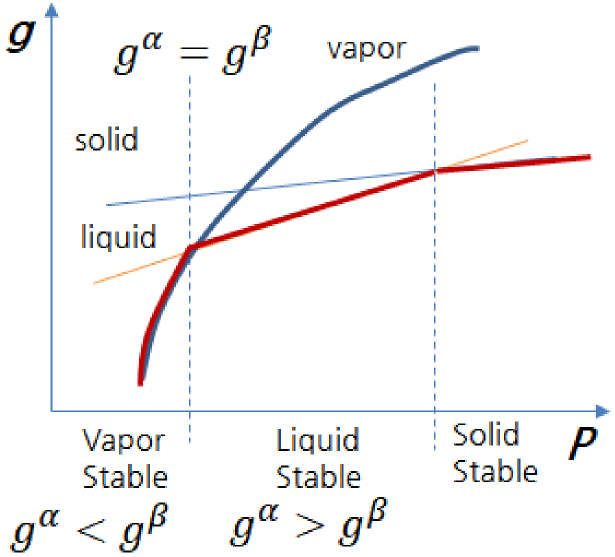
$$\mathcal{P}_i (= y_i P) = P_i^{vap} \left(= x_i P_i^{sat}\right)$$

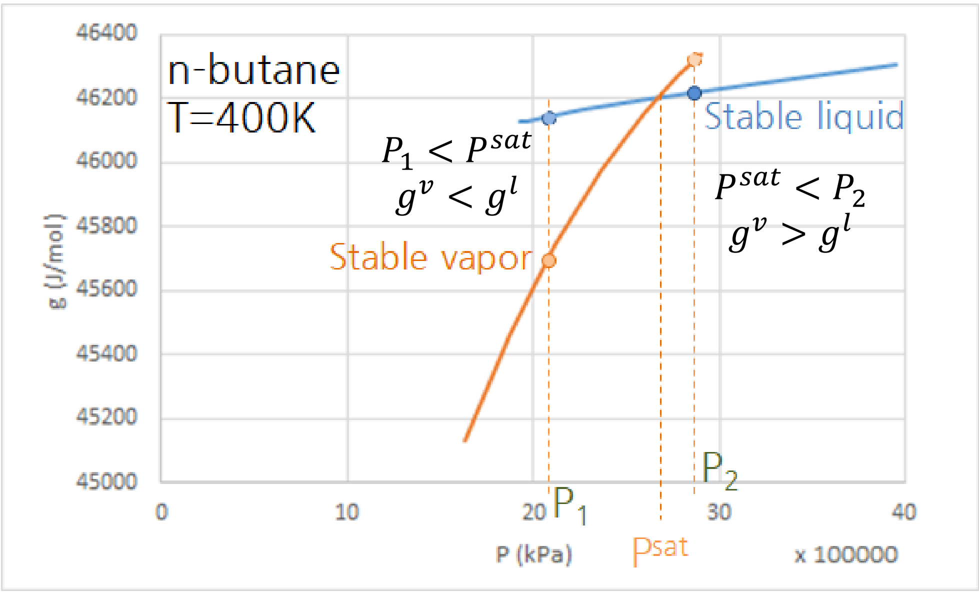
Partial pressure of i in gas mixture

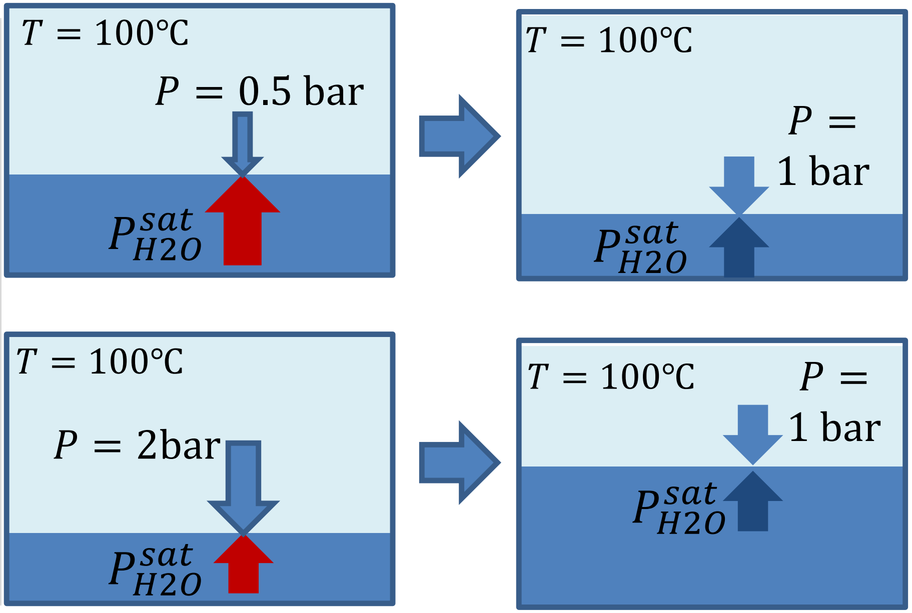
Vapor pressure of i in liquid mixture

Phase Equilibrium for pure substance

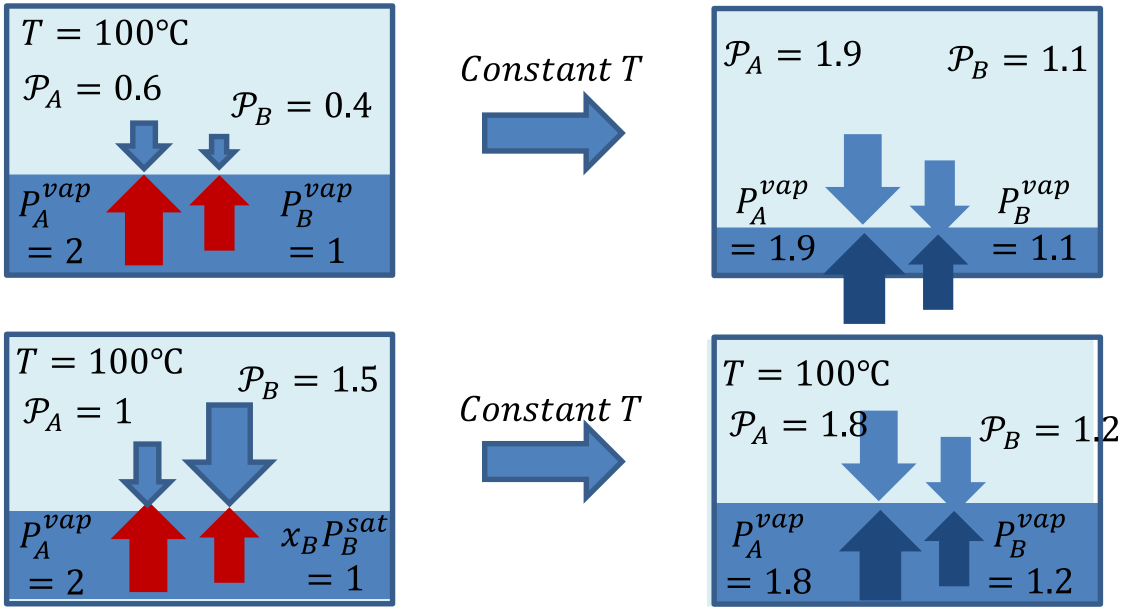








Phase Equilibrium for ideal mixture



With ideal gas mixture and ideal liquid mixture

Phase equilibrium:
Partial pressure of i in gas mixture
= Vapor pressure of i in liquid mixture

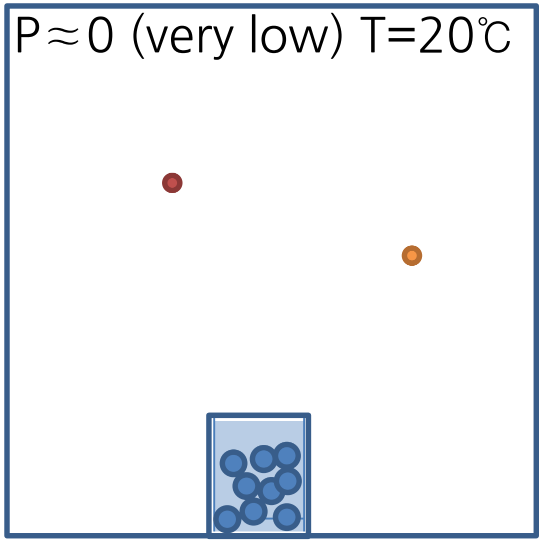
$$\mathcal{P}_i = P_i^{vap}$$

$$\left(y_i P = x_i P_i^{sat}\right)$$

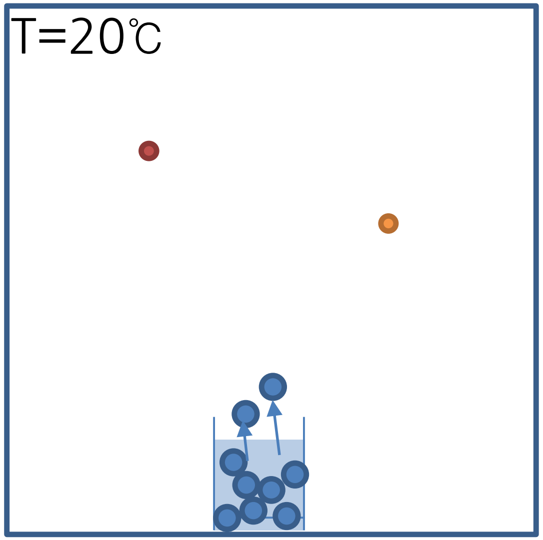
Raoult's law

Phase Equilibrium for pure substance

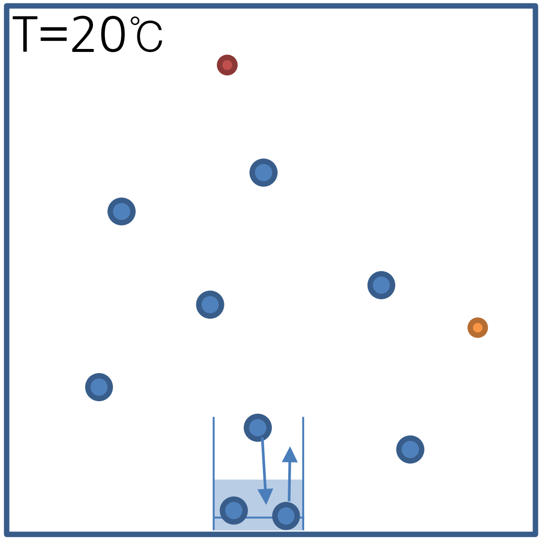
- Let’s imagine water in a cup in vacuum room at const. T



$P(\approx 0) < P_{H2O}^{sat}(= 2.34\ kPa)$

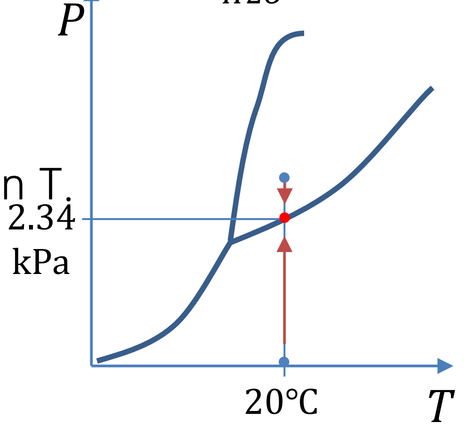


$P < P_{H2O}^{sat} = 2.34\ kPa$

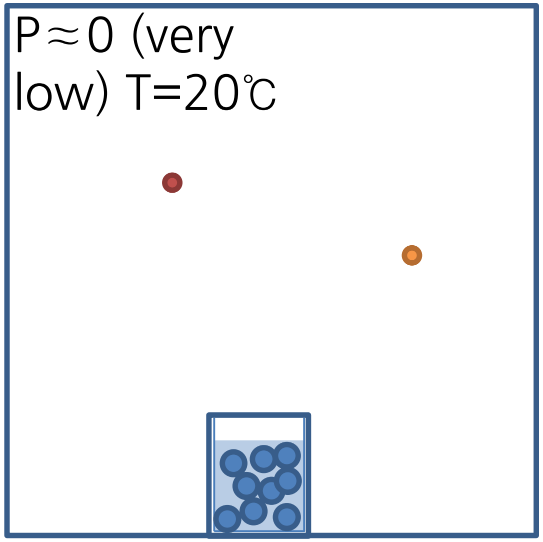


$P = 2.34\ kPa = P_{H2O}^{sat}$

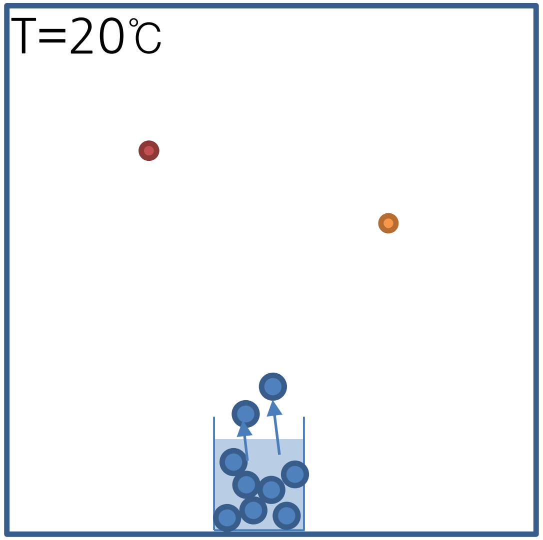
- For pure substance, saturation pressure is
  - P at which a pure substance boils at a given T.
  - P exerted by the vapor that escapes from the liquid at a given T.
  - P at which vaporization rate is same as condensation rate.
  - P at phase equilibrium



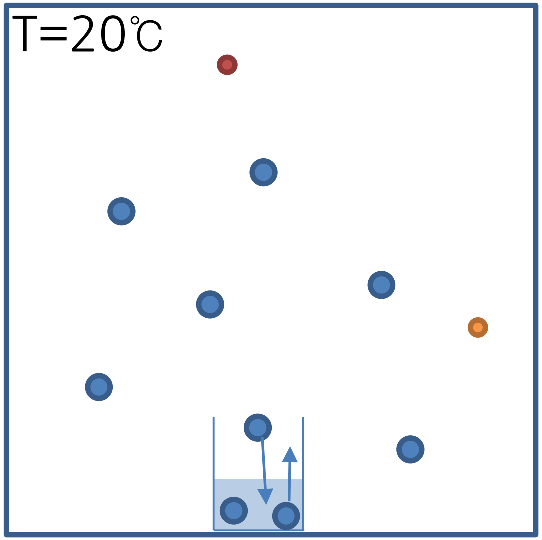
Phase Equilibrium for pure substance



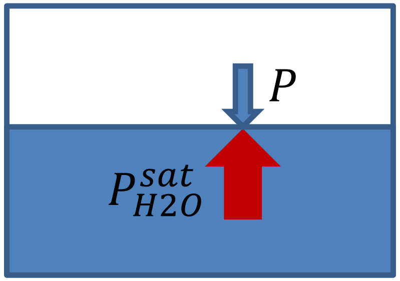
$P(\approx 0) < P_{H2O}^{sat}(= 2.34\ kPa)$



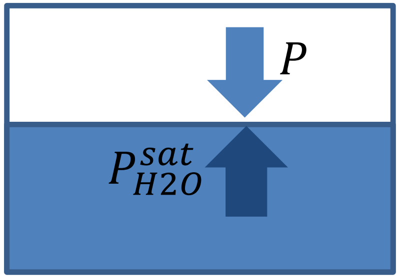
$P < P_{H2O}^{sat} = 2.34\ kPa$



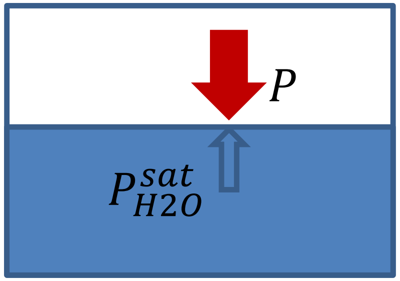
$P = 2.34\ kPa = P_{H2O}^{sat}$



Will vaporize



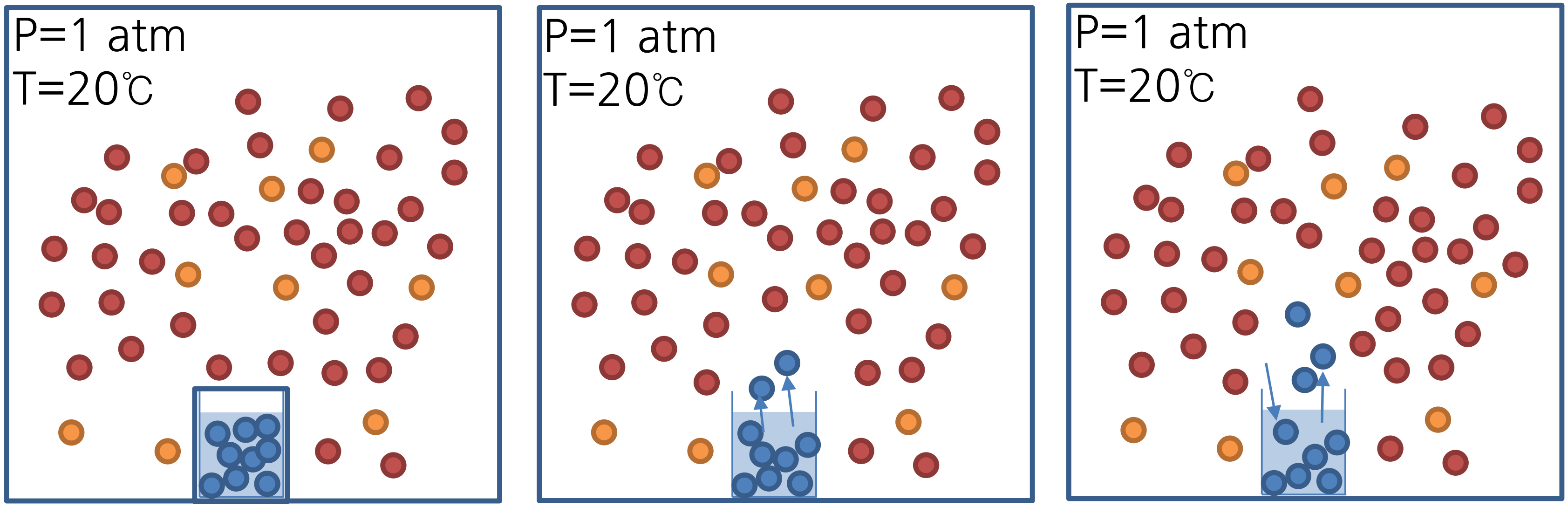
(Phase equilibrium)



Will condense

Phase Equilibrium for ideal mixture
(nonsoluble gas and pure liquid substance)

- Water in a big room



Dalton's partial pressure law

$\mathcal{P}_i = y_i P$ The partial pressure is proportional to the mole fraction of the substance
기체의 분압은 혼합물 중 그 기체 몰분율에 비례한다.

Where

$\mathcal{P}_i$= partial pressure of the component *i* in the gas mixture

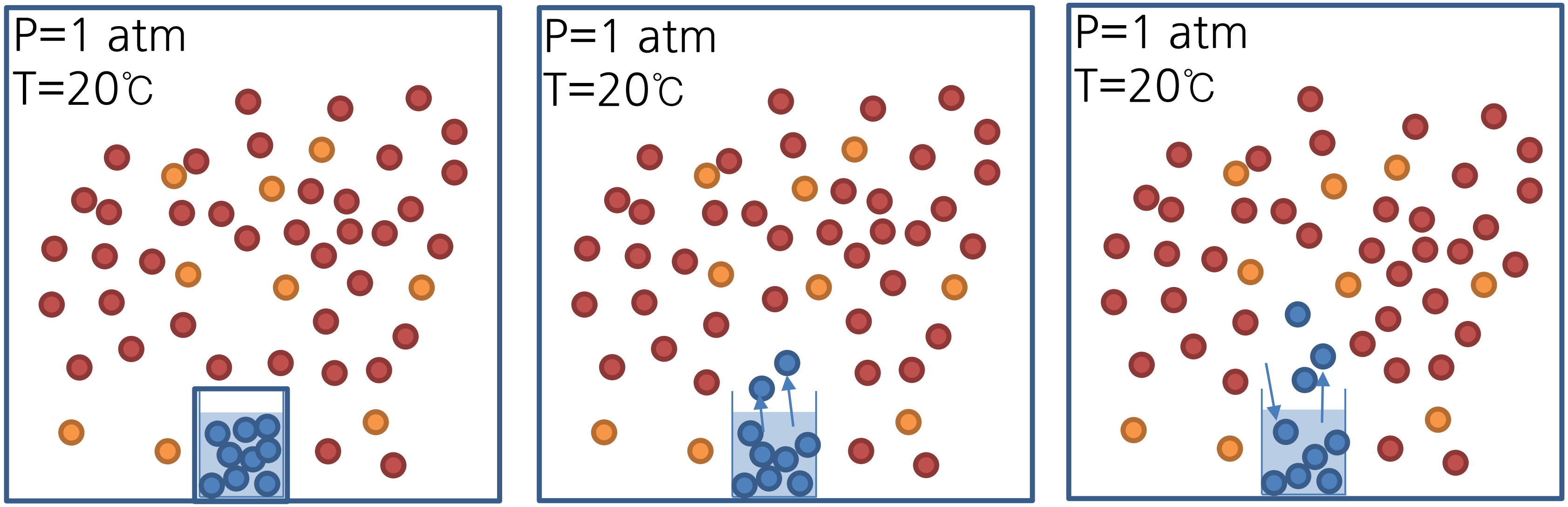
P = pressure in the system

y_i= the mole fraction of the component *i* in the gas mixture

Partial pressure $\mathcal{P}_i$(분압): a hypothetical pressure of gas i if it alone occupied the volume of the mixture at the same temperature

Phase Equilibrium for ideal mixture (nonsoluble gas and pure liquid substance)

- Water in a big room



$\mathcal{P}_{H_2O} = 0 < P^{sat}_{H2O}$

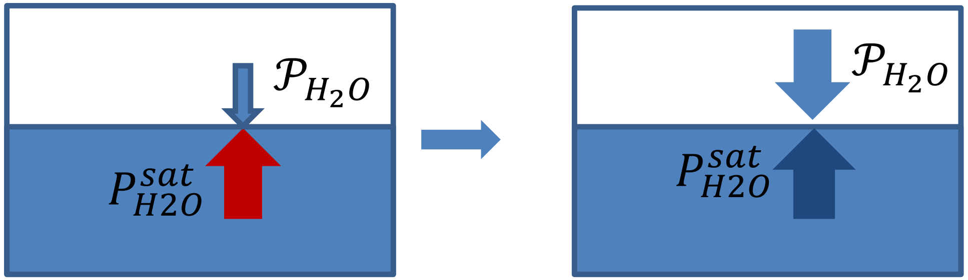
$\mathcal{P}_{H_2O} \neq 0 < P^{sat}_{H2O}$

$\mathcal{P}_{H_2O} = P^{sat}_{H2O} = 2.34\ kPa$

(Phase equilibrium)

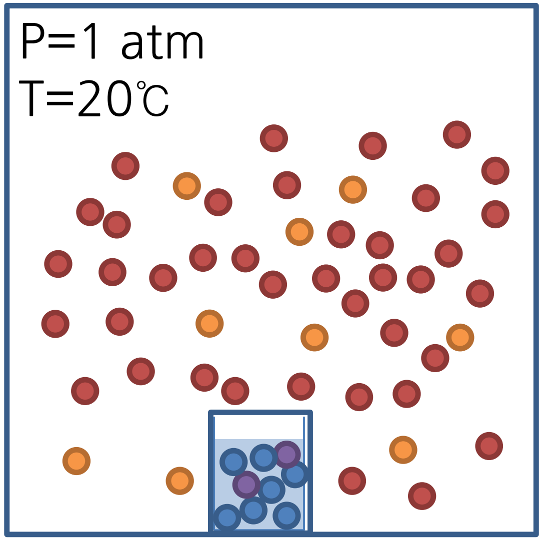
Phase equilibrium: When the saturation pressure of water is same as the partial pressure of water in the gas mixture

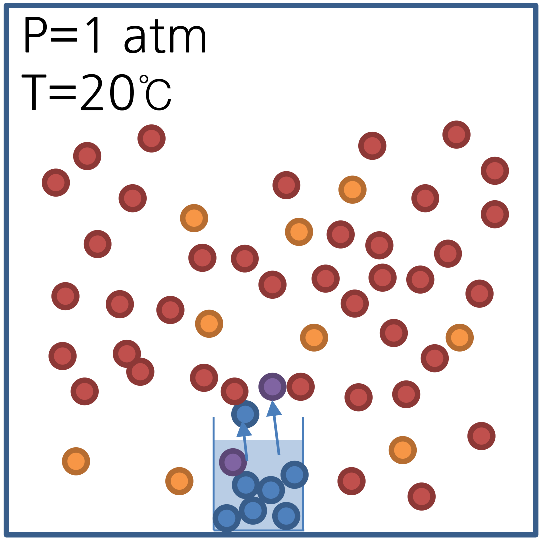
액체상태의 물질 i의 증발하여 형성하는 포화증기압(saturation pressure)이 해당 물질 i의 기체 분압과 같아질 때 상평형에 도달한다.

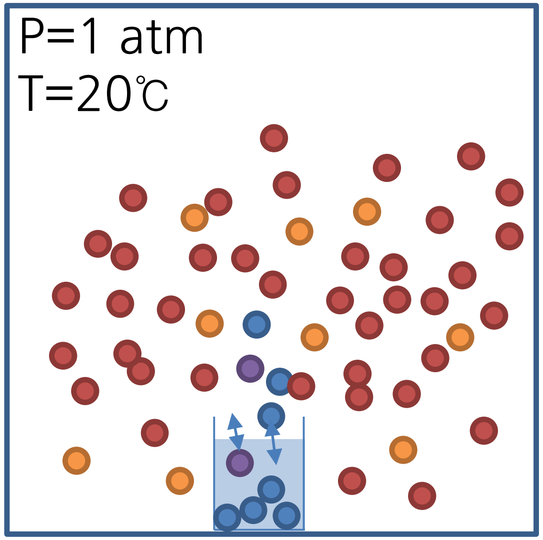


Phase Equilibrium for ideal mixture (nonsoluble gas and liquid mixture)

- H_2O+Ethanol in a big room







Saturation pressure (P_i^{sat}): the pressure exerted from a vaporized pure substance
Vapor pressure (P_i^{vap}): the pressure exerted from a vaporized substance i in a mixture

순물질이 증발하여 형성하는 압력이 포화증기압(saturation pressure), 혼합물 내에서 물질 *i*가 증발하여 형성하는 압력을 i의 증기압(P_i^{vap}, vapor pressure) 즉, 순물질에서 $P^{sat}=P^{vap}$

The vapor pressure of component i of an ideal mixture of liquids is equal to the vapor pressure of the pure component multiplied by its mole fraction in the mixture.

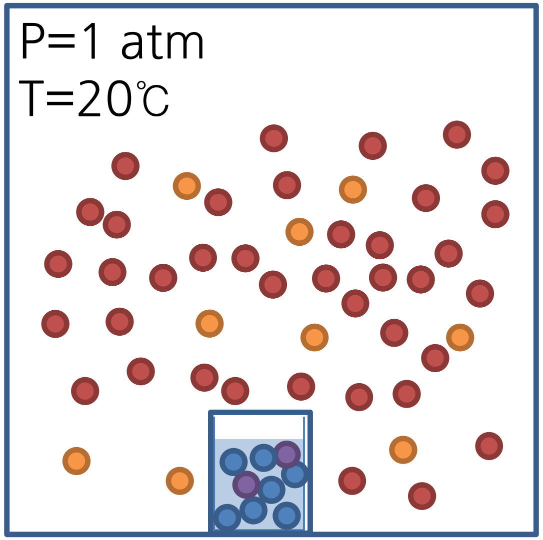
Raoult's law (라울의 법칙)

$$P_i^{vap} = x_i P_i^{sat}$$
$$= y_i P$$

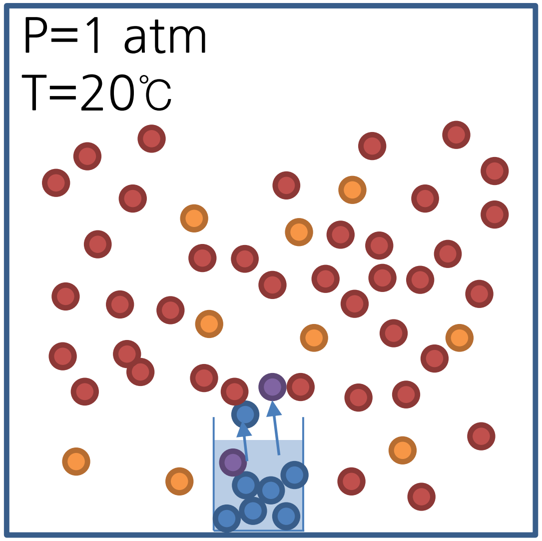
혼합물에서 물질 *i*의 증기압(vapor pressure)은 순물질 i의 포화증기압(saturation pressure)에 비례한다.(다른 액체분자들이 미치는 영향력이 없다고 가정)

Phase Equilibrium for ideal mixture (nonsoluble gas and liquid mixture)

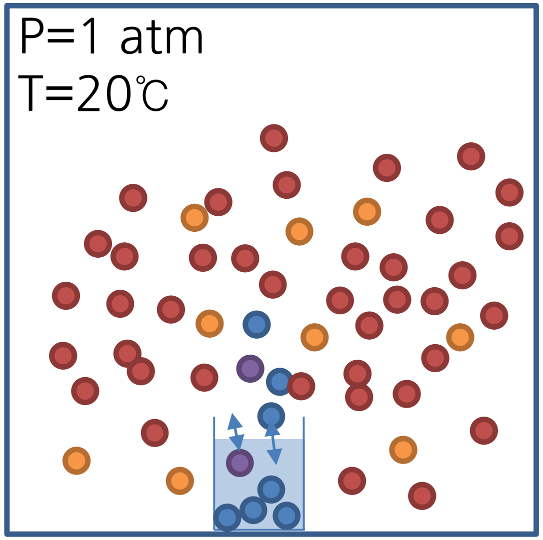
- H_2O+Ethanol in a big room



$$\mathcal{P}_{H_2O} = 0 < P^{vap}_{H_2O} = x_{H_2O}P^{sat}_{H_2O}$$
$$\mathcal{P}_{EtOH} = 0 < P^{vap}_{EtOH} = x_{EtOH}P^{sat}_{EtOH}$$



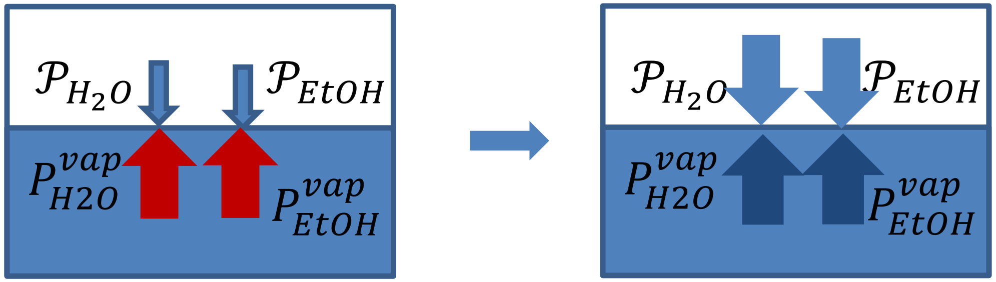
$$\mathcal{P}_{H_2O} \neq 0 < P^{vap}_{H2O}$$
$$\mathcal{P}_{EtOH} \neq 0 < P^{vap}_{EtOH}$$



$$\mathcal{P}_{H_2O} = P^{vap}_{H2O}$$
$$\mathcal{P}_{EtOH} = P^{vap}_{EtOH}$$

Phase equilibrium: When the vapor pressure of component i is same as the partial pressure of component i in the gas mixture

가스 혼합물과 액체 혼합물의 경우 각 물질의 증기압(vapor pressure)이 해당 물질의 분압과 같아질 때 상평형에 도달함.



Phase equilibrium

- **With ideal gas mixture and ideal liquid mixture**

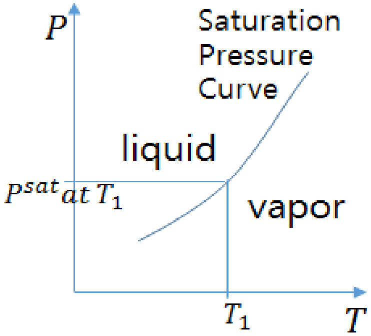
Phase equilibrium:
Partial pressure of i in gas mixture
= Vapor pressure of i in liquid mixture

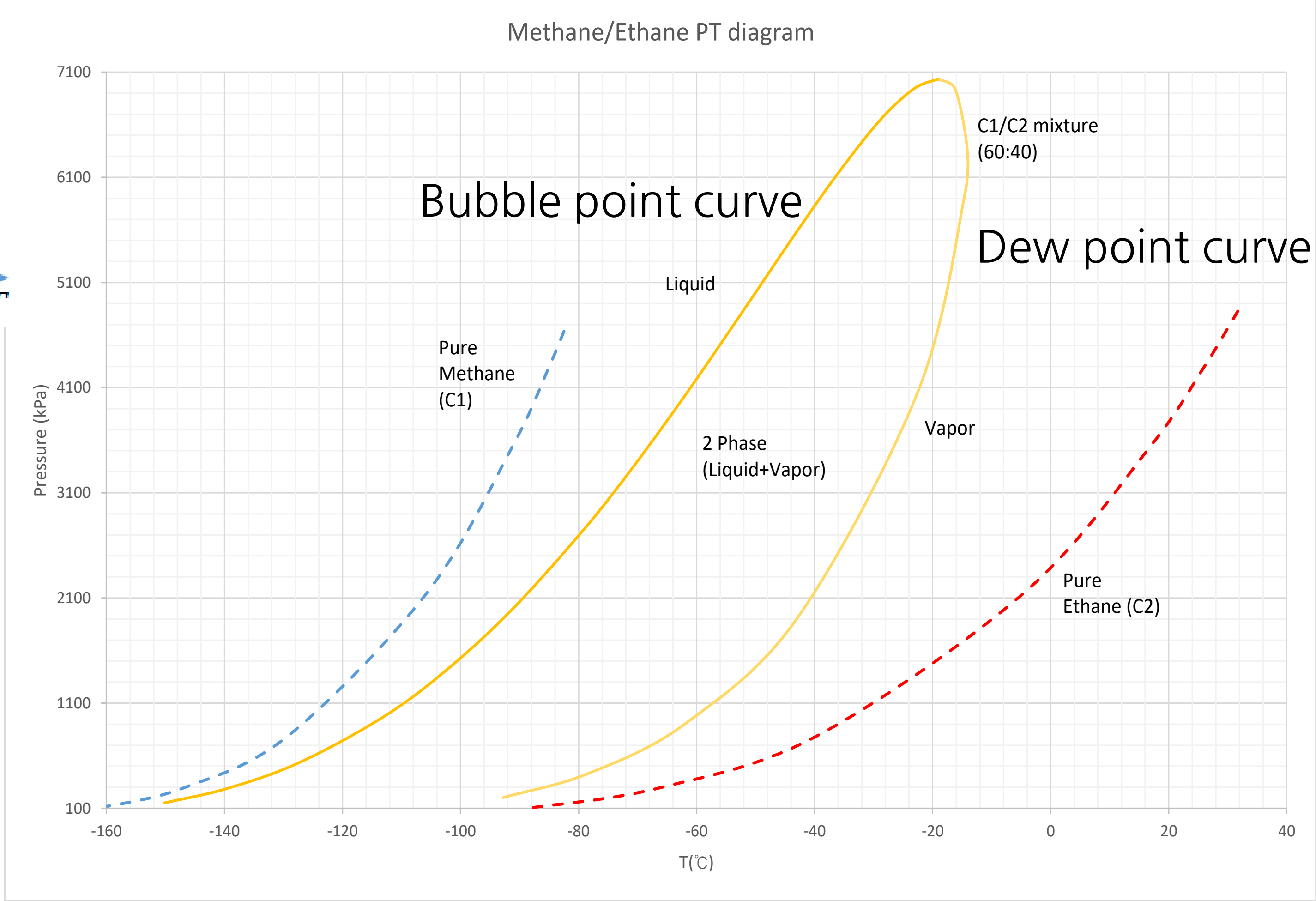
$$\mathcal{P}_i (= y_i P) = P_i^{vap} (= x_i P_i^{sat})$$

*Unfortunately, in real gas and liquid mixture, molecules interact each other. Therefore, Raoult's law does not work very well. This caused to give birth to other thermodynamic properties, fugacity and activity to calculate properties for a non-ideal mixture.
* However, for non-polar mixture such as hydrocarbon mixture, ideal mixture assumption is still effective.

PT diagram of Mixture

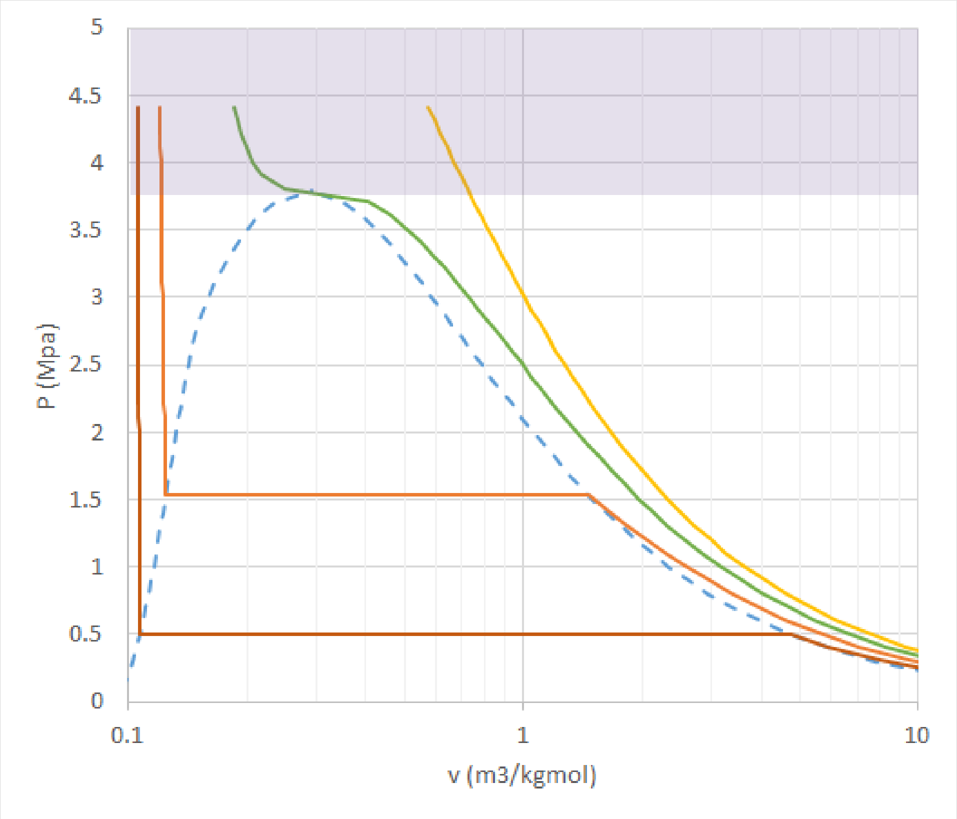
- Pure component
- Mixture



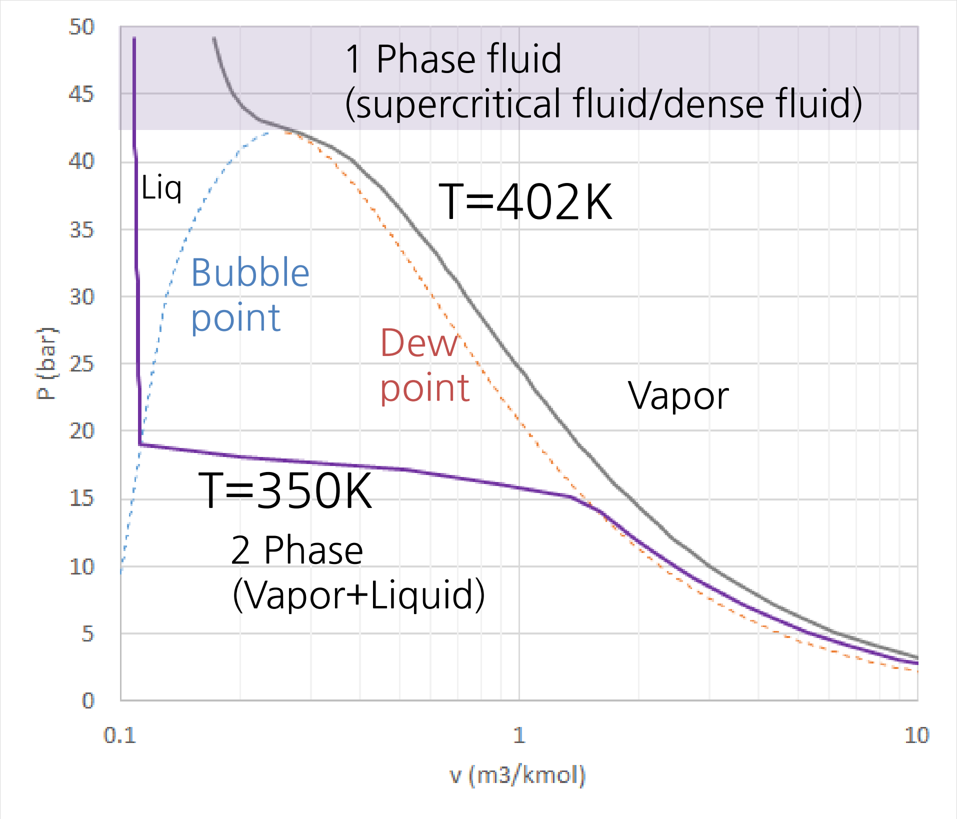


Pv diagram of mixture

- n-butane

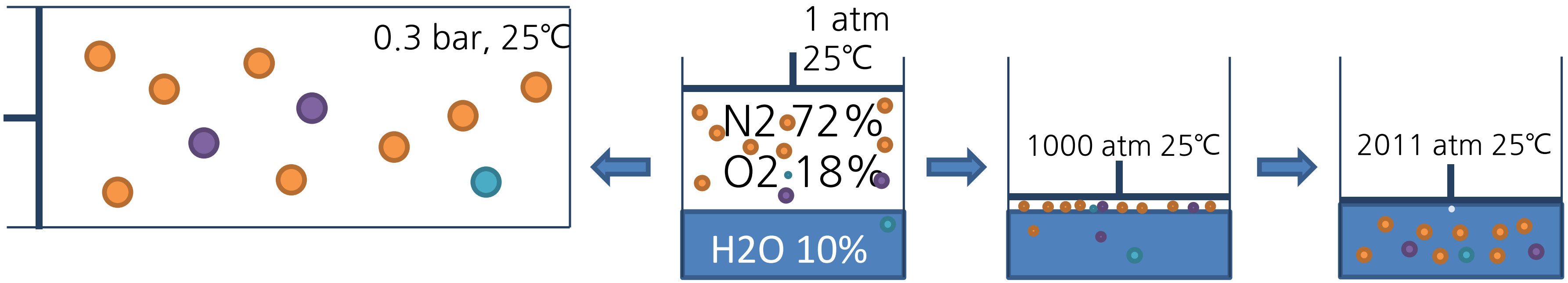


- C3/nC4 1:1



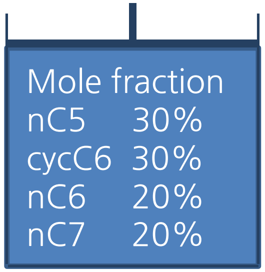
Bubble point/dew point

- **Bubble point**
  - T where the first bubble of vapor is formed at the given P
  - P where the first bubble of vapor is formed at the given T
- **Dew point**
  - T where the first dew of liquid is formed at the given P
  - P where the first dew of liquid is formed at the given T



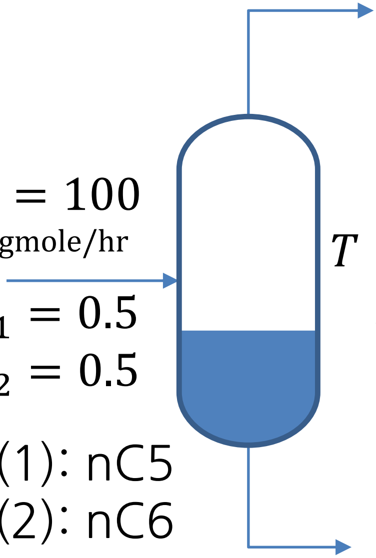
Ex 8.1

- **Bubble point?**
  - When T=333K
  - When P=1 bar



Mole fraction	
nC5	30%
cycC6	30%
nC6	20%
nC7	20%

Ex 8.3



$V = F/3$

$y_1 = ?$

$y_2 = ?$

$F = 100$ kgmole/hr

$z_1 = 0.5$

$z_2 = 0.5$

(1): nC5

(2): nC6

$T = 20°\text{C}$

$P = ?$

$L = ?$

$x_1 = ?$

$x_2 = ?$