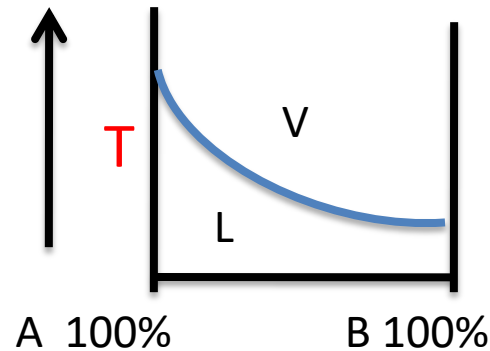
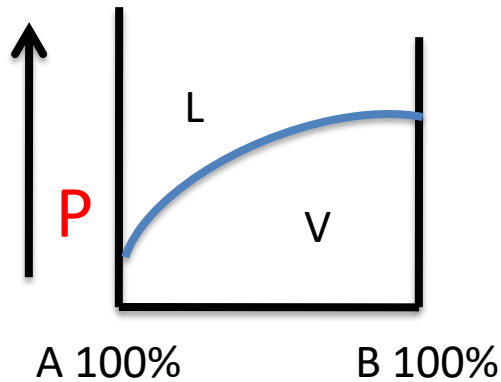


Distillation of

Real solution

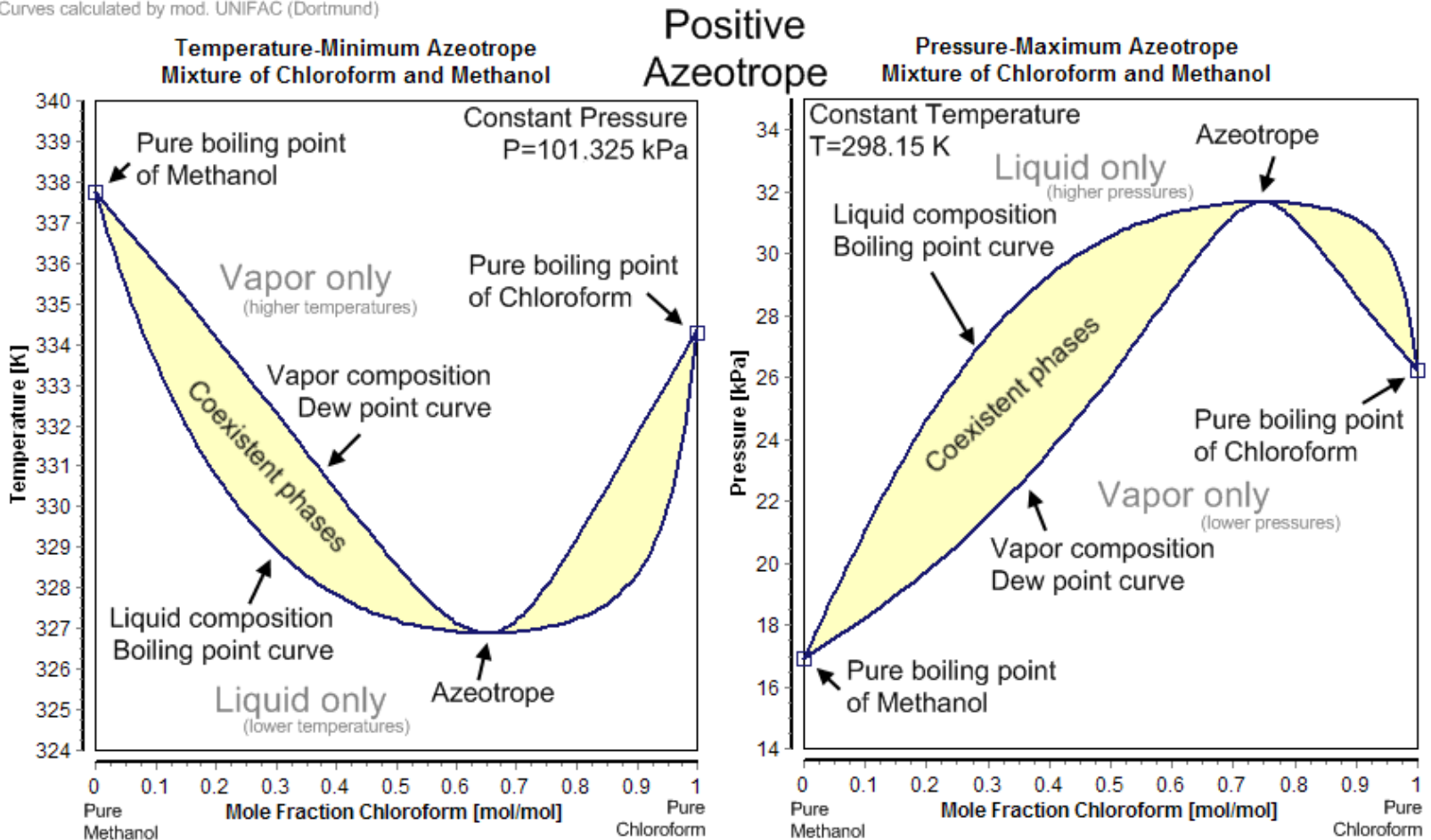
A- Positive deviation

- The distillation give azeotropic mixture which produce more volatile constituent **plus** mixture of constant composition and constant T_b .



Distillation diagram

Curves calculated by mod. UNIFAC (Dortmund)

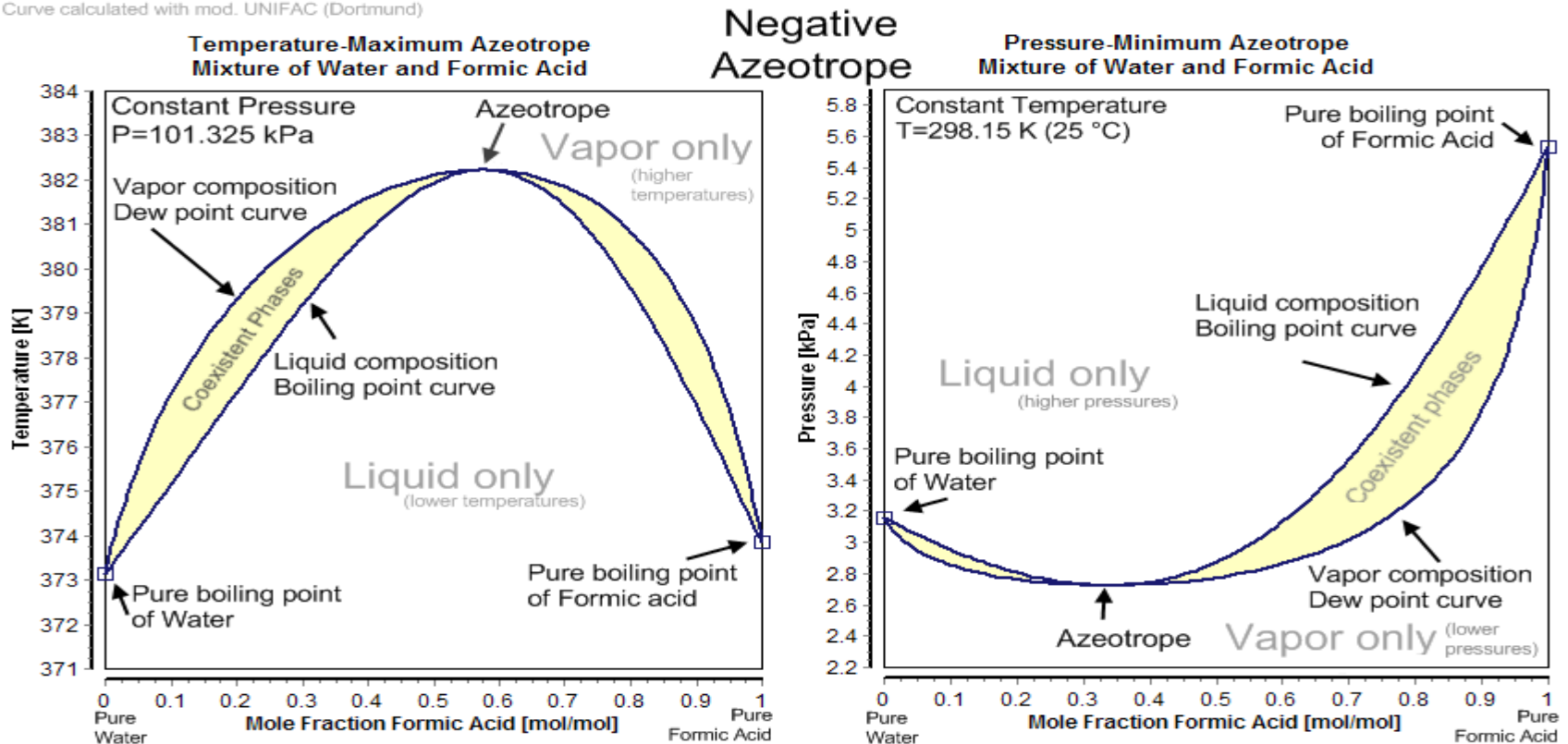


The distillation give **low** boiling point azeotrope or **high** V.P azeotrope
For example (EtOH+H₂O) and (MeOH+ C₆H₆)

B- Negative deviation

- The distillation give **high** boiling azeotrope or **low** V.P. azeotrope for example
- (H₂O+HOAC) and (CHCl₃+ Me₂CO)

Curve calculated with mod. UNIFAC (Dortmund)



- Distillation of HCl+H₂O azotropic mixture with 20.22% composition at 108.08 °C (High boiling) or (Low V.P.) azotrope.
- The composition of this mixture is constant and sufficiently accurate and reproducible so that the solution at 20.22% composition can be used a standard solution in analytical chemistry

C- Immiscible liquids

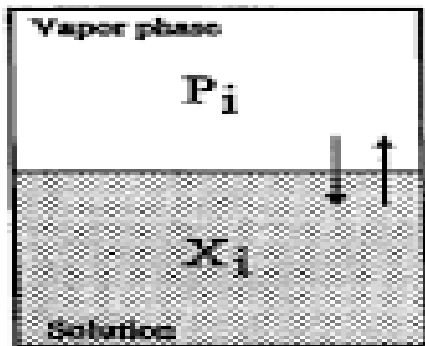
- When a mixture of two immiscible liquids heated, the distillation may be effected when the sum of the partial pressure ($\sum P_i$) is exceeds to atmospheric pressure.
 - $\sum P_i = 1$ atmosphere
- This principle is applied in steam distillation for many organic compound insoluble in water.

- Steam distillation occurs below the normal boiling temperature so that it is useful to obtaining volatile oils from plant tissues without decomposing the oils.
- Example:
- Bromobenzene boils in steam distillation at $95\text{ }^{\circ}\text{C}$
- T_b Bromobenzene = $156.2\text{ }^{\circ}\text{C}$
- T_b water = $100\text{ }^{\circ}\text{C}$

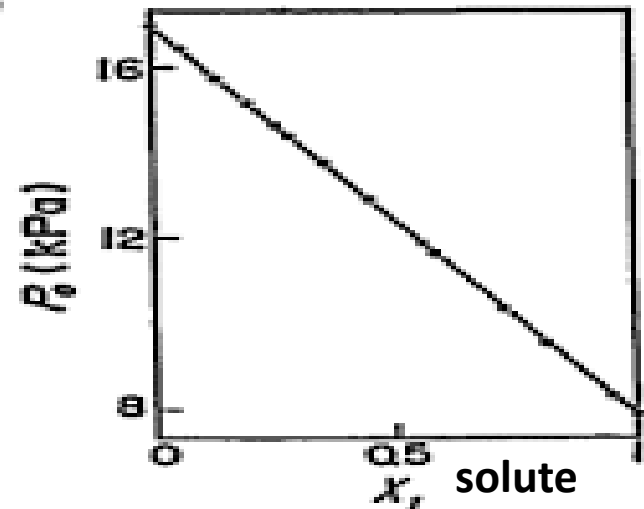
Colligative properties

When a non volatile (solute) combined with a volatile (solvent), the solute reduces the escaping tendency (V.P.) of solvent on basis of Rault's law.

(a)



(b)



The colligative properties can be summarized as the following:

- 1- lowering of V.P. ($\Delta P \propto C$)
- 2- Osmotic pressure ($\pi \propto C$)
- 3- Depression of T_f ($\Delta T_f \propto C$)
- 4- Elevation of T_b ($\Delta T_b \propto C$)

These 4 properties called colligative properties depend chiefly on the **number** rather than the nature of the constituents (on the **concentration**)

Lowering of vapor pressure

For a dilute solution, according to Raoult's law

$$P = X_1 P_1^0$$

$$X_1 = 1 - X_2 \quad \dots\dots\dots (1) \text{ solvent, (2) solute}$$

$$P = (1 - X_2) P_1^0 \longrightarrow P = P_1^0 - P_1^0 X_2 \longrightarrow P_1^0 - P = P_1^0 X_2$$

$$(P_1^0 - P) / P_1^0 = X_2 \quad \text{or} \quad \Delta P / P_1^0 = X_2 = n_2 / (n_1 + n_2)$$

Where ΔP : lowering vapor pressure

$\Delta P / P_1^0$: relative V.P, lowering

Now:

In very dilute solution $n_1 \gg n_2$ so that

$$n_2/(n_1+n_2) \approx n_2/n_1$$

$$\text{And } \Delta P/P^0_1 = X_2 = n_2/n_1 = (W_2/Mw_2) / (w_1/Mw_1)$$

$$[(W_2/Mw_2)/(w_1/Mw_1) * 1000/1000]$$

$$= m * Mw_1/1000$$

$$\Delta P/P^0_1 = X_2 = m * Mw_1/1000$$

$$\Delta P/P^0_1 = 0.018 m \quad \text{..... for aqueous solution}$$