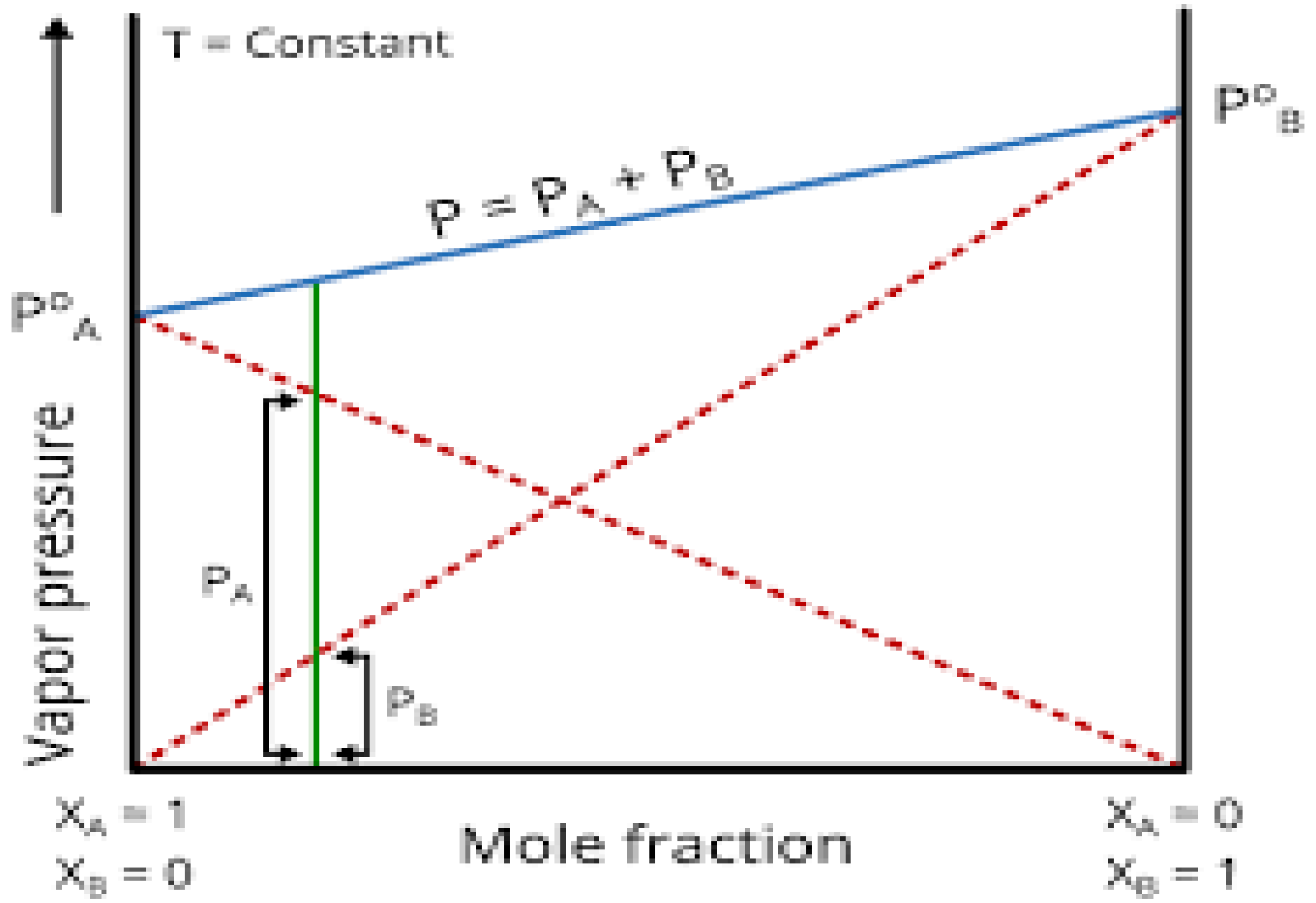


**Ideal solution  
and  
Raoult's law**

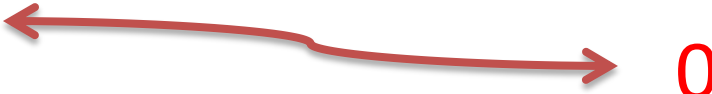
# Rault's law

- The partial vapor pressure ( $P_i$ ) of each volatile constituents in **ideal** solution is equal to vapor pressure of the pure constituent  $P^{\circ}_i$  multiplied by the mole fraction ( $X_i$ ) in the solution.
- $P_A = X_A * P^{\circ}_A$  ,  $P_B = X_B * P^{\circ}_B$
- $X_A = n_A / (n_A + n_B)$  ,  $X_B = n_B / (n_A + n_B)$
- $X_A + X_B = 1$

- The total vapor pressure  $P_t$  is
- $P_t = P_A + P_B$
- $P_t = P_A^0 * X_A + P_B^0 * X_B$



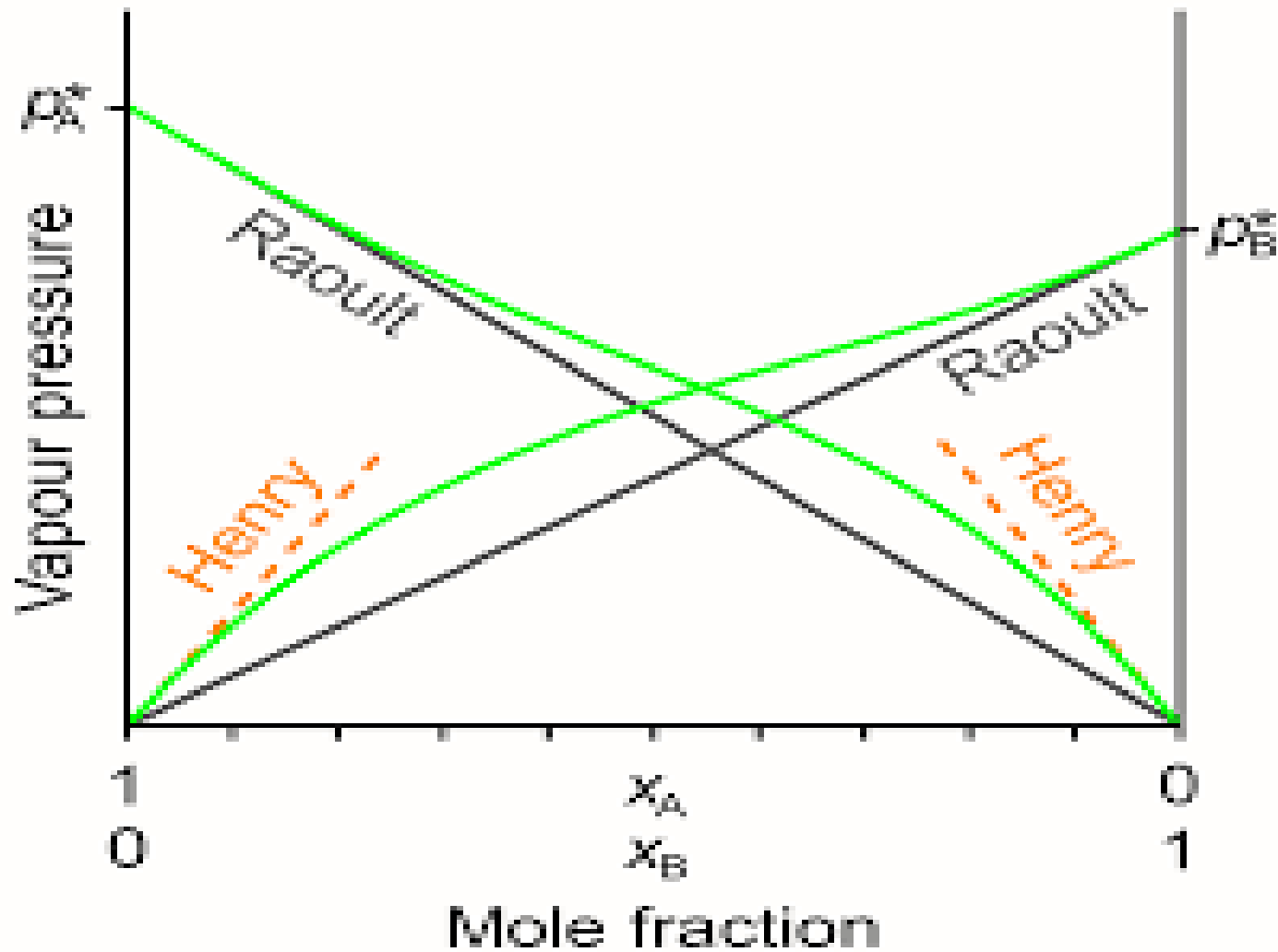
- The vapor pressure (V.P.) is quantitative expression of **escaping** tendency (**free energy**) of each constituent
- For example:
- When  $X_i$  of **more** volatile constituent increased  $\uparrow$  so the total  $P_t$  increased  $\uparrow$
- When  $X_i$  of **less** volatile constituent increased  $\uparrow$  the total pressure  $P_t$  decreased  $\downarrow$

- Raoult's law does not apply in real solution
- But may be in **very dilute** real solution, when the solvent is high  $X \rightarrow 1$
- So Raoult's law will be expressed as:
- $P_{\text{solvent}} = X_{\text{solvent}} P^0_{\text{solvent}}$
- $P_t = P_{\text{solvent}}$  because  $X_{\text{solvent}} \gg X_{\text{solute}}$
- Or  $X_{\text{solute}} \rightarrow 0$
- $P_t = X_{\text{solvent}} P^0_{\text{solvent}} + X_{\text{solute}} P^0_{\text{solute}}$ 


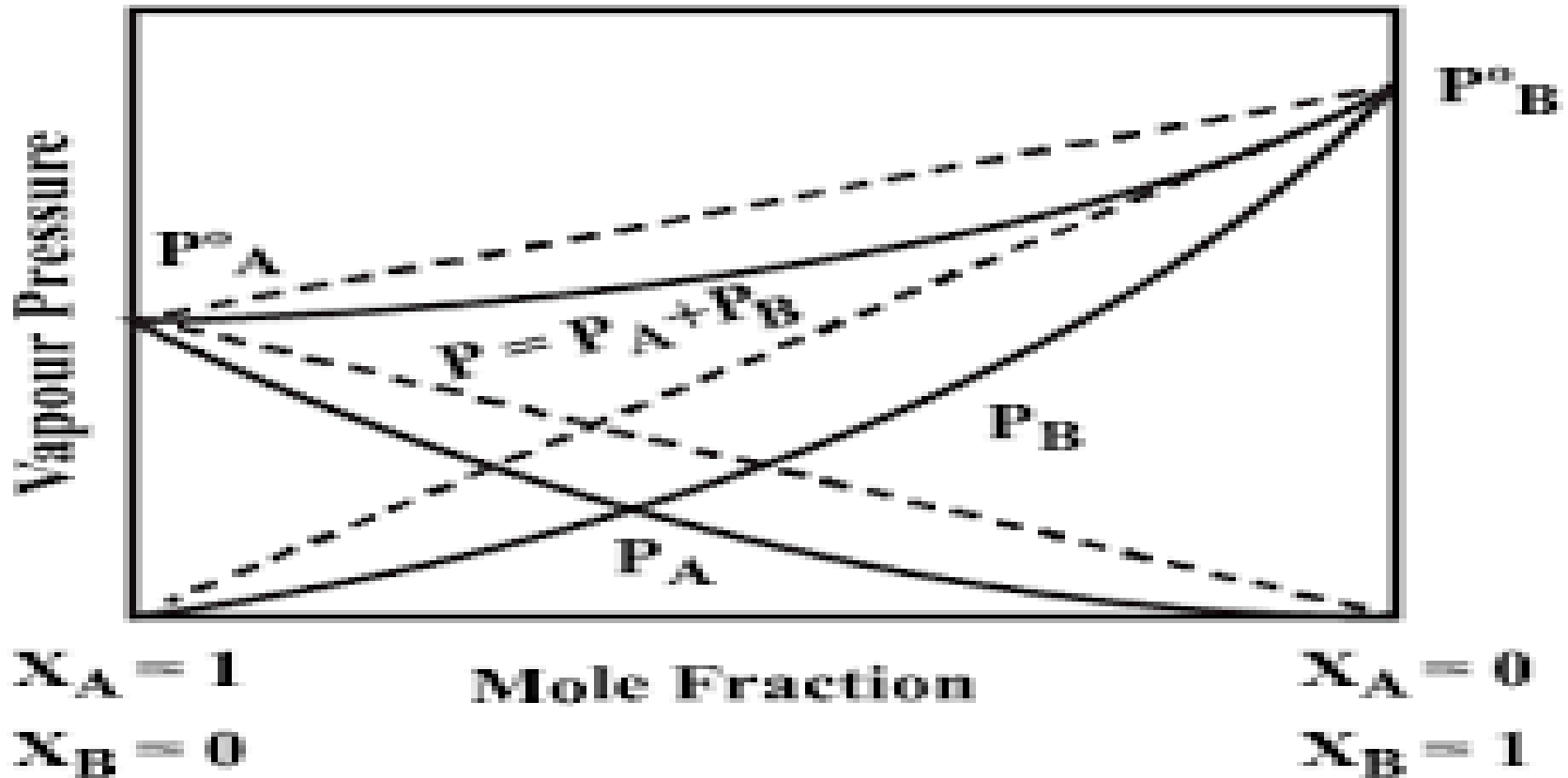
# Henry's law

- For real solution
- Form Raoult's law the **+ev** or **-ev** deviation at low  $X_i$  of each constituent, the v.p. ( $P_i$ ) or escaping tendency will be proportional to its  $X_i$ .
- But the proportionality constant is not  ${}^0P_i$
- The v.p. ( $P_i$ ) of each constituent (solute) can be expressed by Henry's law:
- $P_{\text{solute}} = X_{\text{solute}} K_{\text{solute}}, \quad K_{\text{solute}} \neq P_{\text{solute}}^{\circ}$

# Positive deviation

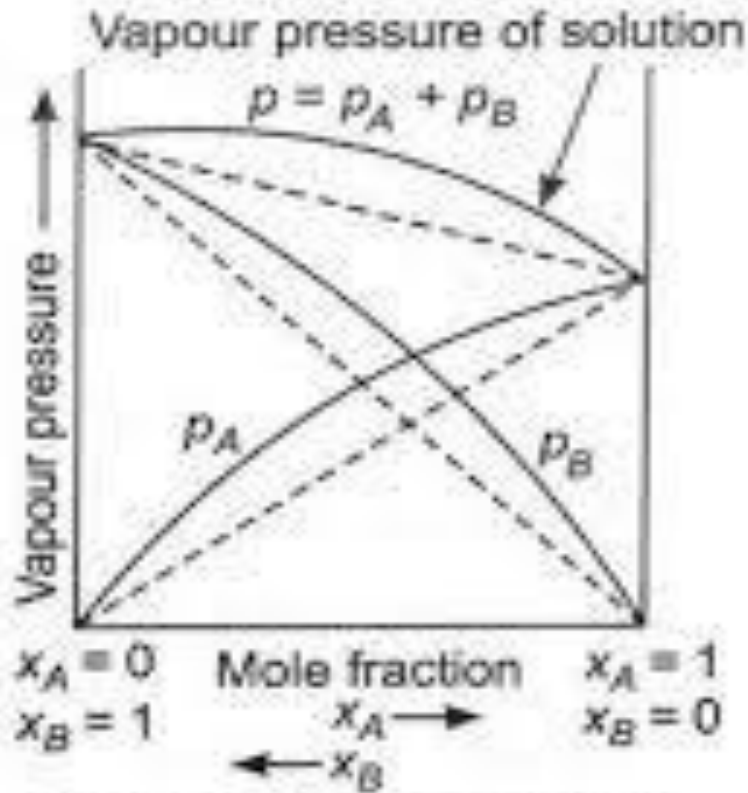


# Negative deviation

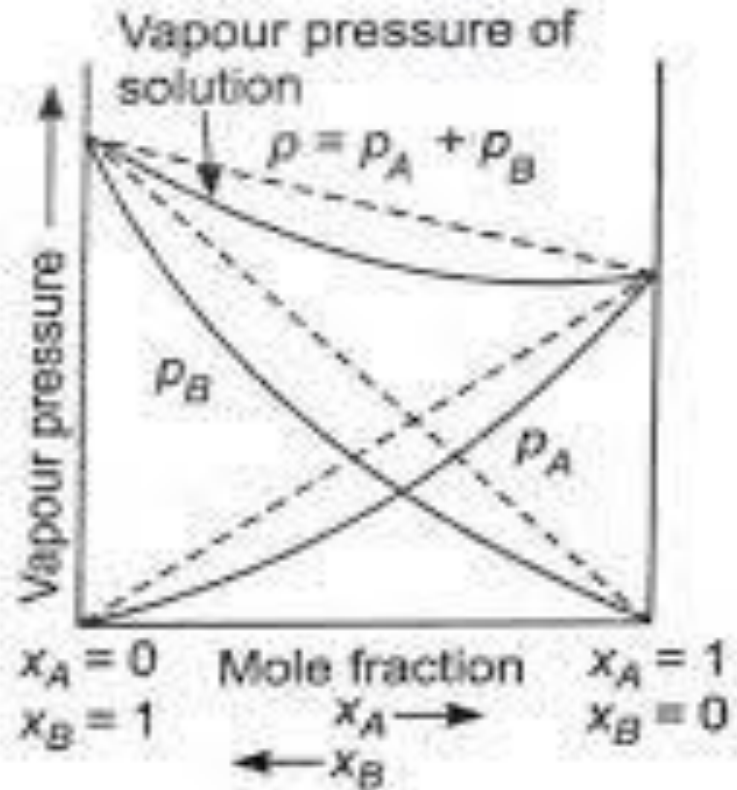


**Negative deviation from  
Raoult's law behaviour**

# +ev and -ev deviation



Vapour pressure diagram showing positive deviation



Vapour pressure diagram showing negative deviation