Ideal and Non-Ideal solution.

(1) **Ideal solution:**An ideal solution may be defined as the solution which obeys Raoult's law over the entire range of concentration and temperature and during the formation of which no change in enthalpy and no change in volume takes place. So for ideal solutions the conditions are,

(i) It should obey Raoult's law, i.e., $P_A = P_A^0 X_A$ and $P_B = P_B^0 X_B$.

(ii) $\Delta H_{\text{mixing}} = 0$

(iii) $\Delta V_{\text{mixing}} = 0$

The solutions in which solvent-solvent and solute-solute interactions are almost of the same type as solvent-solute interactions, behave nearly as ideal solutions.

This type of solutions are possible if molecules of solute and solvent are almost of same size and have identical polarity. For example, solutions of following pairs almost behave as ideal solutions,

n-Heptane and n-hexane.; Chlorobenzene and bromobenzene.

Benzene and toluene; Ethyl bromide and ethyl iodide.

Ethylene bromide and ethylene chloride; Carbon tetrachloride and silicon tetrachloride.

For such solutions the vapor pressure of the solution is always intermediate between the vapor pressures of pure components A and B, i.e., P_A^0 and P_B^0.

(2) **Non-Ideal solution:**The solutions which do not obey Raoult's law and are accompanied by change in enthalpy and change in volume during their formation are called non-ideal solutions. So, for non-ideal solutions the conditions are:

(i) It does not obey Raoult's law. $P_A \neq P_A^0 X_A ; P_B \neq P_B^0 X_B$

(ii) $\Delta H_{\text{mixing}} \neq 0$

(iii) $\Delta V_{\text{mixing}} \neq 0$

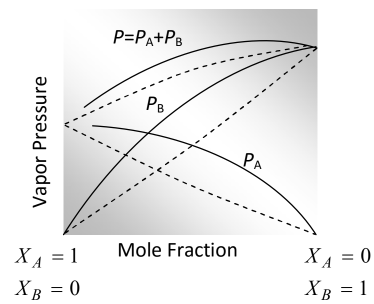
Either component of non-ideal binary solution do not follow Raoult's law. The non-ideal solutions are further divided into two types:

(a) Solutions showing positive deviations. (b) Solutions showing negative deviations.

(a) **Solutions showing positive deviation:**In this type of deviations, the partial vapor pressure of each component (say A and B) of solution is greater than the vapor pressure as expected according to Raoult's law. This type of deviations are shown by the solutions in which solvent-solvent and solute-solute interactions are stronger than solvent-solute interactions.

For the non-ideal solutions exhibiting positive deviation.

$P_A > P_A^0 X_A, P_B > P_B^0 X_B$; $\Delta H_{\text{mixing}} = +ve$; $\Delta V_{\text{mixing}} = +ve$



Partial and total vapor pressure curves for solutions that show positive deviations

E.g. of solutions showing positive deviations

$(CH_3)_2CO + CS_2$; $(CH_3)_2CO + C_2H_5OH$

$C_6H_6 + (CH_3)_2CO$; $CCl_4 + C_6H_6$

$CCl_4 + CHCl_3$; $CCl_4 + C_6H_5CH_3$

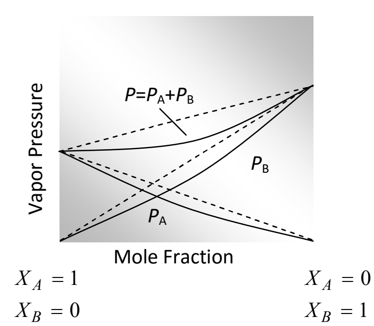
$H_2O + CH_3OH$; $H_2O + C_2H_5OH$

$CH_3CHO + CS_2$; $CHCl_3 + C_2H_5OH$

(b) **Solutions showing negative deviation:**In this type of deviations the partial vapor pressure of each component of solution is less than the vapor pressure as expected according to Raoult's law. This type of deviations are shown by the solutions in which solvent-solvent and solute-solute interactions are weaker than solvent-solute interactions.

For non-ideal solution showing negative deviation.

$P_A < P_A^0 X_A, P_B < P_B^0 X_B$; $\Delta H_{\text{mixing}} = -ve$; $\Delta V_{\text{mixing}} = -ve$



A vapor pressure curve showing negative deviation (solid lines) from ideal

E.g. of solutions showing negative deviations

$CH_3COOH + C_5H_5N$ (pyridine)

$CHCl_3 + (CH_3)_2CO$; $CHCl_3 + C_6H_6$

$CHCl_3 + (C_2H_5)_2O$; $H_2O + HCl$

$H_2O + HNO_3$; $(CH_3)_2CO + C_6H_5NH_2$

Differences between ideal and non-ideal solutions

Ideal solutions	**Solutions with positive deviations**	**Solutions with negative deviations**
A……B interactions are similar to A……A and B……B interactions	A……B interactions are smaller than A……A and B……B interactions	A……B interactions are greater than A……A and B……B interactions
$P_A = P_A^0 X_A ; P_B = P_B^0 X_B$	$P_A > P_A^0 X_A ; P_B > P_B^0 X_B$	$P_A < P_A^0 X_A ; P_B < P_B^0 X_B$
$\Delta H_{\text{sol.}} = 0$	$\Delta H_{\text{sol.}} > 0$	$\Delta H_{\text{sol.}} < 0$
$\Delta V_{\text{mix}} = 0$	$\Delta V_{\text{mix}} > 0$	$\Delta V_{\text{mix}} < 0$
Do not form azeotrope	Exhibit minimum boiling point azeotropy	Exhibit maximum boiling azeotropy