

Non Ideal Solutions

Solution which do not follow Raoult's law are called non ideal solutions. These are of two types:

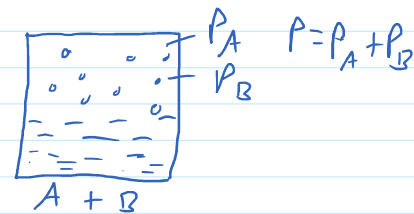
- i) Solutions showing positive deviation
- ii) Solutions showing negative deviation

Negative deviation solutions

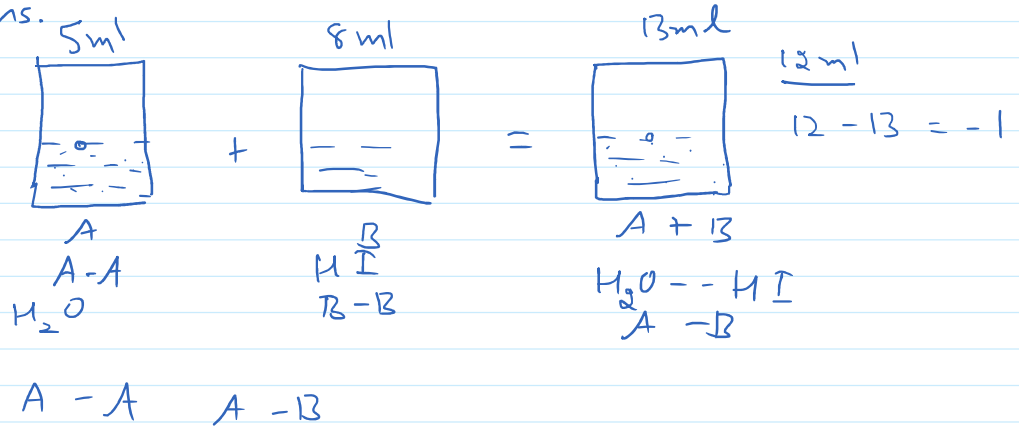
- i) Vapour pressure (P) of these solution is less than that predicted by Raoult's law.

$$P_A < P_A^0 x_A \quad P_B < P_B^0 x_B$$

$$P < P_A^0 x_A + P_B^0 x_B$$



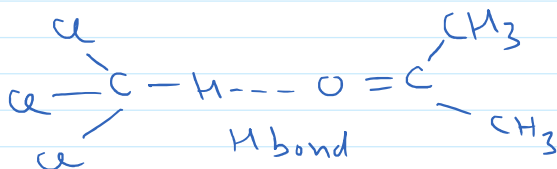
- ii) A-B interactions are stronger than A-A interaction and B-B interactions.



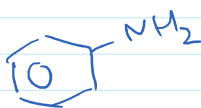
- iii) $\Delta V_{mix} < 0$ (ideal $\Delta V_{mix} = 0$)
- iv) $\Delta H_{mix} < 0$ (ideal $\Delta H_{mix} = 0$)
- v) $\Delta S_{mix} > 0$ (ideal $\Delta S_{mix} > 0$)
- vi) $\Delta G_{mix} < 0$ (ideal $\Delta G_{mix} < 0$)

vii) Examples:

- a) Chloroform + acetone

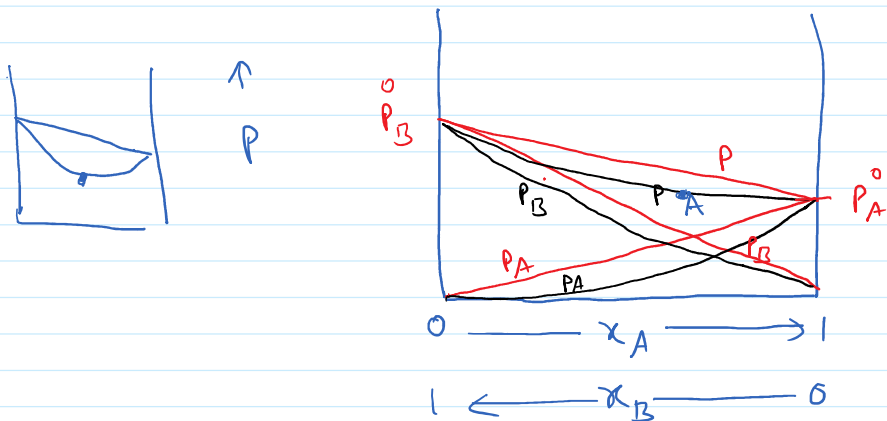


b) Phenol + aniline.



c) strong acid + water

(HClO_4 , H_2SO_4 , HNO_3 , HBr , HI , HCl) + H_2O



Black \rightarrow negative deviation
 $P = P_A + P_B$

Red \rightarrow ideal solution
 $P = P_A + P_B$

A \rightarrow Maximum boiling azeotrope

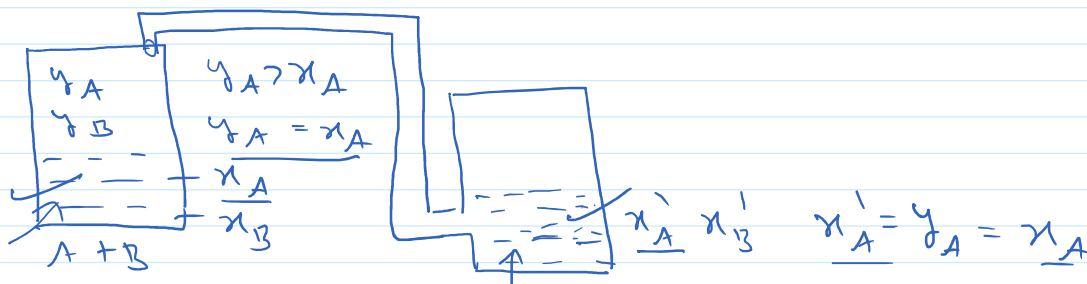
VIII)

Boiling point of these solution is more than expected value.

Azeotropes

- i) These are solutions which have same composition in liquid phase, as well as vapour phase ($x_A = y_A$, $x_B = y_B$).
- ii) These boil at constant temperature.

A $>$ B
 (more volatile)



iii) Solutions showing negative deviation form maximum boiling azeotropes

iv) For solutions showing negative deviation, azeotropic mixture is formed at a point where vapour pressure is minimum.

Solutions showing positive deviation

i) For these solutions vapour pressure is more than that predicted by Raoult's law.

$$P_A > P_A^0 x_A \quad P_B > P_B^0 x_B \quad P > P_A^0 x_A + P_B^0 x_B$$

ii) A-B interactions are weaker than A-A interactions and B-B interactions.

iii) $\Delta V_{mix} > 0$ (ideal $\Delta V_{mix} = 0$)

iv) $\Delta H_{mix} > 0$ (ideal $\Delta H_{mix} = 0$)

v) $\Delta S_{mix} > 0$ ($\Delta S_{mix} > 0$)

vi) $\Delta G_{mix} < 0$ ($\Delta G_{mix} < 0$)

vii) Example

a) $H_2O + C_6H_6$ (Benzene breaks H bonding between H_2O)
 \downarrow
 H bonding

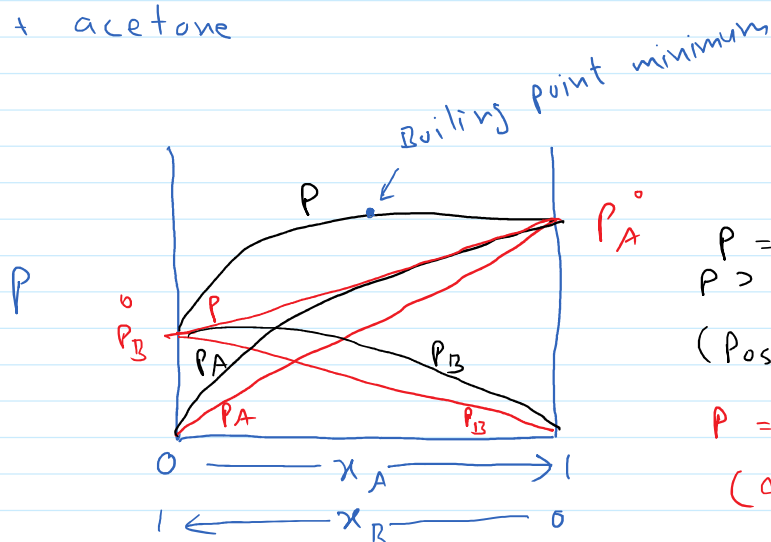
b) $H_2O + C_2H_6$

c) ethanol + water

d) ethanol + acetone

e) $CS_2 + acetone$

viii)



$$P = P_A + P_B$$

$$P > P_A^0 x_A + P_B^0 x_B$$

(Positive deviation)

$$P = P_A + P_B = P_A^0 x_A + P_B^0 x_B$$

(ideal)

ix) Boiling point of these solution is less than expected value.

x) These form minimum boiling azeotropes.

21) Azeotropic mixture is formed at a point where vapour pressure is maximum.