

5. Azeotrope - This type of liquid mixture which boils at the same temperature without undergoing any change in composition is ~~known~~ known as constant boiling mixture or azeotropic mixture or azeotrope. ~~The solute~~ There are two types of azeotropes - Minimum boiling azeotrope and maximum boiling azeotrope. (Table 2.6, 2.7).

5.1. Minimum boiling azeotrope - ~~at~~ These solutions show large <sup>positive</sup> deviation from Raoult's law at a specific composition.

For example; ethanol-water mixture. (By fermentation)

Ethanol	- 95.57 mass %
Water	- 4.43 mass %

This will be boiling at 351.1 K temperature which is less than boiling point of both ethanol (351.3 K) and Water (373 K).

This is known as minimum boiling azeotrope because the partial vapour pressure of the two components in the mixture are the maximum while their boiling points are the minimum. So, alcohol and water will behave as if they were constituents of a pure liquid and they will distil together.

5.2. Maximum boiling azeotrope - These solutions show large negative deviation from Raoult's law at a specific composition.

i) In this case, the vapour pressure will be lowered and consequently the boiling point will be raised.

ii) The partial vapour pressure of the two constituents present will be minimum and boiling points the maximum.

iii) Ex: HCl - 20.2 mass %,  $H_2O$  - 79.8 mass %.  
It boils at 383 K and this temperature is more than the bp temperature of both HCl (188 K) and water (373 K).

Thus, in the case of minimum boiling azeotrope, the boiling point of the azeotropic mixture is less than the boiling points of any of the two pure components. In the case of maximum boiling azeotrope, the boiling point of the mixture is more than the boiling point of any of the two components in pure state.

Teacher's Signature \_\_\_\_\_

▼ TABLE 2.6. Minimum Boiling Azeotropes

Components		Mass % of B in the azeotrope	Boiling points (K)		
A	B		A	B	Azeotrope
Water, H <sub>2</sub> O	Ethanol, C <sub>2</sub> H <sub>5</sub> OH	95.57	373	351.3	351.1
Chloroform, CHCl <sub>3</sub>	Ethanol, C <sub>2</sub> H <sub>5</sub> OH	67.00	334	351.3	332.3
Benzene, C <sub>6</sub> H <sub>6</sub>	Ethanol, C <sub>2</sub> H <sub>5</sub> OH	32.40	353.2	351.3	341.2
Acetone, (CH <sub>3</sub> ) <sub>2</sub> C=O	Carbon disulphide, CS <sub>2</sub>	67.00	329.25	319.25	312.25

▼ TABLE 2.7. Maximum Boiling Azeotropes

Components		Mass % of B in the azeotrope	Boiling points (K)		
A	B		A	B	Azeotrope
Water, H <sub>2</sub> O	Hydrochloric acid, HCl	20.20	373	188	383
Water, H <sub>2</sub> O	Nitric acid, HNO <sub>3</sub>	68.00	373	359	393.5
Chloroform, CHCl <sub>3</sub>	Acetone, (CH <sub>3</sub> ) <sub>2</sub> CO	20.00	334	329.25	347.7
Chloroform, CHCl <sub>3</sub>	Methyl acetate, CH <sub>3</sub> COOCH <sub>3</sub>	23.00	334	330	347.8

v.8) The vapour pressure of pure liquids A and B are 450 and 700 mm Hg respectively, at 350 K. Find out the composition of the liquid mixture if total vapour pressure is 600 mm Hg. Find the composition of the vapour phase.

Sol: Vapour pressure of pure liquid A ( $P_A^{\circ}$ ) = 450 mm  
 Vapour pressure of pure liquid B ( $P_B^{\circ}$ ) = 700 mm  
 Total vapour pressure of solution ( $P$ ) = 600 mm

According to Raoult's law,

$$P = P_A^{\circ} x_A + P_B^{\circ} x_B = P_A^{\circ} x_A + P_B^{\circ} (1 - x_A)$$

$$\Rightarrow 600 \text{ mm} = 450 \text{ mm} \times x_A + 700 \text{ mm} (1 - x_A)$$

$$\Rightarrow 600 = 700 \text{ mm} + x_A (450 - 700) \text{ mm}$$

$$\Rightarrow 600 = 700 - x_A (250 \text{ mm})$$

$$\Rightarrow x_A = \frac{(600 - 700) \text{ mm}}{-250 \text{ mm}} = 0.40$$

$$\text{Mole fraction of A } (x_A) = 0.40$$

$$\text{Mole fraction of B } (x_B) = 1 - 0.40 = 0.60$$

$$p_A = p_A^{\circ} x_A = (450 \text{ mm}) \times 0.40 = 180 \text{ mm}$$

$$p_B = p_B^{\circ} x_B = (700 \text{ mm}) \times 0.60 = 420 \text{ mm}$$

$$\text{Mole fraction of A in vapour phase} = \frac{p_A}{p_A + p_B} = \frac{180}{180 + 420}$$

$$= 0.30$$

Mole fraction of B in the vapour phase =

$$= \frac{P_B}{P_A + P_B} = \frac{420}{180 + 420} = 0.70$$