

Today's Goal



Non-Ideal Solution + Azeotropes





Non-Ideal Solution



Definition



The solution which do not obey Raoult's law over the entire range of concentration are known as non ideal solutions.

There are two types of non ideal solutions

1. Positive deviation
2. Negative deviation





Properties of Positive deviation

1. $\Delta_{\text{mix}} H > 0$, $\Delta_{\text{mix}} V > 0$, $\Delta_{\text{mix}} P > 0$
2. $\Delta_{\text{mix}} S > 0$, $\Delta_{\text{mix}} G < 0$
3. If the intermolecular attractive forces between the A-A and B-B are greater than those between A-B, this leads to the formation of positive deviation.
4. Examples –
 - Ethanol + Acetone
 - CS_2 + Acetone
 - Ethanol + H_2O



Graph of Positive deviation





Properties of Negative Deviation

1. $\Delta_{\text{mix}} H < 0$, $\Delta_{\text{mix}} V < 0$, $\Delta_{\text{mix}} P < 0$
2. $\Delta_{\text{mix}} S > 0$, $\Delta_{\text{mix}} G < 0$
3. If the intermolecular attractive forces between the A-A and B-B are lesser than those between A-B, this leads to the formation of negative deviation.
4. Examples –
 - Phenol + Acetone
 - Chloroform + Acetone
 - $\text{HNO}_3 + \text{H}_2\text{O}$



Trick to find positive and negative deviation



1. $\text{CCl}_4 + \dots\dots\dots$
2. $\text{CHCl}_3 + \dots\dots\dots$
3. Acid + Water
4. Important example $\text{CHCl}_3 + \text{Acetone}$



Graph of Negative deviation





Azeotropes



Definition



1. Some liquids on mixing, form azeotropes which are binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature.
2. In such cases, it is not possible to separate the components by fractional distillation.
3. There are two types of azeotropes called minimum boiling azeotropes and maximum boiling azeotropes.



Types of Azeotropes



1. Solution which show a large positive deviation from Raoult's law form minimum boiling azeotropes.
2. The solutions that show large negative deviation from Raoult's law form maximum boiling azeotropes.





Q.1 Which of the following liquid pairs shows a positive deviation from Raoult's law?



Acetone-Chloroform



Benzene-methanol



Water-nitric acid



Water-hydrochloric acid





2. Which of the following solutions can have boiling point less than that of both the individual components ?



n-Hexane and n- Heptane



HNO_3 and H_2O



$\text{HCl} + \text{H}_2\text{O}$



$\text{C}_2\text{H}_5\text{OH}$ and H_2O





Azeotropic mixture :



Are those which can be fractionally distilled



Have definite constant boiling point



Have same definite composition at any pressure



Are those which have different composition in liquid and vapour state





Select the mixture in which volume of solution is less than $2V$. V mL on mixing V mL each of the two miscible liquids :



$\text{CCl}_4 + \text{CS}_2$



Benzene + Toulene



$\text{CHCl}_3 + \text{CH}_3\text{COCH}_3$



Hexane + Pentane





Which of the following does not show negative deviation from Raoult's law ?



Chloroform-Acetone



Acetone-Benzene



Chloroform-Ether



Chloroform-Benzene



Q Which will form maximum boiling azeotrope ?



- A** $\text{C}_6\text{H}_6 + \text{C}_6\text{H}_5\text{CH}_3$ Solution
- B** $\text{HNO}_3 + \text{H}_2\text{O}$ solution
- C** $\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$ solution
- D** n-hexane and n-heptane





The azeotropic mixture of water (B.P = 100°C) and HCl (B.P = 86°C) boils at about 120°C . During fractional distillation of this mixture, it is possible to obtain :



Pure HCl



Pure H_2O



Pure H_2O as well as pure HCl



Neither H_2O nor HCl





Azeotropic mixture of water and HCl boils at 381.5 K. By distilling the mixture, it is possible to obtain:



Pure HCl only



Pure water only



Neither water nor HCl



Both water and HCl in pure state





An azeotropic mixture of two liquids has a boiling point higher than either of them when it :



Shows positive deviation from Raoult's law



Shows negative deviation from Raoult's law



Shows ideal behaviour



N.O.T.A





The boiling point of an azeotropic mixture of water-ethanol is less than that of both water and ethanol. Then :



The mixture will show negative deviation from Raoult's law



The mixture will show positive deviation from Raoult's law



The mixture will show no deviation from Raoult's law



This mixture cannot be considered as true solution





Total vapour pressure of mixture of 1 mol X ($P^\circ_x=150$ torr) and 2 mol Y ($P^\circ_y=300$ torr) is 240 torr. In this case:



There is negative deviation from Raoult's law



There is positive deviation from Raoult's law



There is no deviation from Raoult's law



Can not be decided





In a mixture of A and B, components show positive deviation when :



A-B interaction is stronger than A-A and B-B interaction



A-B interaction is weaker than A-A and B-B interaction



$\Delta V_{\text{mix}} < 0$, $\Delta S_{\text{mix}} > 0$



$\Delta V_{\text{mix}} = 0$, $\Delta S_{\text{mix}} > 0$





A solution of acetone In ethanol :



Behaves like a near ideal solution



Obeys Raoult's law



Show a negative deviation from Raoult's law



Shows a positive deviation from Raoult's law

