BE TRUE

Deviations from Raoult's law

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Why do solutions deviate from Raolut`s law/Ideal behaviour.

- Non ideal solutions deviate from Raoult`s law because the intermolecular forces between molecules of different kinds in solution, are not uniform with the intermolecular forces between molecules in pure liquids.
- On mixing the liquids, the intermolecular forces between the molecules can be weaker or stronger, as compared to the intermolecular forces between the molecules in pure liquids.
- This gives rise to two types of deviations from Raoult`s law namely;

a) Negative deviation.

b) Positive deviation

NEGATIVE DEVIATION

- It arises when the intermolecular forces of attraction between molecules of different components in the solution, are stronger than the intermolecular forces of attraction between molecules of the pure components.
- As a result, the escaping tendency of the molecules of each of the components in the mixture is lower than when the components are pure on heating at the same temperature.
- This causes the vapour pressure of the mixture to be lower than what Raoult`s law predicts or that of an ideal solution.

Negative Deviation Cont`d

Due to strong intermolecular forces of attraction formed in the solution;

- there is reduction in total volume (the total volume of the solution formed is less than the expected volume) on mixing the liquids.
- heat is given out on forming the solution i.e. the process of forming the mixture is exothermic.

Question:

a) Explain why some solutions deviate negatively from Raoult`s law.

b) State any three characteristics of solutions that show negative deviation from Raoult`s law. Explain what causes these characteristics.

Negative Deviation Cont`d.

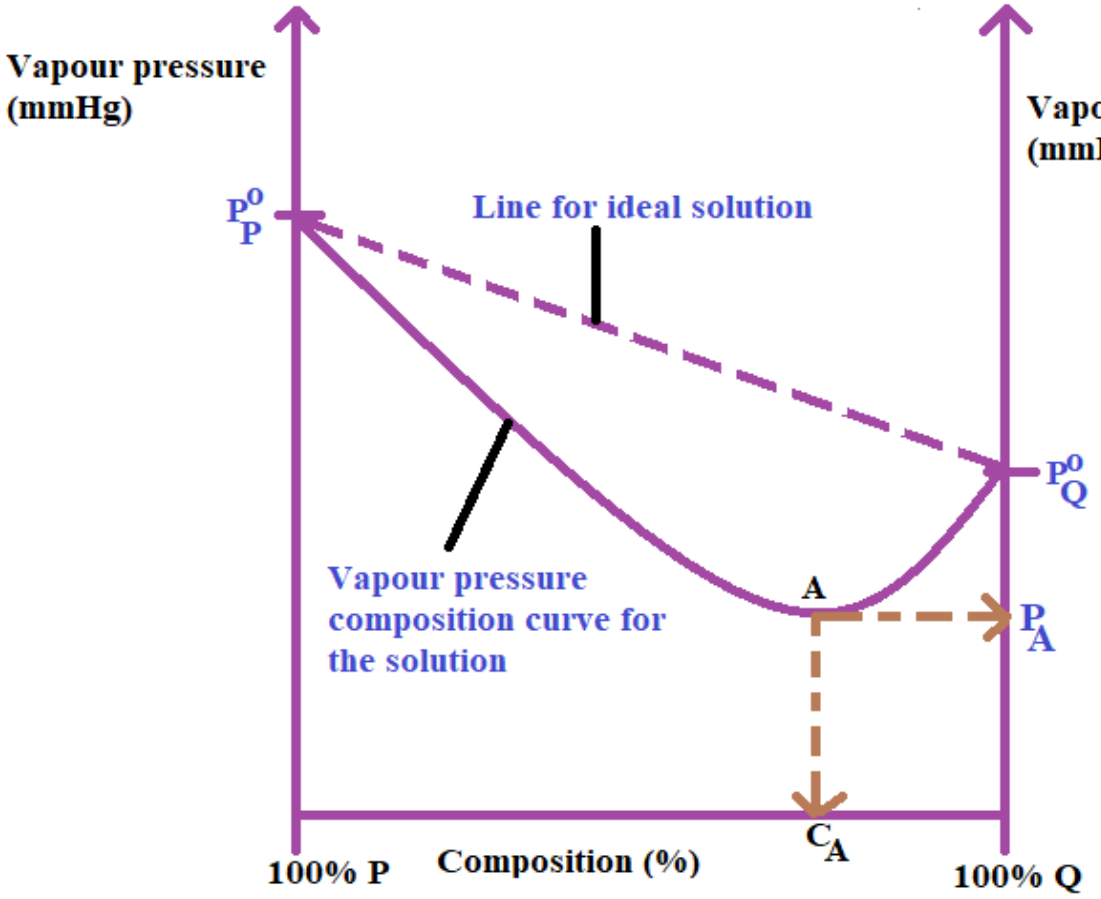
Examples of miscible liquids that form mixtures with negative deviation from Raoult`s law include;

- Water and sulphuric acid
- Water and nitric acid
- Water and hydrochloric acid
- Aniline (Aminobenzene) and pyridine

Question.

Explain why a solution of sulphuric acid in water deviates **negatively** from Raoult`s law.

Vapour pressure-composition diagram for solutions with negative deviation



P_P^o is vapour pressure of pure P

P_Q^o is vapour pressure of pure Q

A is the azeotropic point

C_A is the composition of the azeotropic mixture

P_A is the vapour pressure of the azeotropic mixture

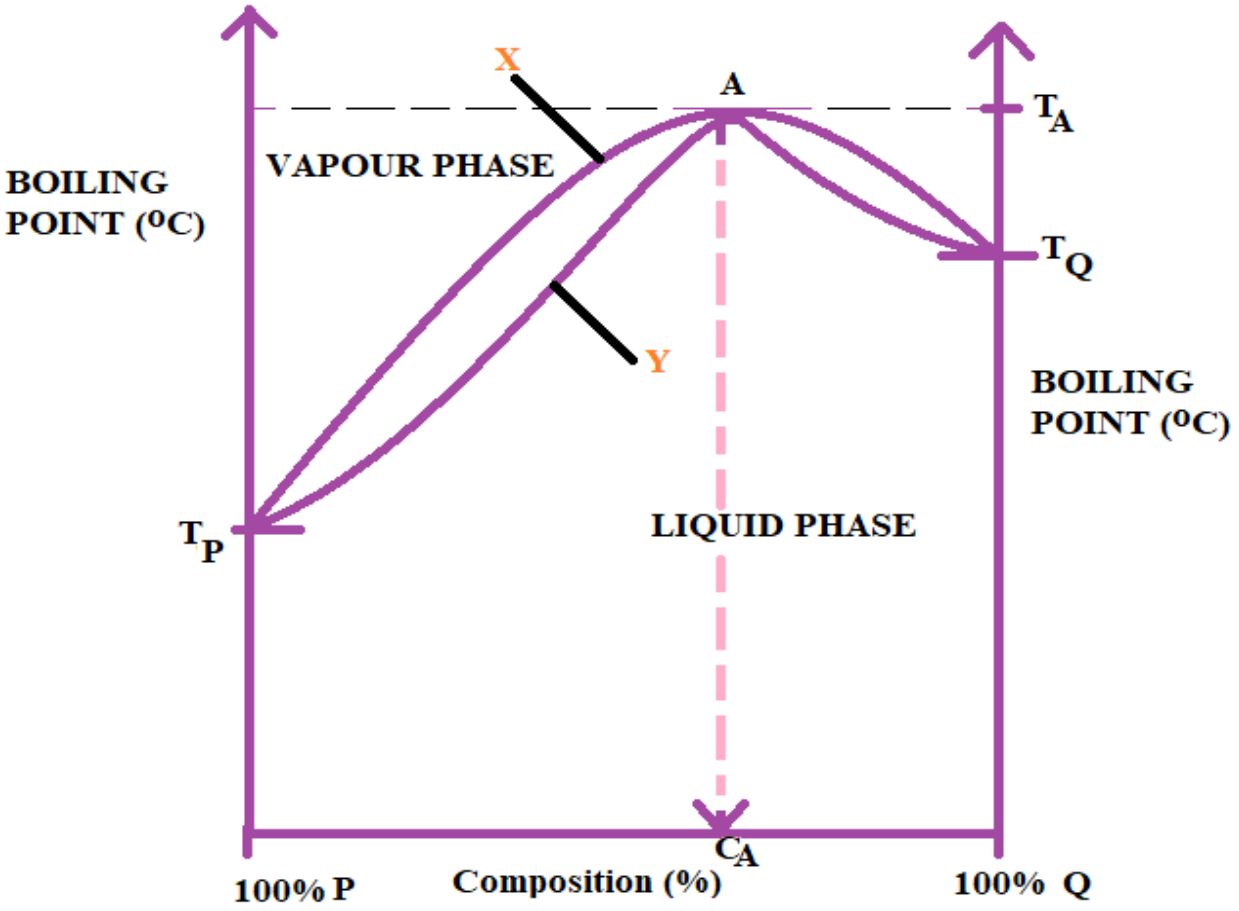
BenSegu Diagrams

Vapour Pressure Diag. Cont`d.

Explain the shape of the graph above.

- On adding liquid Q to liquid P, strong intermolecular forces of attraction between their molecules are formed. These forces increase in strength with increase in composition of Q till maximum.
- The escaping tendency of the molecules goes on reducing and the vapour pressure of the solution becomes increasingly lower than that predicted by Raoult`s law.
- At the minimum point, the azeotropic mixture is formed, that has the strongest intermolecular forces of attraction between the different molecules, causing it to have the lowest escaping tendency of the molecules and the minimum vapour pressure.
- Beyond the azeotropic point, the vapour pressure increases due to increase in the composition of Q, which is more volatile than the azeotropic mixture.

Boiling point-composition diagram for solutions with negative deviation



Features of the diagram.

- X is the boiling point composition curve for the equilibrium vapour.
- Y is the boiling point composition curve for the liquid mixture.
- T_P is the boiling point of pure liquid P
- T_Q is the boiling point of pure liquid Q
- A is the azeotropic point
- T_A is the boiling point of the Azeotropic mixture
- C_A is the composition of the azeotropic mixture

Diagram cont`d

Describe the trend of the curve Y from point Tp to point A.

Boiling point of the mixture increases with increase in composition of Q up to point A.

Diagram cont`d

Explain the shape of curve Y from point Tp to point A.

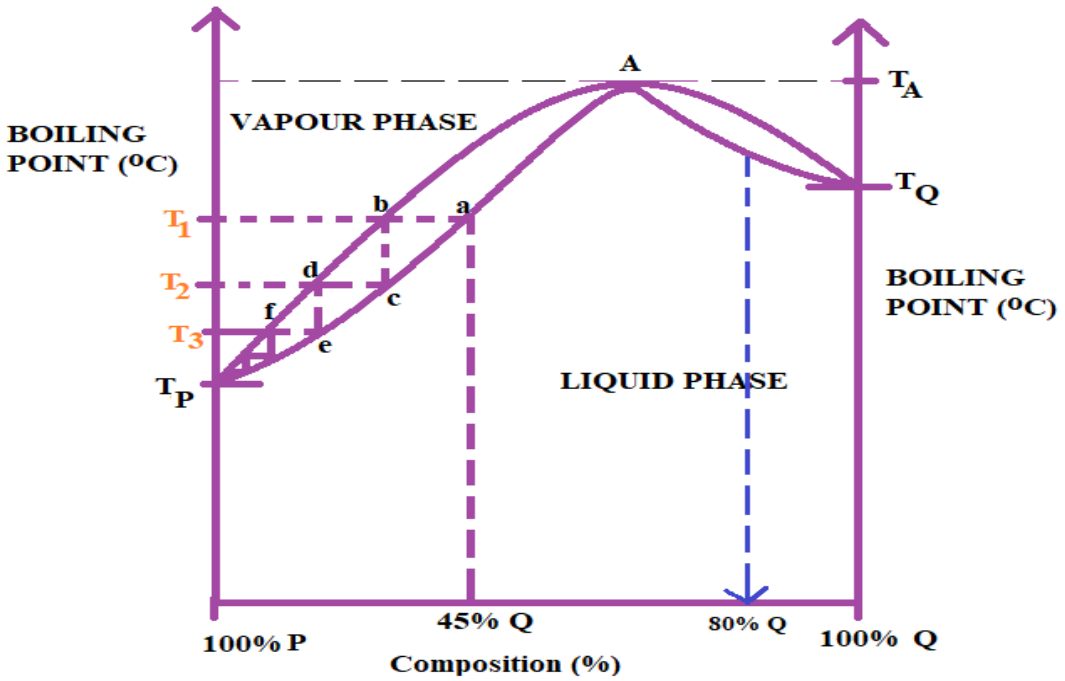
- On adding liquid Q to liquid P, strong intermolecular forces of attraction are formed between their molecules. These forces increase in magnitude with increase in the composition of Q.
- This causes the escaping tendence of the molecules in the mixture to go on reducing on heating.
- The vapour pressure of the mixture goes on reducing
- Therefore, a higher temperature is required to raise the vapour pressure of the solution to be equal to the external pressure. This causes the boiling point to go on increasing up to the maximum.
- This maximum boiling point is the boiling point of the azeotropic mixture whose composition is C_A.

Fractional Distillation of solutions with negative deviation

Consider the mixture above of P and Q with negative deviation from Raoult`s law. Use the Diagram to **describe what happens** if a mixture containing **45% Q** is **fractionally distilled**.

Important aspects:

- Successive boiling points of liquid mixtures (show that they are reducing)
- Composition of the vapour (always rich in the more volatile component)
- What is collected as distillate and residue.



Fractional Distillation of solutions with negative deviation cont`d

- Using the diagram above, describe what would happen if a mixture containing 20% P is fractionally distilled.

POSITIVE DEVIATION

- This arises due to weak intermolecular forces of attraction formed between the molecules of the different components in the solution, and are weaker than those in the pure components.
- Due to this, the escaping tendency of the molecules from the liquid phase to the vapour phase is higher than in pure components.
- This causes the vapour pressure to be higher than what Raoult`s law predicts.

Positive Deviation cont`d

Due to weak intermolecular forces of attraction formed in the solution;

- there is increase in total volume (the total volume of the solution formed is higher than the expected volume)
- heat is absorbed on forming the solution.

Question:

a) Explain why some solutions deviate **positively** from Raoult`s law.

b) State any **three** characteristics of solutions that show **positive** deviation from Raoult`s law. Explain what causes these characteristics.

Positive Deviation cont`d

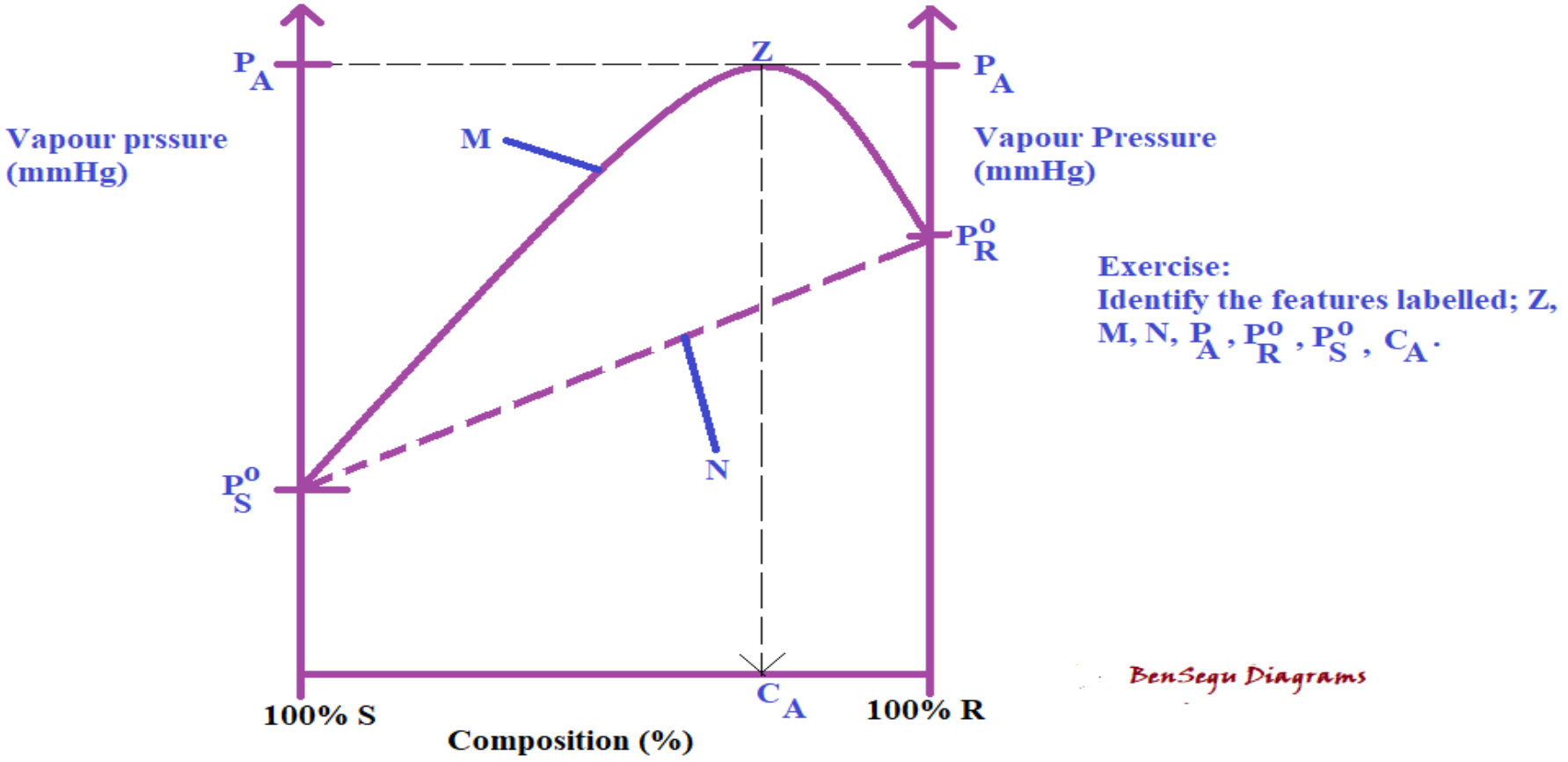
Examples of miscible liquids that form solutions with positive deviation from Raoult`s law include;

- Water and ethanol.
- Propanone and water.
- Propan-1-ol and water

Question:

Explain why the solution of propanone in water deviates positively from Raoult`s law.

Vapour Pressure Composition Diagram for Solutions with Positive Deviation



Exercise:
Identify the features labelled; Z, M, N, P_A, P^o_R, P^o_S, C_A.

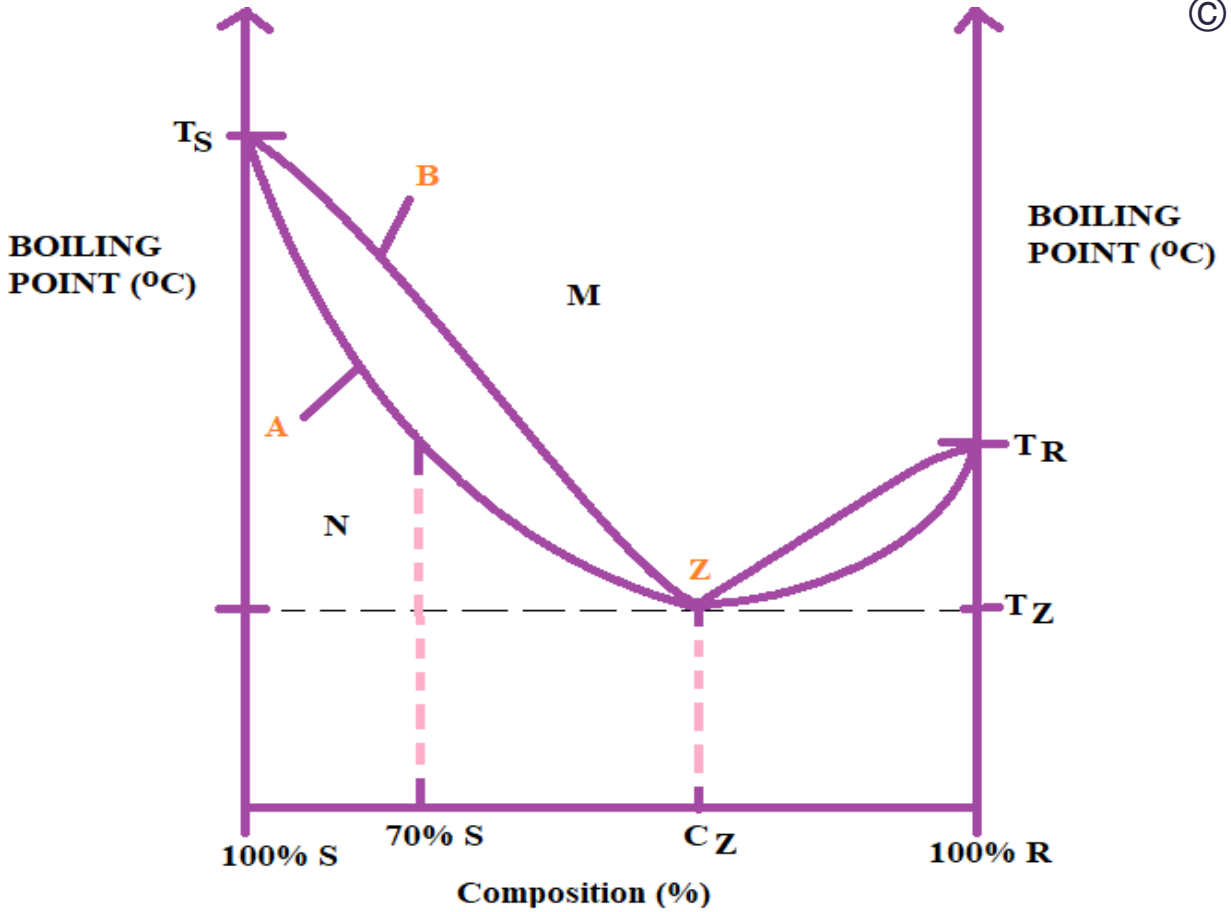
BenSegu Diagrams

Diag. Cont`d

Exercise:

Explain the shape of the graph above. (Refer to audio-video and relate to the explanation for negative deviation)

Boiling Point-Composition Diagram for a solution with positive deviation



Consider two miscible liquids S and R where R is more volatile than S.

Diagram cont`d

Exercise:

a) Name the features of the diagram labelled; A, B, Z, T_R, T_S,T_Z and c_z.

b) Identify the phases existing in the regions M and N.

c) Describe and explain the shape of curve A from point Ts to point Z.

d) Describe what happens if a liquid mixture containing 70% S is fractionally distilled.

In the Next video;

- Azeotropic Mixtures.
- What are they?
- Methods of separating them.
- Their similarity with pure liquids.

Thanx for your attendance

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