

Ideal and Non-ideal Solutions

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The binary liquid-liquid solution be classified into two types:

- (1) ideal solution
- (2) non-ideal solutions

These may be described as follows:

An ideal solution may be defined as the solution which obeys Raoult's law exactly over the entire range of concentration. Such solutions are formed by mixing of two components which are identical in molecular size, in structure and have almost identical intermolecular forces. In these solutions, the intermolecular interaction between the components (A-B attractions) are of same magnitude as the intermolecular interaction in pure components (A-A and B-B attractions). According to Raoult's law, the partial vapour pressure of two components of the solution may be given as:

$$p_A = p_A^0 X_A \quad \text{and} \quad p_B = p_B^0 X_B$$

$$\text{Total pressure } p = p_A + p_B = p_A^0 X_A + p_B^0 X_B$$

The ideal solutions have also following characteristics:

- (i) Heat change on mixing is zero: Since there is no change in magnitude of the attractive forces in the two components present, the heat change i.e., $\Delta_{\text{mixing}} H$ in such solutions must be zero.
- (ii) Volume change on mixing is zero: In ideal solutions, the volume of the solution is the sum of the volume of the components before mixing i.e., there is no change in volume on mixing or $\Delta_{\text{mixing}} V$ is zero. For example, when we mix 100 cm^3 of benzene with 100 cm^3 of toluene, the volume of the solution is found to be exactly 200 cm^3 . Therefore, there is no change in volume on mixing i.e., $\Delta_{\text{mixing}} V = 0$. It has been noticed that the solutions generally tend to become ideal when they are dilute.

Example of ideal solutions: In fact, ideal solutions are quite rare but many solutions practically behave as ideal.

A few examples of ideal solutions are:

- (i) benzene and toluene
- (ii) n-hexane and n-heptane
- (iii) bromoethane and iodoethane
- (iv) chlorobenzene and bromobenzene

Solutions which obey Raoult's law are called ideal liquid solutions. Composition in vapour phase: The composition of vapour phase in equilibrium with the solution is determined by the partial pressure of the components. If Y_1 and Y_2 are the mole fraction of the two components 1 and 2 respectively in the vapour phase, then according to Dalton's law of partial pressure: Partial pressure of a component = mole fraction of the component \times total pressure

$$\therefore p_1 = y_1 p \quad \text{or} \quad p_2 = y_2 p$$

In general, $p_i = y_i p$

mole fraction of component 1 in vapour phase, $y_1 = p_1/p$

Mole fraction of component 2 in vapour phase $y_2 = p_2/p$

In general, mole fraction of a component in vapour phase = partial vapour pressure of component / total vapour pressure.

Non-ideal solutions: The solution which do not obey Raoult's law over the entire range of concentration are called non-ideal solutions.

Therefore, for such solution $p_A \neq p_A^0 X_A$ and $p_B \neq p_B^0 X_B$

Thus, the vapour pressure of such solutions is either higher or lower than that predicted by Raoult's law. In non-ideal solutions, there is a noticeable change in volume and heat energy when two components are mixed. Most of the solutions are non-ideal because they deviate from ideal behavior to more or less extent. Thus, for non-ideal solutions,

- (i) it does for Round ideal solution none of the components of the route or over the entire composition range is not equal to zero is not equal to zero. Thus, for non-ideal solutions, (i) none of the component obey Raoult's law over the entire composition range, i.e., $p_A \neq p_A^0 X_A$ and $p_B \neq p_B^0 X_B$
- (ii) $\Delta_{\text{mixing}} V$ is not equal to zero
- (iii) $\Delta_{\text{mixing}} H$ is not equal to zero.

Thus, non-ideal solutions do not obey Raoult's law and are accompanied by change in enthalpy and change in volume during their formation.

Types of non-ideal solutions: non-ideal solutions show positive and negative deviations from the ideal behavior depending upon their nature.

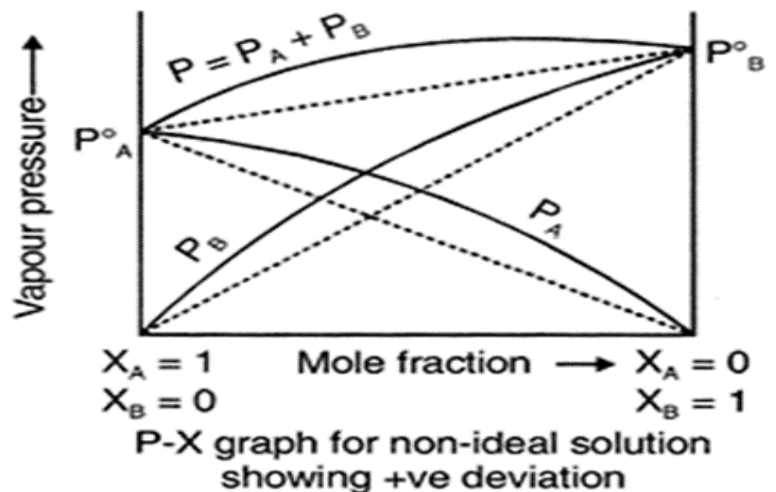
- (i) **Non-ideal solutions showing positive deviations from Raoult's law:** consider a binary solution of two components A and B. If the A-B interaction in the solution is weaker than the A-A and B-B interactions in the two liquids forming the solution, then the escaping tendency of A and B types of molecules from the solution become more than from pure liquids. As a result, each component of the solution has a partial vapour pressure greater than expected on the basis of Raoult's law. The total vapour pressure will be greater than corresponding vapour pressure expected in case of ideal solution of the same composition. This type of behavior of solution is described as positive deviation from Raoult's law. Mathematically, it may be expressed as: $p_A > p_A^0 X_A$ and $p_B > p_B^0 X_B$

The total vapour pressure, $p = p_A + p_B$ is always greater than $(p_A^0 X_A + p_B^0 X_B)$

Positive deviations have been shown in figure, in which dotted lines show the ideal behavior upon mixing while thick lines exhibit the actual behavior. A few examples of solutions showing positive deviation are:

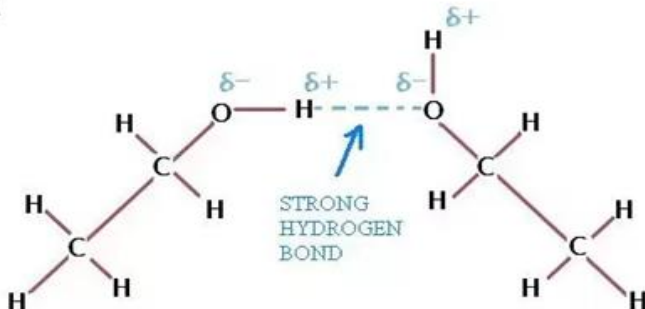
- I) ethyl alcohol and cyclohexane
- II) acetone and carbon disulphide
- III) benzene and acetone
- IV) carbon tetrachloride and chloroform
- V) acetone and ethyl alcohol
- VI) ethyl alcohol and water

Explanation for positive deviations: Let us explain by considering a solution of ethyl alcohol and cyclohexane. In ethyl alcohol, the molecules are held together due to hydrogen bonding as shown below:



When cyclohexane is added to ethyl alcohol, the molecules of cyclohexane tend to occupy the spaces between ethyl alcohol molecules. Consequently, some hydrogen bonds in alcohol molecules break and attractive forces in alcohol molecules are weakened. The escaping tendency of alcohol and cyclohexane molecules from the solution increases. Consequently, the vapour pressure of the solution is greater than the vapour pressure as expected according to Raoult's law.

Ethanol



In such solution, $\Delta_{\text{mixing}} H$ and $\Delta_{\text{mixing}} V$ are also not equal to zero as explained below:

- (i) $\Delta_{\text{mixing}} H$ is positive because energy is required to break A-A or B-B attractive forces. Therefore, dissolution process is endothermic.

(ii) because of the decrease in the magnitude of intermolecular forces in solution, the molecules will be loosely held and therefore, there will be increase in volume of the mixing.

Thus, $\Delta_{\text{mixing}} V$ will be +ive. Since the dissolution process is endothermic, heating will increase the solubility of such a solution.

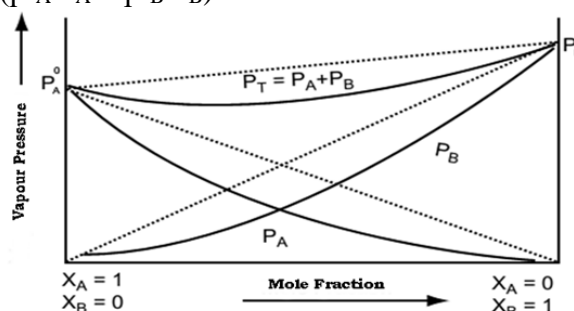
(ii) Non-ideal solution showing negative deviations from Raoult's law: In such solution, the A-B interactions are stronger than the A-A and B-B interactions present in the two liquids forming the solution. Due to stronger A-B interactions, the escaping tendency of A and B types of molecules from the solution becomes less than from pure liquids. Consequently, each component of the solution has a partial vapour pressure less than expected on the basis of Raoult's law. As a result, the total vapour pressure becomes less than the corresponding vapour pressure expected in case of Ideal

solution. The solutions are said to have negative deviation from Raoult's law. Mathematically, $p_A < p_A^0 X_A$ and $p_B < p_B^0 X_B$.

Thus, the total vapour pressure, $p = p_A + p_B$ is always less than $(p_A^0 X_A + p_B^0 X_B)$

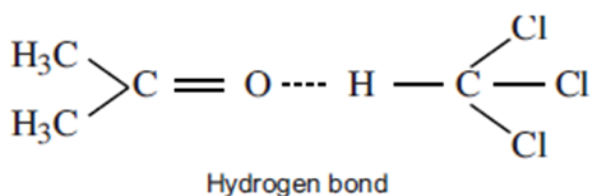
The negative deviation has been shown in figure in which dotted lines show the ideal behavior upon mixing while the thick lines show the actual behavior. A few examples of the solution showing negative deviation are:

- (I) Acetone and chloroform
- (II) chloroform and diethyl ether
- (III) chloroform and nitric acid
- (IV) Acetone and aniline
- (V) water and nitric acid
- (VI) diethyl Ether and chloroform



P-X Diagram for Solutions Showing Negative Deviation from Raoult's Law

Explanation for negative deviation: Let us illustrate by considering a solution of acetone and chloroform. When acetone and chloroform are mixed, there are new attractive forces due to intermolecular hydrogen bonding. Thus, the attractive forces become stronger and the escaping tendency of each liquid from the solution decreases.



Therefore, the vapour pressure of the solution is less than that expected for an ideal solution. In this solution also $\Delta_{\text{mixing}} H$ and $\Delta_{\text{mixing}} V$ are not equal to zero as explained:

(I) $\Delta_{\text{mixing}} H$ is negative because energy is released due to increase in attractive forces. Therefore, dissolution process is exothermic and heating the solution will decrease solubility.

(II) because of the increase in forces of attraction in the solution, the molecules will be held more tightly. Therefore, there will be decrease in volume on mixing i.e., $\Delta_{\text{mixing}} V$ will be negative.

Assignment

1. The solution showing negative deviation -----
 - (A) have $\Delta V (\text{mixing}) = +\text{ive}$
 - (B) have $\Delta H (\text{mixing}) = -\text{ive}$
 - (C) form maximum boiling azeotropes
 - (D) have lower the per pressure of each component in the solution then their pure vapour pressure
2. Non-ideal solutions having negative deviation are:
 - (A) Acetone + ethyl alcohol
 - (B) Acetic Acid + pyridine
 - (C) chloroform + Benzene
 - (D) carbon tetrachloride + toluene

3. Which of the following form nearly ideal solution?
 (A) chlorobenzene + bromobenzene (B) hexane + heptane
 (C) ethanol + cyclohexane (D) acetic acid + pyridine
4. Which of the following liquid pairs show a positive deviation from Raoult's law?
 (A) water -nitric acid (B) benzene – methanol
 (C) water- hydrochloric acid (D) Acetone –chloroform
5. A solution of acetone in ethanol -----
 (A) shows positive deviation from Raoult's Law
 (B) behave like a near ideal solution
 (C) obey Raoult's law
 (D) shows negative deviation from Raoult's law
6. Which of the following statement is correct for non -ideal solutions?
 (A) for solution showing negative deviation ΔV (mixing) and ΔH (mixing) are positive
 (B) for solutions showing negative deviation, the interaction between the compounds are greater than the pure components
 (C) for solution showing positive deviation ΔV (mixing) positive but ΔH (mixing) positive
 (D) for solution showing negative deviation ΔV (mixing) negative but ΔH (mixing) positive

Answers

(A) 2. (B) (C) 3. (A) (B) 4. (B) 5. (A) 6. (B)