

SOLUTION

“A homogeneous mixture of two or more substances, whose composition is variable under certain limits is called solution.”

In binary solutions, the component which is present in lesser quantity is called solute, while that which is present in larger quantity is called solvent. Thus, in binary solution the solute molecules remain homogeneously distributed amongst solvent molecules.

Types of Solution - Depending upon physical state of solute and solvent solution may be of following 9 types -

S.No.	Physical state of solute	Physical state of solvent	Examples
1.	Solid	Solid	Alloys
2.	Liquid	Solid	Gels
3.	Gas	Solid	NH ₃ adsorbed at the surface of Pt, Pumic stone
4.	Solid	Liquid	Sols, Sugar in water, Salt in water
5.	Liquid	Liquid	Alcohol in water
6.	Gas	Liquid	Soft drinks
7.	Solid	Gas	Dust in air, Smoke (Aerosol)
8.	Liquid	Gas	Fog, Aerosols
9.	Gas	Gas	Air

Concentration of Solution - The amount of solute present in given amount of solvent or solution is called conc. of solute in solution or conc. of solution.

Mode of Expression of Conc. of Solutions

(1) Mass Percentage – “The number of parts of solute by mass present in hundred parts of solution is called mass percentage of solute in solution.”

Mathematically,

$$\text{Mass \% age} = \frac{\text{Mass of solute (g)}}{\text{Mass of solution (g)}} \times 100$$

(2) Volume Percentage – “The number of parts of solute by volume present in hundred parts of solution is called volume percentage of solute in solution.”

Mathematically,

$$\text{Volume \% age} = \frac{\text{Volume of solute (ml)}}{\text{Volume of solution(ml)}} \times 100$$

(3) Gram / litre Concentration (Strength of solution) – “The mass of solute in gram present in per litre of solution is called gram / litre conc. (strength) of solution.”

Mathematically,

$$\text{Gram/litre conc. (strength)} = \frac{\text{Mass of solute (g)}}{\text{Volume of solution(l)}}$$

(4) Normality (N) – “The number of gram equivalent mass of solute present in per litre of solution is called normality solution.”

Mathematically,

$$\begin{aligned} \text{Normality, N} &= \frac{\text{Number of Gram Equivalent Mass of Solute}}{\text{Volume of Solution (l)}} \\ &= \frac{\text{Mass of solute (g)}}{\text{GEM of Solute} \times \text{Volume of Solution (l)}} \\ &= \frac{\text{Mass of solute (g)} \times 1000}{\text{GEM of Solute} \times \text{Volume of Solution (ml)}} \end{aligned}$$

If 1 gram equivalent mass of solute is present in per litre of solution, then the solution is called normal solution (N- solution). Similarly, If 2, 3, 4,----- gram equivalent mass of solute is present in per litre of solution, then the solutions are called 2N, 3N, 4N----- solutions respectively.

On the other hand, If 1/2 gram equivalent mass of solute is present in per litre of solution, then it is called semi - normal (N/2) solution and if 1/10 gram equivalent mass of solute is present in per litre of solution, then it is called deci- normal (N/10) solution.

Normality involves volume term and therefore, it is dependent on temperature and changes with change of temperature. Hence, it is not considered to be a good method for expressing the conc. of solutions.

(5) Molarity (M) – “The number of gram molecular mass (moles) of solute present in per litre of solution is called molarity solution.”

Mathematically,

$$\begin{aligned} \text{Molarity, M} &= \frac{\text{Number of GMM (moles) of Solute}}{\text{Volume of solution(l)}} \\ &= \frac{\text{Mass of solute (g)}}{\text{GMM of Solute} \times \text{Volume of solution (l)}} \end{aligned}$$

$$= \frac{\text{Mass of solute (g)} \times 1000}{\text{GMM of Solute} \times \text{Volume of solution (ml)}}$$

If 1 GMM (moles) of solute is present in per litre of solution, then the solution is called molar solution (M- solution). Similarly, If 2, 3, 4,----- GMM (moles) of solute is present in per litre of solution, then the solutions are called 2M, 3M, 4M----- solutions respectively.

On the other hand, If 1/2 GMM(moles) of solute is present in per litre of solution, then it is called semi molar (M/2) solution and if 1/10 GMM (moles) of solute is present in per litre of solution, then it is called deci-molar (M/10) solution.

Molarity involves volume term and therefore, it is dependent on temperature and changes with change of temperature. Hence, it is not considered to be a good method for expressing the conc. of solutions.

(6) Molality (m) – “The number of gram molecular mass (moles) of solute present in per kg of solvent is called molality solution.”

Mathematically,

$$\begin{aligned} \text{Molality, } m &= \frac{\text{Number of GMM (moles) of Solute}}{\text{Mass of Solvent (Kg)}} \\ &= \frac{\text{Mass of solute (g)}}{\text{GMM of Solute} \times \text{Mass of Solvent (Kg)}} \\ &= \frac{\text{Mass of solute (g)} \times 1000}{\text{GMM of Solute} \times \text{Mass of Solvent (g)}} \end{aligned}$$

If 1 GMM (moles) of solute is present in per kg of solvent, then the solution is called molal solution (m- solution). Similarly, If 2, 3, 4,----- GMM (moles) of solute is present in per kg of solvent, then the solutions are called 2m, 3m, 4m----- solutions respectively.

On the other hand, If 1/2 GMM (moles) of solute is present in per kg of solvent, then it is called semi molal (m/2) solution and if 1/10 GMM (moles) of solute is present in per kg of solvent, then it is called deci-molal (m/10) solution.

Molality does not involves volume term and therefore, it is independent of temperature and does not change with change of temperature. Hence, it is considered to be a good method for expressing the conc. of solutions.

(7) Formality (F) - The term formality is specially used to express the conc. of the solution of ionic solutes such as NaCl, KCl, CuSO₄ etc. By definition,

“The number of gram formula mass (moles) of solute present in per litre of solution is called formality of solution.”

Mathematically,

$$\text{Formality, } F = \frac{\text{Number of Gram Formula Mass of Solute}}{\text{Volume of Solution (l)}}$$

$$= \frac{\text{Mass of solute (g)}}{\text{GFM of Solute} \times \text{Volume of Solution (l)}}$$

$$= \frac{\text{Mass of solute (g)} \times 1000}{\text{GFM of Solute} \times \text{Volume of Solution (ml)}}$$

If 1 GFM (moles) of solute is present in per litre of solution, then the solution is called formal solution (F- solution). Similarly, If 2, 3, 4,----- GFM (moles) of solute is present in per litre of solution, then the solutions are called 2F, 3F, 4F----- solutions respectively.

On the other hand, If 1/2 GFM (moles) of solute is present in per litre of solution, then it is called semi formal (F/2) solution and if 1/10 GFM (moles) of solute is present in per litre of solution, then it is called deci- formal (F/10) solution.

Formality involves volume term and therefore, it is dependent on temperature and changes with change of temperature. Hence, it is not considered to be a good method for expressing the conc. of solutions.

(8) Mole Fraction – “The ratio of the number of moles of one component to the total number of moles in solution is called mole fraction of respective component in solution.”

Let, W_B gram of a solute B having molecular mass M_B is present in W_A gram of a solvent A having molecular mass M_A , then,

$$\text{Mole Fraction of solute, } X_B = \frac{\text{No. of moles of solute}}{\text{Total number of moles in solution}}$$

$$= \frac{n_B}{n_B + n_A}$$

$$= \frac{W_B/M_B}{W_B/M_B + W_A/M_A}$$

Similarly,

$$\text{Mole Fraction of solvent, } X_A = \frac{\text{No. of moles of solvent}}{\text{Total number of moles in solution}}$$

$$= \frac{n_A}{n_B + n_A}$$

$$= \frac{W_A/M_A}{W_B/M_B + W_A/M_A}$$

Here,

$$X_B + X_A = \frac{n_B}{n_B + n_A} + \frac{n_A}{n_B + n_A}$$

or

$$\boxed{X_B + X_A = 1}$$

It is clear that, the sum of mole fractions of two components of a binary solution is always equal to one. Thus, if mole fraction of one component of the solution is known then, that of another can be calculated.

Mole fraction does not involve volume term and therefore, it is independent of temperature and does not change with change of temperature. Hence, it is considered to be a good method for expressing the conc. of solutions.

(9) Parts Per Million (ppm) conc. - This method is specially used to express the conc. of very dilute solutions. For example, conc. of chlorine in drinking water, conc. of polluting gases in air etc. are expressed in ppm. By definition,

“The number of parts of solute either by mass or by volume present in 10^6 parts of solution is called ppm conc. of solute in solution.”

Mathematically,

$$\text{PPM conc. of solute (by Mass)} = \frac{\text{Mass of solute (g)}}{\text{Mass of solution (g)}} \times 10^6$$

$$\text{PPM conc. of solute (by Volume)} = \frac{\text{Volume of solute (ml)}}{\text{Volume of solution (ml)}} \times 10^6$$

* If a mode of expressing conc. involves volume term, then it is dependent on temperature and changes with change of temperature. Hence, it is not considered to be a good method for expressing the conc. of solutions. For example, normality, molarity, formality, ppm conc. by volume etc. On the other hand, if it does not involve volume term, then it is independent of temperature and therefore, it does not change with change of temperature. Hence, it is considered to be a good method for expressing the conc. of solutions. For example, molality, mole fraction, mass %age, ppm conc. by mass etc.

*** Relation between normality (N) and gram/litre conc. (strength) of solutions-**

$$\text{Normality, N} = \frac{\text{Mass of solute (g)}}{\text{GEM of Solute} \times \text{Volume of Solution (l)}}$$

$$\text{or} \quad \text{N} = \frac{S}{E}$$

*** Relation between molarity (M) and gram/litre conc. (strength) of solutions-**

$$\text{Molarity, M} = \frac{\text{Mass of solute (g)}}{\text{GMM of Solute} \times \text{Volume of solution (l)}}$$

$$\text{or} \quad \text{M} = \frac{S}{\text{GMM of Solute}}$$

* Relation between normality (N) and molarity (M) of solutions–

$$\text{Normality, } N = \frac{\text{Mass of solute (g)}}{\text{GEM of Solute} \times \text{Volume of Solution (l)}}$$

$$\text{And Molarity, } M = \frac{\text{Mass of solute (g)}}{\text{GMM of Solute} \times \text{Volume of solution (l)}}$$

$$\text{Therefore, } \frac{N}{M} = \frac{\text{GMM of Solute}}{\text{GEM of Solute}}$$

$$\text{or } \frac{N}{M} = x \quad (\text{Where, } x = \text{valency of solute})$$

$$\text{or } N = x \times M$$

For example,

(1) For monobasic acids (HCl, HCN, CH₃COOH etc.) or mono acidic bases (NaOH, KOH, NH₄OH etc) -

$$\text{Hence, } \begin{array}{l} x = 1 \\ \boxed{N = M} \end{array}$$

(2) For dibasic acids (H₂SO₄, H₂CO₃, H₃PO₃ etc.) or di acidic bases (Ca(OH)₂, Mg(OH)₂ etc.) -

$$\text{Hence, } \begin{array}{l} x = 2 \\ \boxed{N = 2 \times M} \end{array}$$

(3) For tri basic acids such as H₃PO₄ or tri acidic bases such as Al(OH)₃, Fe(OH)₃ etc.-

$$\text{Hence, } \begin{array}{l} x = 3 \\ \boxed{N = 3 \times M} \end{array}$$

Vapour Pressure of Pure Solvent

When a volatile solvent is taken in a beaker and is covered with a glass jar then, two opposing processes occur simultaneously i.e evaporation of liquid into vapours and condensation of vapours into liquid. After some time, equilibrium state is achieved where, the rate of evaporation becomes equal to the rate of condensation so that, the amount of vapours in equilibrium with liquid becomes constant. In this state, the pressure exerted by vapour molecules over liquid surface is called vapour pressure of pure solvent. Thus,

“At constant temperature, the pressure exerted by vapour molecules present in equilibrium with a liquid over liquid surface is called vapour pressure of pure solvent.”

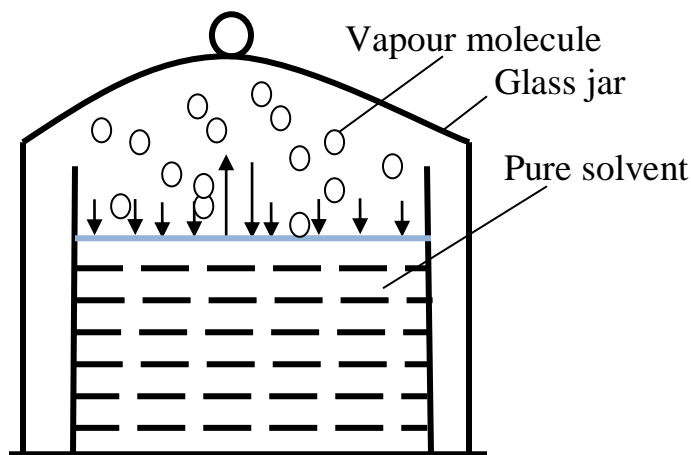


Fig-Vapour pressure of pure solvent

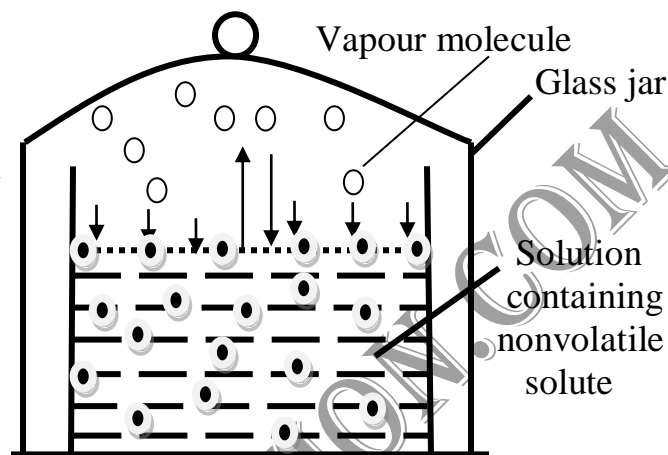


Fig-Vapour pressure of solution

Vapour Pressure of Solution

“At constant temperature, the pressure exerted by vapour molecules present in equilibrium with a solution is called vapour pressure of solution.”

When a nonvolatile solute is added to a volatile solvent, the solute molecules get homogeneously distributed amongst solvent molecules, and some of the surface area of solvent is occupied by solute molecules. Thus, available surface area for evaporation gets decreased and relatively lesser vapour molecules are formed at equilibrium so that, the vapour pressure of solution gets decreased. Thus, vapour pressure of solution containing nonvolatile solute is always lesser than the vapour pressure of pure solvent.

Lowering in vapour pressure

When a nonvolatile solute is added to a volatile solvent, the partial vapour pressure of solvent in solution (vapour pressure of solution) gets decreased. This is called Lowering in Vapour Pressure of solution.

Let, vapour pressure of a pure volatile solvent A is p_A^0 and that of solution containing nonvolatile solute B is p_A , then,

$$\boxed{\text{Lowering in Vapour Pressure} = p_A^0 - p_A}$$

Lowering in Vapour Pressure of solution depends upon the amount of solute added. The larger the amount of solute added more is Lowering in Vapour Pressure of solution.

Raoult's Law

This law governs the partial vapour pressure of a volatile component in solution. According to this law-

“At constant temperature, the partial vapour pressure of a volatile component in solution is directly proportional to its mole fraction in solution.”

Let, W_B gram of a nonvolatile solute B having molecular mass M_B is present in W_A gram of a volatile solvent A having molecular mass M_A . If p_A is partial vapour pressure of solvent in solution and X_A is mole fraction of solvent in solution, then according to Raoult's law -

$$p_A \propto X_A$$

$$p_A = kX_A$$

Where, k is a proportionality constant

If $X_A = 1$ (pure solvent),
Then, $p_A = p_A^0 = k$

Where, $p_A^0 =$ vapour pressure of pure solvent

Thus, $p_A = p_A^0 X_A$

This is mathematical form of Raoult's law. It is clear that, "The partial vapour pressure of a volatile component in solution is equal to the product of vapour pressure of pure component and its mole fraction in solution."

In binary solutions of two volatile liquids A and B, if p_A and p_B are partial vapour pressure of components, X_A and X_B are their mole fraction in solution and p_A^0 and p_B^0 are vapour pressure of pure components, then-

$$p_A = p_A^0 X_A$$

$$p_B = p_B^0 X_B$$

Here,

$$p_{sol} = p_A + p_B$$

$$= p_A^0 X_A + p_B^0 X_B$$

$$= p_A^0 (1 - X_B) + p_B^0 X_B$$

$$= p_A^0 - p_A^0 X_B + p_B^0 X_B$$

$$= p_A^0 + X_B (p_B^0 - p_A^0)$$

If partial vapour pressure of components are plotted against their respective mole fractions in solution, then straight lines are obtained.

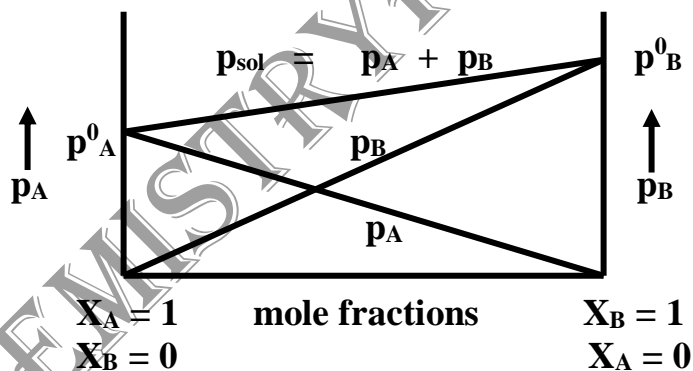


Fig - Plot of partial vapour pressure of components against their respective mole fractions

From the plot, it is clear that, vapour pressure of solution is always in between the vapour pressure of the pure components.

Raoult's law is only applicable on ideal solutions but no solution of nature is ideal. However, in very dilute condition, following solutions behave almost like ideal solutions and follow Raoult's law to a large extent –

- (1) n-Hexane + n-Heptane
- (2) Benzene + Toluene
- (3) Chlorobenzene + Bromobenzene
- (4) Ethyl chloride + Ethyl bromide
- (5) Carbon tetrachloride + Silicon tetrachloride

- The mole fraction of a volatile component in vapour phase is given by Dalton's law of partial pressure and is obtained by following expression-

$$X_i = \frac{p_i}{p_{Total}}$$

Ideal Solutions

“Such solutions which follow Raoult's law at all the temperatures and compositions are called ideal solutions.”

Thus, for ideal solutions,

$$p_A = p_A^0 X_A$$

$$p_B = p_B^0 X_B$$

Here,

$$p_{sol} = p_A + p_B$$

$$= p_A^0 X_A + p_B^0 X_B$$

Where, p_A and p_B are partial vapour pressure of components A and B, X_A and X_B are their respective mole fractions in solution and p_A^0 and p_B^0 are vapour pressure of pure components.

If partial vapour pressure of components are plotted against their respective mole fractions in solution, then straight lines are obtained.

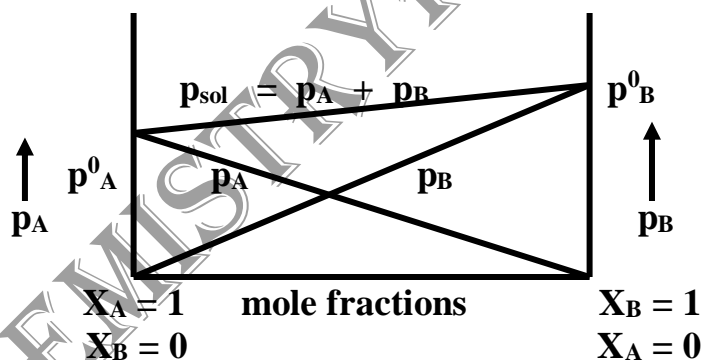


Fig - Plot of partial vapour pressure of against their respective mole fractions

Ideal solutions are obtained by mixing the components having same structure and polarity. Here, interactional force does not change on mixing the components, so that heat is neither released nor absorbed on mixing the components. Thus, for ideal solutions, the enthalpy change on mixing the components is zero.

$$\Delta H_{\text{mix}} = 0$$

Here, molecules neither come close together nor go farther from one another. Hence, change in volume on mixing the components is zero.

$$\Delta V_{\text{mix}} = 0$$

No solution of nature is ideal and therefore, no solution of nature completely follow Raoult's law at all the temperatures and compositions. However, in very dilute condition, following solutions behave almost like ideal solutions and follow Raoult's law to a large extent -

- (1) n-Hexane + n-Heptane
- (2) Benzene + Toluene
- (3) Chlorobenzene + Bromobenzene
- (4) Ethyl chloride + Ethyl bromide
- (5) Carbon tetrachloride + Silicon tetrachloride

Non-Ideal Solutions

“Such solutions which do not follow Raoult's law at all the temperatures and compositions are called non-ideal solutions.”

Thus, for non-ideal solutions,

$$p_A \neq p_A^0 X_A$$

$$p_B \neq p_B^0 X_B$$

Here,

$$p_{\text{sol}} = p_A + p_B$$

$$\neq p_A^0 X_A + p_B^0 X_B$$

Where, p_A and p_B are partial vapour pressure of components A and B, X_A and X_B are their respective mole fractions in solution and p_A^0 and p_B^0 are vapour pressure of pure components.

Non-ideal solutions are obtained by mixing the components having different structure and polarity. Here, interactional force changes appreciably on mixing the components, so that heat is either released or absorbed on mixing the components. Thus, for non-ideal solutions enthalpy change on mixing the components is not equal to zero.

$$\Delta H_{\text{mix}} \neq 0$$

Here, the molecules either come close together or go farther from one another. Hence, change in volume on mixing the components is not equal to zero.

$$\Delta V_{\text{mix}} \neq 0$$

For these solutions, if partial vapour pressure of components are plotted against their respective mole fractions in solution, then instead of straight lines, curves having either maxima or minima are obtained. On this basis, non-ideal solutions are of following 2 types -

- (1) Non-ideal solutions showing positive deviation from Raoult's law
- (1) Non-ideal solutions showing negative deviation from Raoult's law

(1) Non-ideal solutions showing positive deviation from Raoult's law

If solvent-solute interaction in solution is weaker than solvent-solvent and solute-solute interactions, then the solution shows +ve deviation from Raoult's law. Here, escaping tendency of both the components gets increased in solution, so that, relatively more vapours of both the components are formed. Hence, partial vapour pressure of both solvent and solute in solution is greater than that expected according to Raoult's law. Thus, for non-ideal solutions showing positive deviation from Raoult's law-

Here,

$$\begin{aligned}
 p_A &> p_A^0 X_A \\
 p_B &> p_B^0 X_B \\
 p_{\text{sol}} &= p_A + p_B \\
 &> p_A^0 X_A + p_B^0 X_B
 \end{aligned}$$

Here, interactional force in solution becomes weaker, so that, energy is absorbed on mixing the components. Thus, for these solutions enthalpy change on mixing the components is more than zero i.e. +ve.

$$\Delta H_{\text{mix}} > 0 \text{ (+ve)}$$

Here, molecules go farther from one another and volume gets increased. Hence, change in volume on mixing the components is +ve.

$$\Delta V_{\text{mix}} > 0 \text{ (+ve)}$$

For these solutions, if partial vapour pressure of components are plotted against their respective mole fractions in solution, then curves having maxima are obtained.

For these solutions, there is a definite composition for which vapour pressure is highest and therefore, boiling point of solution is least. This mixture behaves like azeotropic mixture (constant boiling mixture) and like a pure substance, it boils at a definite temperature without any change in composition. The components present in this mixture cannot be separated by simple distillation process.

Thus, non-ideal solutions showing +ve deviation from Raoult's law form high vapour pressure low boiling point azeotropes.

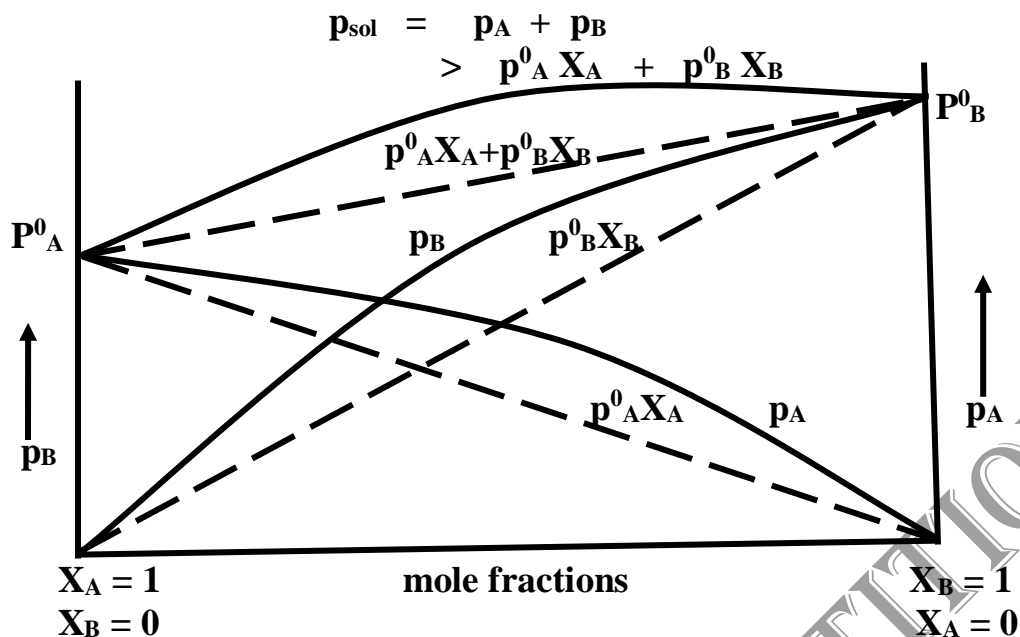


Fig – Positive deviation from Raoult's law

Examples - Some most common examples of non-ideal solutions showing +ve deviation from Raoult's law are as under -

- | | |
|--------------------------------------|---|
| (1) Ethanol + Water | (2) Ethanol + Cyclohexane |
| (3) Acetone + Ethanol | (4) Acetone + Benzene |
| (5) Acetone + CS_2 | (6) CCl_4 + Toluene |
| (7) CCl_4 + CHCl_3 | (8) CCl_4 + CH_3OH |

Cause of +ve deviation from Raoult's law

Cause of +ve deviation from Raoult's law can be explained by taking the example of the solution of ethanol and cyclohexane. Here, molecules of cyclohexane occupy the space between ethanol molecules by breaking the inter-molecular hydrogen bonds of ethanol.

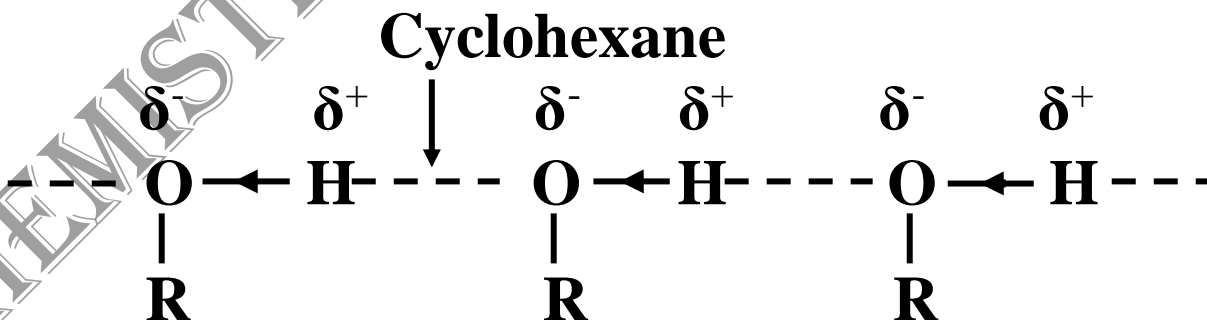


Fig - Cause of +ve deviation from Raoult's law

Thus, escaping tendency of both solvent and solute molecules gets increased in solution, so that relatively more vapours of both the components are formed. Thus, partial vapour

pressure of both solvent and solute in solution becomes greater than that expected according to Raoult's law.

(2) Non-ideal solutions showing negative deviation from Raoult's law

If solvent-solute interaction in solution is stronger than solvent-solvent and solute-solute interactions, then the solution shows -ve deviation from Raoult's law. Here, escaping tendency of both the components gets decreased in solution, so that, relatively lesser vapours of both the components are formed. Thus, partial vapour pressure of both solvent and solute in solution is lesser than that expected according to Raoult's law. Thus, for Non-ideal solutions showing -ve deviation from Raoult's law-

Here,

$$\begin{aligned} p_A &< p_A^0 X_A \\ p_B &< p_B^0 X_B \\ p_{\text{sol}} &= p_A + p_B \\ &< p_A^0 X_A + p_B^0 X_B \end{aligned}$$

Here, interactional force in solution becomes stronger, so that, energy is released on mixing the components. Thus, for these solutions enthalpy change on mixing the components is lesser than zero i.e. -ve.

$$\Delta H_{\text{mix}} < 0 \text{ (-ve)}$$

Here, molecules come close together and volume gets decreased. Hence, change in volume on mixing the components is -ve.

$$\Delta V_{\text{mix}} < 0 \text{ (-ve)}$$

For these solutions, if partial vapour pressure of components are plotted against their respective mole fractions in solution, then curves having minima are obtained.

For these solutions, there is a definite composition for which vapour pressure is least and therefore, boiling point of solution is highest. This mixture behaves like azeotropic mixture (constant boiling mixture) and like a pure substance, it boils at a definite temperature without any change in composition. The components present in this mixture cannot be separated by simple distillation process.

Thus, non-ideal solutions showing -ve deviation from Raoult's law form low vapour pressure high boiling point azeotropes.

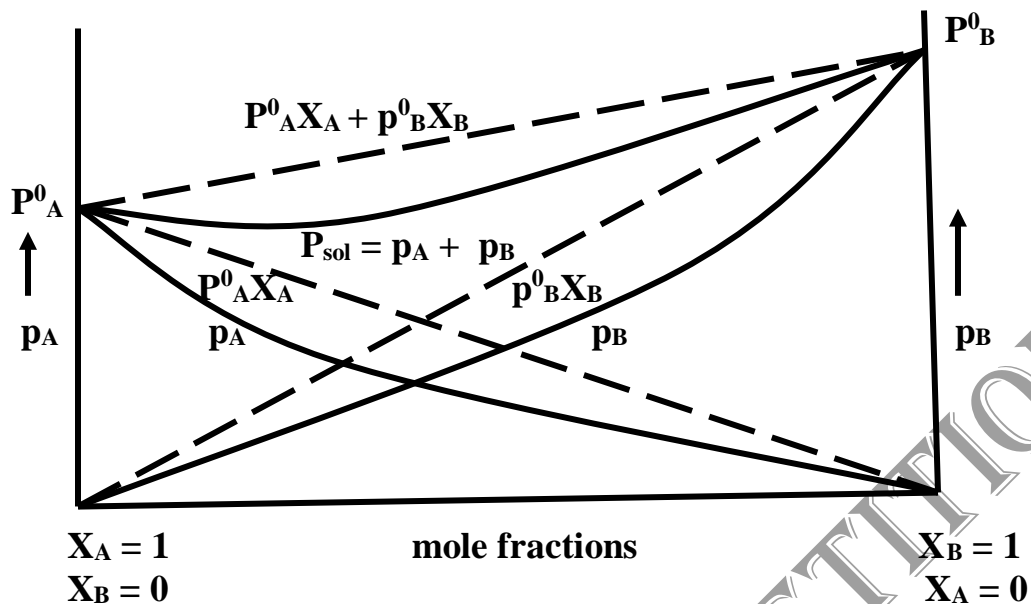


Fig – Negative deviation from Raoult's law

Examples - Some most common examples of non-ideal solutions showing -ve deviation from Raoult's law are as under –

- | | |
|---|--------------------------------|
| (1) Acetone + Chloroform | (2) Acetone + Aniline |
| (3) Nitric acid + Water | (4) HCl + Water |
| (5) CH ₃ OH + CH ₃ COOH | (6) Chloroform + Benzene |
| (7) Acetic acid + Pyridine | (8) Chloroform + Diethyl ether |

Cause of -ve deviation from Raoult's law–

Cause of -ve deviation from Raoult's law can be explained by taking the example of the solution of acetone and chloroform. Here, inter-molecular hydrogen bonds get formed between the molecules of both the components.

Inter-molecular hydrogen bond

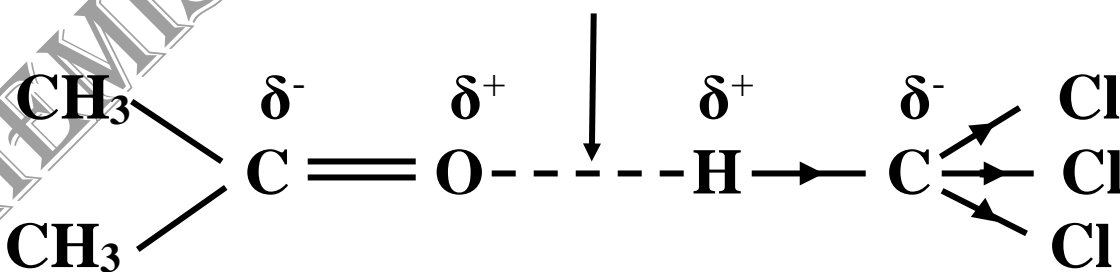


Fig - Cause of -ve deviation from Raoult's law

Thus, escaping tendency of both solvent and solute molecules gets decreased in solution, so that, relatively lesser vapours of both the components are formed. Thus, partial vapour pressure of both solvent and solute in solution becomes lesser than that expected according to Raoult's law.

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