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Ideal and Non-Ideal Solutions

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ABSTRACT:
Solutions are homogeneous mixtures with two components: a solvent and a solute. The larger component is called the solvent, and the smaller component is called the solute. If both components are present in equal 50% amounts in a solution, either can be called the solvent or solute, or the more common/widely used substance can be designated as the solvent. When two liquids dissolve in each other, they are respectively labeled solvent and solute depending on their relative amounts in the solution. Most chemical reactions occur in solutions. Solutions also play an essential role in our daily lives. The air we breathe, the water we drink, and all the fluids in our bodies are all solutions.
Now what do ideal and non-ideal solutions mean?
Among solutions, there are those that exhibit different behaviors by following or not following certain laws. This research attempts to concisely and usefully cover ideal and non-ideal solutions, their properties, and examples.

Keywords: Solution, ideal and non-ideal solutions, Raoult's law

INTRODUCTION:

Ideal and Non-Ideal Solutions

In 1886 A.D., François-Marie Raoult, a French chemist, proposed a relationship between partial pressure and mole fraction of volatile liquids. Raoult stated in his law that: The vapor pressure of a solution depends on the vapor pressures of the chemical components and the mole fractions of the components present in the solution.

According to Raoult's law, liquid-liquid solutions can be of two types: (1,2)
5. Ideal solutions
6. Non-ideal solutions

Ideal Solutions

Solutions that obey Raoult's law at any concentration and temperature are ideal. In an ideal solution of A and B, the A-B interactions are identical to the A-A and B-B interactions. Under such conditions, the relationship between solution concentration and partial pressure of the gas phase for each component is given by Raoult's law. In an ideal solution, the vapor above the solution is enriched in the volatile components which can be separated by fractional distillation. The non-volatile solute components cause a decrease in the vapor pressure above the solution. Such solutions exhibit a decrease in freezing point and an increase in boiling point. These properties in an ideal solution depend only on the concentration and are independent of the type of volatile solute.

In an ideal gas, the atoms or molecules do not interact with each other. Specifically, such a model is not suitable for a liquid because a gas without attractive interactions will not condense. The difference in boiling points of elements indicates a large variation in attractive interactions in liquids. For example, the boiling point of helium is quoted as 4.2 K whereas hafnium has a boiling point of 5400 K.(3)

In developing a model for solutions, the vapor phase in equilibrium with the solution must also be considered. Consider pure liquid benzene in a flask in a closed room. Since the liquid is in equilibrium with its vapor phase, there is a non-zero partial pressure of benzene in the environment around the flask. This pressure is known as the vapor pressure of benzene at the temperature of the liquid. Now what happens if toluene is added to the flask? It is observed that the partial pressure of benzene decreases.

For such a mixture, the partial pressure of component i above the liquid is given by the relation

$$p_i = x_i p_i^* \qquad i = 1,2$$

where x_i is the mole fraction of component i in the liquid.

This relation states that the partial pressure of each component is directly proportional to the vapor

pressure (p_i^*)[1] of the pure liquid component, with the proportionality constant being the mole fraction. This relation is known as Raoult's law and is, in fact, the definition of an ideal solution. In a binary solution, the component with the higher x_i is called the solvent and the one with lower x_i is the solute. Few solutions actually obey Raoult's law.(4)

The above relation is valid only if the A-A, A-B and B-B interactions are all equal. This criterion is satisfied for a benzene-toluene mixture because the molecules of the two substances are similar in size, shape and chemical properties, but the law does not hold for all solutions and has limitations. A solvent in an ideal solution obeys Raoult's law only when it is highly diluted.

Examples of Ideal Solutions (1)
· n-hexane and n-heptane
· Bromoethane and chloroethane
· Benzene and toluene
· Chlorobenzene and bromobenzene
· Ethyl bromide and ethyl iodide
· n-butyl chloride and n-butyl bromide
· Silicon tetrachloride and carbon tetrachloride

Non-Ideal Solutions
Solutions that do not obey Raoult's law over any range of concentration and temperature are non-ideal solutions. Solutions that deviate from ideal solutions are known as non-ideal solutions.

The image below shows the P-X diagram of a non-ideal solution that deviates from an ideal solution.

P-X graph for non-ideal solution showing +ve deviation
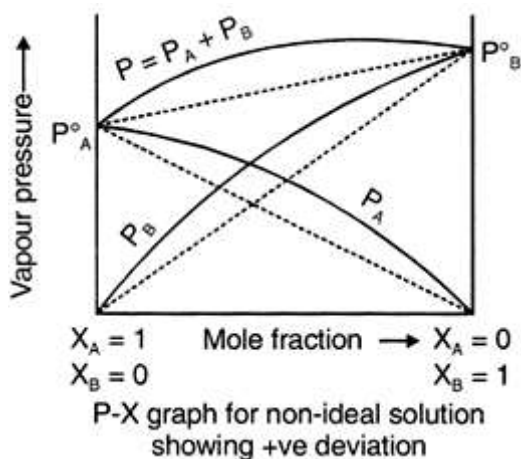
Properties of Non-Ideal Solutions
The solvent-solvent and solute-solute interactions are different from the solvent-solute interactions.
The heat of mixing or mixing enthalpy (ΔmixH) is the heat released or absorbed when two chemical substances that do not react with each other are combined. Whenever the enthalpy of the combined material is positive, the mixture is endothermic, and whenever it is negative, the mixture is exothermic. In an ideal solution, the mixing enthalpy is zero, and in non-ideal solutions, the thermodynamic activity of

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each component differs from the product of its concentration and activity coefficient, and ΔmixH ≠ 0. There are two types of non-ideal solutions: (1)
2.   Non-ideal solutions that show a positive deviation from Raoult's law.
3.   Non-ideal solutions that show a negative deviation from Raoult's law.
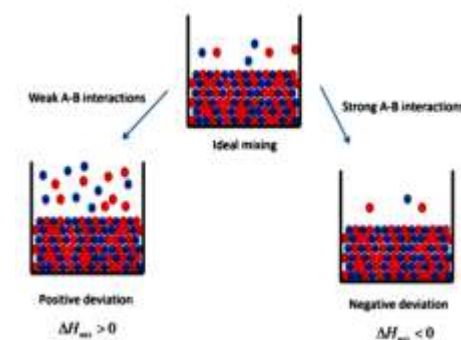
Positive Deviation from Raoult's Law
A positive deviation from Raoult's law occurs when the vapor pressure of a component is greater than what is expected from the law. This type of deviation is observed when the attractive forces between A and B molecules are weaker than the attractive forces between two A molecules or two B molecules. In this case, A molecules can readily escape from the solution, and therefore the partial pressure of A is greater than the predicted value. The behavior of B molecules is also similar. (4)
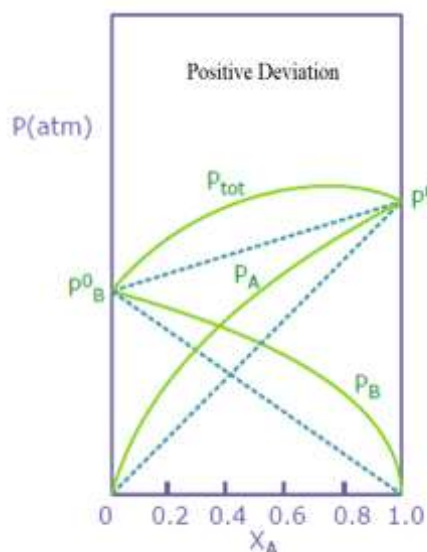
The image opposite shows sample curves of the total vapor pressure and partial pressures for solutions that exhibit a positive deviation from Raoult's law.

Examples of Positive Deviation (1)
Below are some examples of solutions that show a positive deviation from Raoult's law:
4.   Acetone and carbon disulfide
5.   Acetone and benzene
6.   Carbon tetrachloride and toluene or chloroform
7.   Methyl alcohol and water
8.   Acetone and ethanol

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9.   Ethanol and water

Negative Deviation from Raoult's Law
In this deviation, the partial pressures of A and B and the total vapor pressure are less than the predicted pressures. The A-B attractions are stronger than the A-A or B-B attractions. In this case, A molecules cannot readily escape from the solution, and therefore the vapor pressure of A is less than the predicted value. The behavior of B molecules is also similar.(4)
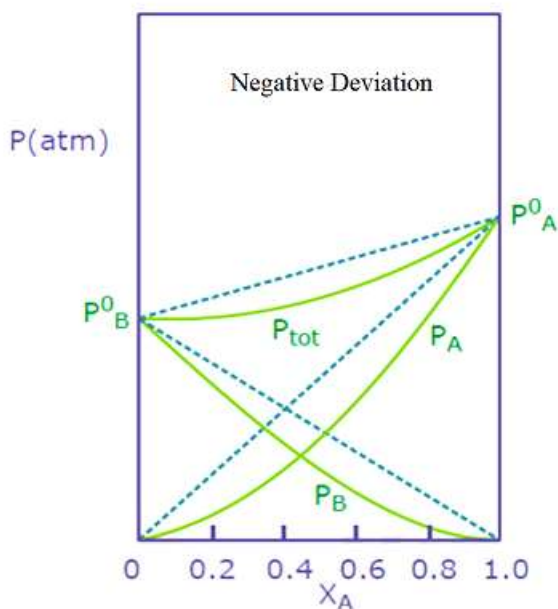
Sample curves of total pressure and partial pressures for solutions exhibiting negative deviation from Raoult's law.

Examples of Negative Deviation (1)
Below are some examples of solutions that show a negative deviation from Raoult's law:
10.   Chloroform and benzene
11.   Chloroform and diethyl ether
12.   Acetone and aniline
13.   Nitric acid and water
14.   Acetic acid and pyridine
15.   Hydrochloric acid and water

Differences Between Ideal and Non-Ideal Solutions (1)

Ideal Solutions	Non-Ideal Solutions

Raoult's Law	
Obey Raoult's law	Do not obey Raoult's law
Molecular Interactions	
Intermolecular interactions between solute and solvent are similar to pure components	Intermolecular interactions between solute and solvent are weaker or sronger than between pure components
Total Vapor Pressure	
Total vapor pressure is as predicted by Raoult's law	Total vapor pressure is less or more than predicted by Raoult's law
Heat of Mixing (Enthalpy of Mixing)	
No heat is released or absorbed, therefore enthalpy of mixing is zero	Heat is either absorbed or released, therefore enthalpy of mixing is positive or negative
Volume of Mixing	
Total volume equals sum of volumes of components, therefore volume of mixing is zero	Contraction or expansion occurs, therefore volume of mixing is non-zero
Separation of Components	
Components can be separated by fractional distillation	Components cannot be separated into pure forms by fractional distillation
Formation of Azeotropes	
Does not form azeotropes	Forms azeotropic mixtures

Solutions : On the basis of Raoult's law.

Ideal
- Obey Raoult's law over the entire range of concentration
- $\Delta_{mix} H = 0$
- $\Delta_{mix} V = 0$

$P_{Total} = P_A + P_B$

- A-A and B-B interactions are equal to A-B interactions

A-B interaction

Non-ideal
- Do not obey Raoult's law over the entire range of concentration

Negative deviation
- $\Delta_{mix} H = -ve$
- $\Delta_{mix} V = -ve$

- A-B interactions are stronger than those between A-A or B-B

Positive deviation
- $\Delta_{mix} H = +ve$
- $\Delta_{mix} V = +ve$

- A-B interactions are weaker than those between A-A or B-B
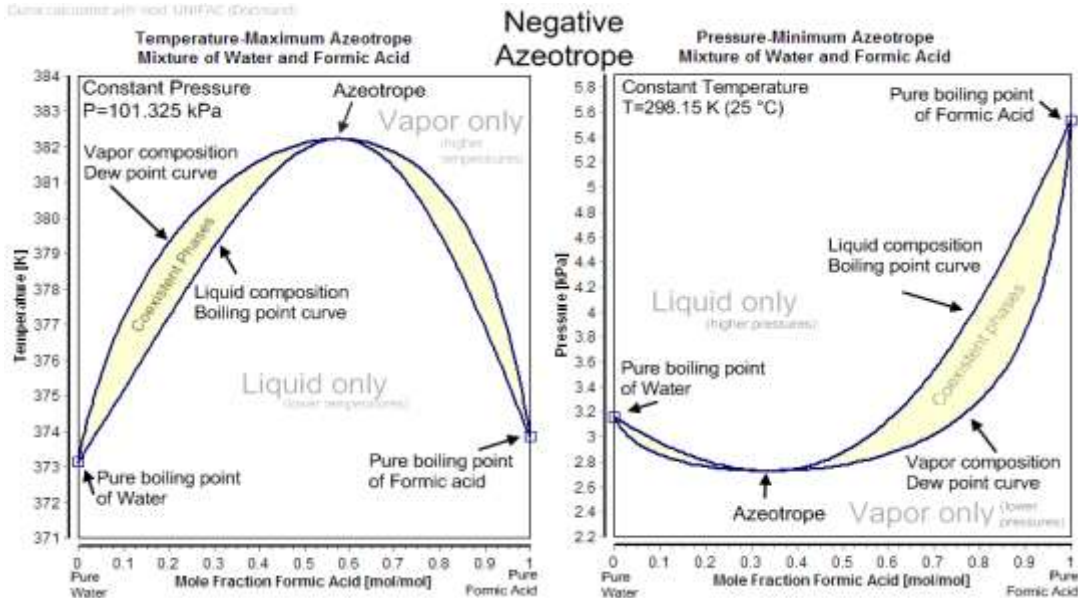
Azeotropes

In the terminology of chemical thermodynamics, azeotropes refer to mixtures that cannot be separated by simple distillation. Raoult's law, under conditions of vapor-liquid equilibrium and for an ideal solution, states that the vapor pressure depends on the chemical composition and the molar decomposition of its particles. As a result, the vapor pressure will have a linear relationship with the mole fraction of the particles. However, in azeotropic mixtures, this relationship deviates from the linear form.

Positive Azeotrope of Chloroform and Methanol Mixture
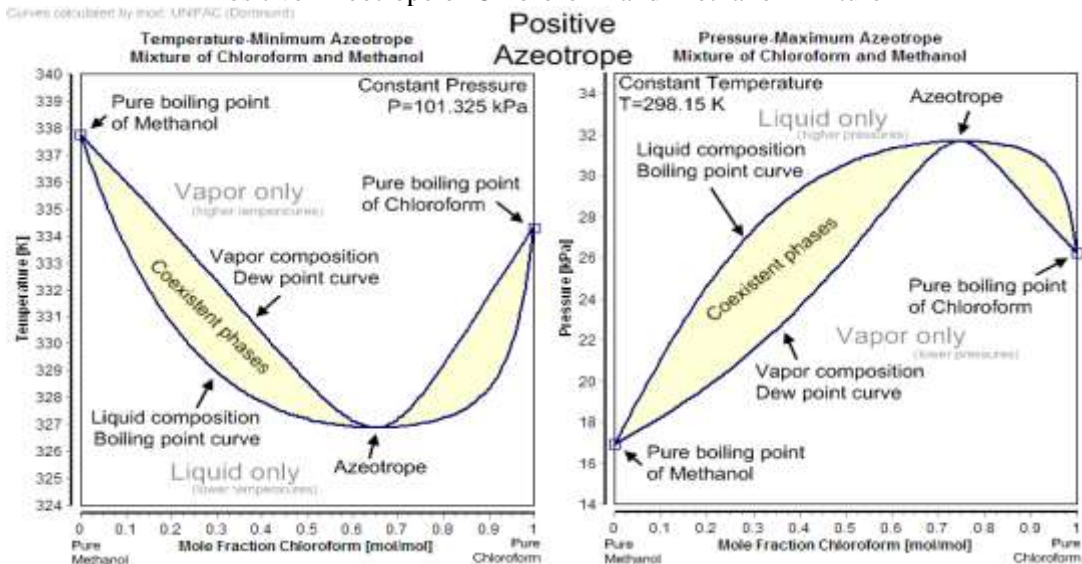
Negative Azeotrope of Formic Acid and Water Mixture

Temperature-Maximum Azeotrope Mixture of Water and Formic Acid — Negative Azeotrope — Pressure-Minimum Azeotrope Mixture of Water and Formic Acid

For a positive deviation, the pressure-mole fraction plot has a maximum and the temperature-mole fraction plot has a minimum. This indicates the dominance of forces between like molecules over forces between unlike molecules.

For a negative deviation, the pressure-mole fraction plot has a minimum and the temperature-mole fraction plot has a maximum. This indicates the dominance of forces between unlike molecules over forces between like molecules.(5)

Raoult's Law and its Proof

Raoult's law states that the vapor pressure of a solvent above a solution is equal to the vapor pressure of the pure solvent at the same temperature scaled by the mole fraction of the solvent present. At any given temperature for a specific solid or liquid, there exists a pressure at which the vapor formed above the liquid or solid phase is in dynamic equilibrium with it. At equilibrium, the rate of evaporation of the solid or liquid equals the rate of condensation of the gas.

Let the rate of evaporation (R_{evap}) and the rate of condensation (R_{cond}) of the solvent at the surface of the pure liquid solvent be defined as follows, where A is the surface area and k represents the rate constants for evaporation and condensation:

$R_{\mathrm{evap}} = \mathrm{A}k_{evap}$
$R_{\mathrm{cond}} = \mathrm{A}k_{cond}P^*_{solvent}$

For the pure solvent, the equilibrium vapor pressure is calculated by equating the rates of evaporation and condensation:

$R_{\mathrm{evap}} = R_{\mathrm{cond}}$
$\mathrm{A}k_{evap} = \mathrm{A}k_{cond}P^*_{solvent}$
$P^*_{solvent} = \dfrac{k_{evap}}{k_{cond}}$

Next, consider an ideal solution. In this case, the evaporation rate gets reduced by the mole fraction factor since only a fraction of the surface will be available for solvent evaporation.

$R_{\mathrm{evap}} = \mathrm{A}k_{evap}\, x_{\mathrm{solvent}}$
$R_{\mathrm{cond}} = \mathrm{A}k_{cond}\, P_{\mathrm{solvent}}$

At equilibrium, we will have:

$R_{\mathrm{evap}} = R_{\mathrm{cond}}$
$\mathrm{A}k_{evap}\, x_{\mathrm{solvent}} = \mathrm{A}k_{cond}\, P_{\mathrm{solvent}}$
$P_{\mathrm{solvent}} = \dfrac{k_{evap}}{k_{cond}}\, x_{\mathrm{solvent}} = x_{\mathrm{solvent}}P^*_{solvent}$

The resulting relation is Raoult's law. (6,7)

Chemical Potential in Gas and Solution Phases

If the liquid and vapor phases are in equilibrium, the following relation holds for each component of the solution, where μ_i is the chemical potential of component i. The chemical potential of a substance in the gas phase is related to its partial pressure by:

$$\mu_i^{vapor} = \mu_i^{\circ} + RTln\frac{P_i}{P^{\circ}}$$

Here μ_i° is the chemical potential for the pure component i in the gas phase at the standard pressure of 1 bar.

Since the chemical potentials of the solution and vapor phases are equal at equilibrium, the above relation can be written as:

$$\mu_i^{solution} = \mu_i^{\circ} + RTln\frac{P_i}{P^{\circ}}$$

For a pure liquid in equilibrium with its vapor, the following applies:

$$\mu_i^* liquid = \mu_i^* vapor = \mu_i^*$$

Therefore, the chemical potential of the pure liquid is given by:

$$\mu_i^* = \mu_i^\circ + RT ln \frac{P_i^*}{P^\circ}$$

Combining the above relations with Raoult's law gives the key relation for an ideal solution:

$$\mu_i^{solution} = \mu_i^* + RT ln x_i$$

This relates the chemical potential of a component in an ideal solution to the chemical potential of the pure liquid component i and the mole fraction of that component in the solution. This relation is useful in describing the thermodynamics of solutions in which all components are volatile and miscible in all proportions. (8)

Henry's Law
In physical chemistry, Henry's law states that the amount of gas dissolved in a liquid is proportional to the partial pressure above the liquid surface. The proportionality factor is known as Henry's law constant, formulated by the English chemist William Henry in 1803. Examples where Henry's law can be observed include the dependence of the dissolution of oxygen and nitrogen gases in the blood flow of divers during diving. Another example is in carbonated beverages containing dissolved carbon dioxide. Before opening the bottle cap, the gas above the liquid is pure carbon dioxide at a pressure higher than atmospheric pressure. After opening the cap and gas escaping, the partial pressure of carbon dioxide decreases. Due to this, the dissolved gas in the beverage comes out of the solution in a process known as "degassing".

There are different ways to define Henry's law constant, which can be divided into two main categories. In the first case, if the solution phase is placed in the numerator and the gas phase in the denominator, we arrive at the solubility constant H in Henry's law. As solubility increases, this value also increases. In another approach, the numerator and denominator can be interchanged, in which case we obtain the volatility constant in Henry's law K_H. As solubility increases, the value of K_H increases.

Typically for solutions, molar concentration of c_a, molality b, and mole fraction x are used. For the gas phase, molar concentration of c_g and partial pressure are used. Ultimately, for a more precise description of Henry's law, two superscripts are employed. For example, H^{cp} refers to Henry's solubility as c/p. The relation for Henry's law regarding solubility with concentration is defined as:

$$H^{cp} = c_a/p$$

In the above relation, c_a is the concentration of the components in the solution phase, and p is the partial pressure of those components in the gas phase under equilibrium conditions. The SI unit for it is defined as mol/(m^3 Pa).

Henry's law can be applied over a wide range of solute particles and under conditions of infinite dilution. In this case, the chemical potential must be considered in Henry's law. For a solute in an ideally dilute solution, the chemical potential depends only on the concentration. In non-ideal solutions, the activity coefficient of the components must also be taken into account. The relation for chemical potential is defined as:

$$\mu = \mu_c^\circ + RT ln \frac{\gamma_c^c}{c^\circ}$$

$$\gamma_c = \frac{K_{H,c}}{p^*}$$

For a volatile solute: $c^\circ = 1 mol/L$

In a non-ideal solution, the activity coefficient (γc) depends on concentration and must be determined based on the desired concentration. Also, for non-volatile solutes where the pure substance vapor pressure can be neglected, the activity coefficient can be calculated using the Gibbs-Duhem equation:

$$\sum_{i=1}^{I} N_i d\mu_i = -SdT + Vdp$$

Absolute temperature: T
Volume: V
Pressure: p
Number of moles of component N$_i$: i
Change in chemical potential: $d\mu_i$
Entropy: S

By measuring the changes in vapor pressure and consequently the changes in the chemical potential of a solvent, the chemical potential of the solute can be obtained. Considering the behavior at infinite dilution, the standard state of a dilute solution can also be defined.

The standard state is a hypothetical 1mol/L solution where the solute exhibits infinite dilution properties. In this regard, all the stated relations can be rewritten in terms of molality b: (9)

$$\mu = \mu_b^\circ + RT ln \frac{\gamma_b^b}{b^\circ}$$

$$\gamma_b = \frac{K_{H,b}}{p^*}$$

For volatile solutions: $b^\circ = 1 \frac{mol}{kg}$

Comparison of Henry's Law and Raoult's Law
Henry's law is a limited law applied to dilute solutions. While Raoult's law is applicable to many solutions, it is specific to when the liquid phase is pure or a mixture of similar substances. The more the system deviates from ideal behavior, the lower the concentration range where Henry's law can be used. In other words, in this

case, the solvent is chemically more different from the solute.

For a dilute solution, the concentration of a solute is relatively dependent on the mole fraction x, and Henry's law can be written as:

$P = K_H x$

This can be compared to Raoult's law:

$P = x\, p^*$

Where p^* is the vapor pressure of the pure component.

At first glance, Raoult's law appears to be a special case of Henry's law. This view is correct for two similar substances, such as benzene and toluene, and Raoult's law holds for their various mixtures (called ideal mixtures).

In general, each of these laws has limitations. In fact, when the mole fraction approaches 1 and the concentration is high, the solution follows Raoult's law, and when the mole fraction approaches 0 and the solution is dilute, it follows Henry's law. These limitations can be shown formulaically and graphically as follows:(10)
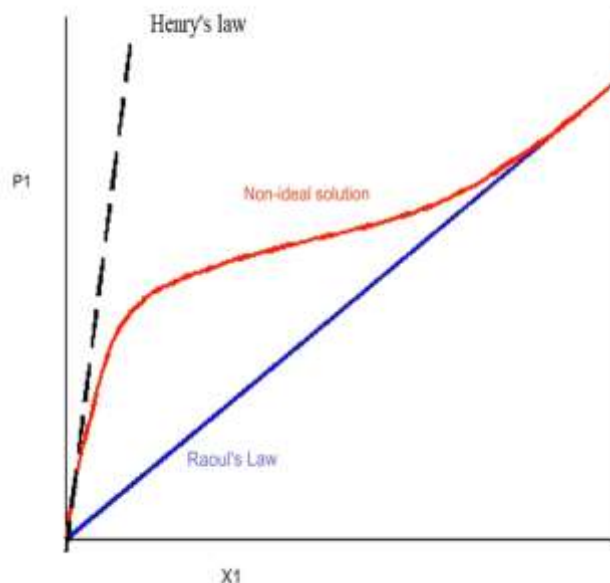
1. Raoult's law: $\lim_{x \to 1}\left(\frac{p}{x}\right) = p^*$

2. Henry's law: $\lim_{x \to \circ}\left(\frac{p}{x}\right) = K_H$

CONCLUSION
The concept of an ideal solution is fundamental to chemical thermodynamics and its applications, such as the use of colligative properties(3). An ideal solution is one where the enthalpy of mixing is zero. As the enthalpy of the solution approaches zero, the solution behavior becomes more ideal. Since the enthalpy of mixing of the solution is zero, the change in Gibbs free energy upon mixing is determined solely by the entropy of mixing.

A non-ideal solution is one that does not follow the rules of an ideal solution, where the intermolecular interactions are the same (or very close) to the interactions between molecules of the different components. Meaning that no force acts between the components, neither van der Waals nor Coulombic forces. We assume ideal properties for dilute solutions and use non-ideal solutions for concentrated solutions. Various forces act on real mixtures, making the prediction of such solution properties difficult. A non-ideal solution is characterized by determining the strength and characteristics of the intermolecular forces between different molecules in the specific solution.

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