A non-ideal solution is a solution that does not abide to the rules of an ideal solution where the interactions between the molecules are identical (or very close) to the interactions between molecules of different components. That is, there is no forces acting between the components: no Van-der-Waals nor any Coulomb forces. We assume ideal properties for dilute solutions.

Introduction

We use the concept of non-ideal solutions for concentrated solutions. A variety of forces act on real mixtures, making it difficult to predict the properties of such solutions. Non-ideal solutions are identified by determining the strength and specifics of the intermolecular forces between the different molecules in that particular solution.

Non-ideal solutions can occur two ways:

- When intermolecular forces between solute and solvent molecules are less strong than between molecules of similar (of the same type) molecules.
- When intermolecular forces between dissimilar molecules are greater than those between similar molecules.

Reminder: A solvent is the major component of a mixture (i.e. water, air) while a solute is the minor component (sugar, carbon dioxide, etc...). A concrete example would be your daily cup of coffee: the coffee itself is the solvent, and anything you add (may it be sugar or cream) will be the solute.

As mentioned above, non-ideal solutions are under study because their properties are not easily predictable, as forces between molecules can fluctuate over time. Non-ideal solutions cannot be defined by Raoult's law or by Henry's law, which are properties specifically unique to ideal mixtures:

- **Raoult's Law**: The vapor pressure of a solvent is proportional to its mole fraction. (for solutions)
- **Henry's Law**: The partial pressure of a gas is proportional to its mole fraction. (for gases)

Since these laws assume that there are no intermolecular interactions, it is evident that they cannot be used for real mixtures, since the mathematical formulas will not hold true anymore due to the fact that the forces will have to be taken into account. However, non-ideal solutions are limited on both sides by these two laws.

There are two main situations that can cause non-ideal solutions to form:

**Situation 1**: Non-ideal solutions can form when forces of attraction between dissimilar molecules are weaker than between similar molecules. At this point, a heterogeneous (non-mixing) solution may still occur, but it is not always the case. The resulting solution has a larger enthalpy of solution than pure components of the solution, causing the process to be endothermic (heat is absorbed to move the reaction forward).

Example 1

A common example of a type of solution where this behavior is seen is in mixtures of carbon disulfide and acetone. Carbon disulfide is non-polar and acetone is polar. Since carbon disulfide is non-polar, the intermolecular attractions are London dispersion forces, which are known to be weak compared to other types of intermolecular forces. However, since
acetone is polar, it has dipole-dipole forces, which are known to be very strong.

Putting these two components together in a mixture results in dipole-induced dipole interactions. Since dipole-dipole induced forces are not nearly as strong as the dipole-dipole interactions between acetone molecules in a pure substance, carbon disulfide-acetone mixtures are non-ideal solutions.

**Situation 2:** Non-ideal solutions can also form when intermolecular forces between dissimilar molecules are larger than those between similar molecules. In this case, interactions between these two types of molecules release more energy than is taken in to separate the two types of molecules. This energy is released in the form of heat, making the solution process exothermic.

Example 2

An example of this kind of non-ideal solution is a mixture of acetone and chloroform.

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**Activity Coefficients**

The chemical activity of a compound corresponds to the active concentration of that particular compound. However, due to intermolecular forces we known is not the case; therefore, we introduce an activity coefficient, labeled \(\gamma\), as a unitless correctional factor. This coefficient takes into account the non-ideal characteristics of a mixture and it is between 0 and 1.

For example, the relationship between the activity of a component and its concentration for ideal mixtures is defined by:

\[
\gamma a_1 = \frac{C}{C_{pure}}
\]

While the same relationship for real (non-ideal) mixtures is defined as follows:

\[
\gamma a_1 = \frac{\gamma C}{C_{pure}}
\]

- If the interactions attract each other: \(\gamma < 1\)
- If the interactions repel one another: \(\gamma > 1\)
- If there are no interactions: \(\gamma = 1\)

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**References**

Inside Links

- Ideal Solutions
- Intermolecular Forces In Mixtures And Solutions
- Van der Waals Forces

Outside Links

- http://wikis.lib.ncsu.edu/index.php/CH_431/Lecture_14#Vapor_pressures_on_non-ideal_solutions

Problems

1. What is the definition of a nonideal solution?
2. What kinds of non-ideal solutions can be represented through Raoult's Law?
3. What kind of solution would a carbon disulfide (CS₂) and acetone ((CH₃)₂CO) mixture form? Why?
4. What kind of solution would a mixture of acetone ((CH₃)₂CO) and chloroform (CHCl₃) form?
5. Is the volume of a non-ideal solution the sum of the volumes of its components?

Answers

1. A non-ideal solution is a solution whose properties are generally not very predictable on account of the intermolecular forces between the molecules.
2. None. Non-ideal solutions by definition cannot be dealt with through Raoult's Law. Raoult's Law is strictly for ideal solutions only.
3. A non-ideal solution. The interactions between the two types of molecules are weaker than interactions between acetone molecules (pure substance). An explanation is given in further detail in the text above.
4. A non-ideal solution. Hydrogen bonding between the two molecules would produce forces of attraction between unlike molecules that exceed those between like molecules.
5. No. If the solution were ideal, this statement would be true. However, for non-ideal solutions, this is usually not the case.

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