Abnormal Molar Masses

In chemistry, when the molar masses are calculated and if they are higher or lower than the expected value are known as abnormal molar masses. These are calculated using the colligative properties. Colligative properties include; elevation of boiling point, lowering relatively of vapor pressure, freezing point depression, and ease of osmotic pressure. The name in itself has abnormal in it which suggests the abnormality of how the molar masses are being calculated, using the Van't Hoff factor. Let's find out.

Introduction to Abnormal Molar Masses

To understand the abnormal molar masses, first, we need to understand the total number of particles left either after the association or dissociation of the solute molecules present in a solution or a solvent. To study and understand more about more about the abnormalities, Dutch chemist Van't Hoff, discovered (i), which is known as the Van't Hoff's factor.

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- Colligative Properties and determination of Molar Mass

- Expressing Concentration of Solutions
- Ideal and Non-ideal Solutions
- Osmosis and Osmotic Pressure
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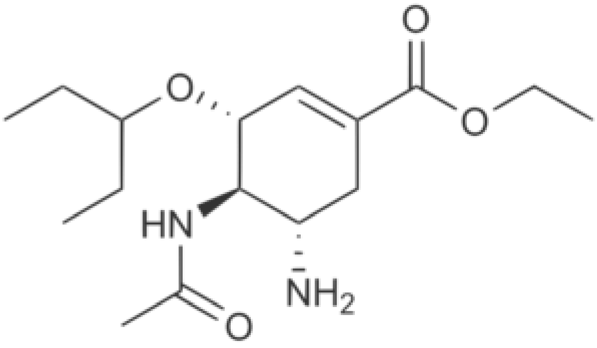
This factor represents the extension of dissociation or association of a solute. This factor alone accounts for all the abnormalities in the molar mass. We will study about the Van’t Hoff’s factor later on, but first, we need to know about the association and dissociation of the solute particles.



Association of the Solute Particles

In a solution, some solute molecules start to associate with each other. Thus, now there is less number of these particles inside a solution. The colligative properties will vary with a number of solute particles in the solution. As a result, they will now, start to decrease with the number of solute particles being less.

The molecular mass of the solute is inversely proportional to its colligative properties. Thus a decrease in colligative properties will lead to an increase in the molecular masses.

Example: acetic acid or ethanoic acid associate in the solution, when dissolved in benzene, dimerizes, because the number of particles and hydrogen bondings are reduced. This happens usually with the solvents which have low dielectric constants. This experiment increases the molar mass more than the expected value achieved theoretically.

Dissociation of Solute Particles

Contrary to the association, some solute particles will dissociate into more ions or particles when they are dissolved in the solution. Thus, this will increase the number of solute particles in the solution and thereby the colligative properties of the solution.

Now, the molar mass being inversely proportional to the colligative properties will reduce the molar mass in the solution. This will result in the lower number of molar mass than the expected value. Thus the molar mass will be abnormal molar mass.

Example: The weak electrolytes are dissolved in the water, ions are formed. Hydrofluoric acid will dissociate into fluorine anion and hydrogen cation.

Van’t Hoff factor

To understand the concept of abnormalities, Van’t Hoff introduced a factor called Van’t Hoff factor. This factor is used to sort out the dissociation and association problem while calculating the molar mass of the solute. The factor is denoted by ‘i’ and is obtained when the normal mass or the expected value is divided by the abnormal mass.

Mathematically, the factor is represented by, i = Normal molar mass/Abnormal molar mass or i = observed or expected colligative properties/calculated colligative properties or i = Total moles in the particles after dissociation or association/total moles in the particles before dissociation or association

Watch Solved Numericals on Molar Masses –

How to calculate i?

Firstly, we will write whether the solute is being dissociated or associated.

For association, $\alpha = n$

$i-1$

$(n-1)$

where n is the no. of particles being associated and α is the degree of association. The equation is derived as follows:

$n\alpha \rightarrow \alpha_n$

Initial moles: 1 mol and 0 mol

Moles at equilibrium: $1 - \alpha$ and

α

n

Therefore, total moles = $1 - \alpha +$

α

n

Thus, $\alpha = n$

$1-i$

$(n-1)$

For solute which depicts the association, the Van't Hoff factor will always be less than 1. For dissociation, $i = 1 + (n - 1)\alpha$. Here, α (alpha) will be the degree of dissociation and n will be a number of dissociated particles. The above equation will be derived from,

$\alpha_n \rightarrow n\alpha$

Initial moles: 1 mole and 0 moles

At the equilibrium: $1-\alpha$ and $n\alpha$

Total no. at equilibrium: $1 - \alpha + n\alpha$

Therefore, $i = 1 - \alpha +$

$n\alpha$

1

Thus, $\alpha =$

$i-1$

$n-1$

For solutes depicting dissociation, Van’t Hoff factor will always be greater than 1. For particles, that shows neither association or dissociation, the Van’t Hoff factor is considered as 1. Thus, after the inclusion of Van’t Hoff’s factor, the equation of the colligative properties will be,

- Boiling point elevation, $\Delta T_b = i \text{ x } K_b \text{ x } m$
- Vapour pressure of the relatively lowering solvent,
- p
- 1
- ^{o}–
- p
- 1

- p
- 1
- o
- =
- i.
- n
- 2
- n
- 1
-
- Freezing point depression, $\Delta T_f = i \times k_f \times m$

Solved Examples for You!

Question 1: The depression of freezing point of the hydrofluoric acid solution is -0.201C° with molality being 0.10 m. Find the Van't Hoff factor. Take off as $1.86C°m^{-1}$.

Solution: As discussed earlier, the solution of hydrofluoric acid will dissociate into fluorine anion and hydrogen cation. Given data,

$\Delta T_f = -0.201C°$

m = 0.10

$K_f = 1.86\ C°m^{-1}$

Taking into account Van’t Hoff factor, the formula for depression of freezing point is, ΔT_f = if Thus, 0.201 = i x 1.86 x 0.10 So, i = 1.08. Thus the Van’t Hoff factor value will be 1.08.

Question 2: Find the Van’t Hoff factor for $Sr(OH)_2$.

Solution: For $Sr(OH)_2$, when it dissolves, the solution is separated into two ions; OH^- ions and Sr^{2+}. It will break up into 2 OH ions and 1 Sr ion. Thus, it will break up into 3 ions and so it’s Van’t Hoff factor will be 3.

Colligative Properties and Determination of Molar Mass

The presence of innumerable elements and substances around us present a unique opportunity to understand their properties. We need to study different properties of such matter because then it becomes easy to comprehend the nature and action of these substances. Determination of molar mass of such matter helps the most in learning the different properties of these substances.

Every matter, whether in solid or liquid or gaseous form, tends to behave in a certain way, which is highly dependent upon its properties. Therefore, all liquid substances can be studied in terms of their colligative properties. This helps in the study of the vapor pressure of the solution. So, let's understand the colligative properties of matter and the determination of molar mass.

Colligative Properties of Liquids

Colligative properties are those properties of a liquid which depend on the number of solute particles and not on the concentration of the solution. These properties are studied in liquids. As per these properties, the mixing of a non-volatile solution in a volatile solution shows a decrease in the relative vapour pressure of the solution.

Furthermore, this decrease in the vapour pressure can be further used to quantify and study the properties of all liquid solutions. Specifically, colligative properties are dependent upon the solute particles present in a given solution. Derived from the Latin word ‘Coligare’, the word, colligative refers to ‘binding together’.

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There are four colligative properties namely- relative lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmosis and osmotic pressures. Related to these properties, the following deductions can be made:

1) Relative Lowering of Vapour Pressure

When a non-volatile solute is added to a solvent, the vapour pressure gets lower. This phenomenon is the lowering of vapour pressure. A relation between the pressure of the solution, the vapour pressure of the pure solvent and the mole fraction of the solute was discovered by a French Chemist.

It was also observed by him that it is mainly the concentration of the solute particles which was responsible for the lowering of vapour pressure. As per the laws devised by scientists at that time, Decrement in Vapour Pressure = Vapour Pressure of Pure Solvent – Vapour Pressure of Solvent. It is through this *equation* that we can determine the ultimate molar mass of a solute.

$(P_{solvent} = X_{solvent}\ P_{osolvent})$

2) Elevation of Boiling Point

The vapour pressure of a solute tends to decrease as a non-volatile solute is added in a solvent. What is to be noted here is that the boiling point of such solution is always greater than the pure solvent in which it is added. This happens because the pressure of vapour is in direct proportion to the temperature of the solution.

If the solution is to be boiled, the temperature of such a solution has to be raised. This phenomenon comes to be identified as the elevation of boiling point. The solute particles in the solvent, along with the vapour pressure, together play a role in this phenomenon.

Formula: $\Delta T = iK_bm$

where ΔT= change in temperature

i = the van’t Hoff factor, which is the number of particles into which the solute dissociates

m = the molality, which is the moles of solute per kilograms of solvent

K_b = the molal boiling point constant (for water, K_b = 0.5121oC/m)

Watch Solved Numericals on Molar Masses

3) Depression of Freezing Point

Decreasing the vapor pressure of a solution results in decreasing the freezing of the solution as well. The freezing point of a solution can be identified as a point at which the vapor pressure of a given substance is equal in the liquid and vapor state. As per the law, the freezing point for a given dilute solution also stays directly proportional to molality of the solute, same as the boiling elevation point.

Formula: $\Delta T = iK_f m$

ΔT= change in temperature

i = the van’t Hoff factor, which is the number of particles into which the solute dissociates

m = the molality, which is the moles of solute per kilograms of solvent

K_f = the molal freezing point constant (for water, $K_f = -1.86\ {}_{o}\mathrm{C}/m$)

4) Osmosis and Osmotic Pressure

You may have observed raw mangoes shriveling when placed in salt water or wilted flowers reviving when placed in fresh water. This happens due to a process called osmosis. Osmosis is the flow of solvent molecules from pure solvent to the solution through a membrane. The flow continues until equilibrium is reached.

The process of osmosis occurs through a membrane that looks continuous but contains small pores that allow small solvent molecules like water to pass through, but not bigger solute molecules. Such membranes are called semipermeable membranes (SPM).

The flow of solvent towards the solution side across the semipermeable membrane can be stopped by applying extra pressure on the solution. This pressure is known as the osmotic pressure of the solution.

Few important things to note –

- During osmosis, the solvent flows from the dilute (lower concentration) to concentrated (high concentration) side across the semipermeable membrane.
- Osmotic pressure depends on the concentration of the solution.

The osmotic pressure of a solution is the excess pressure applied to the solution to prevent osmosis. It is also a colligative property and depends on the number of solute molecules and not their identity.

For dilute solutions, osmotic pressure is directly proportional to the molarity (C) of the solution at a given temperature (T).

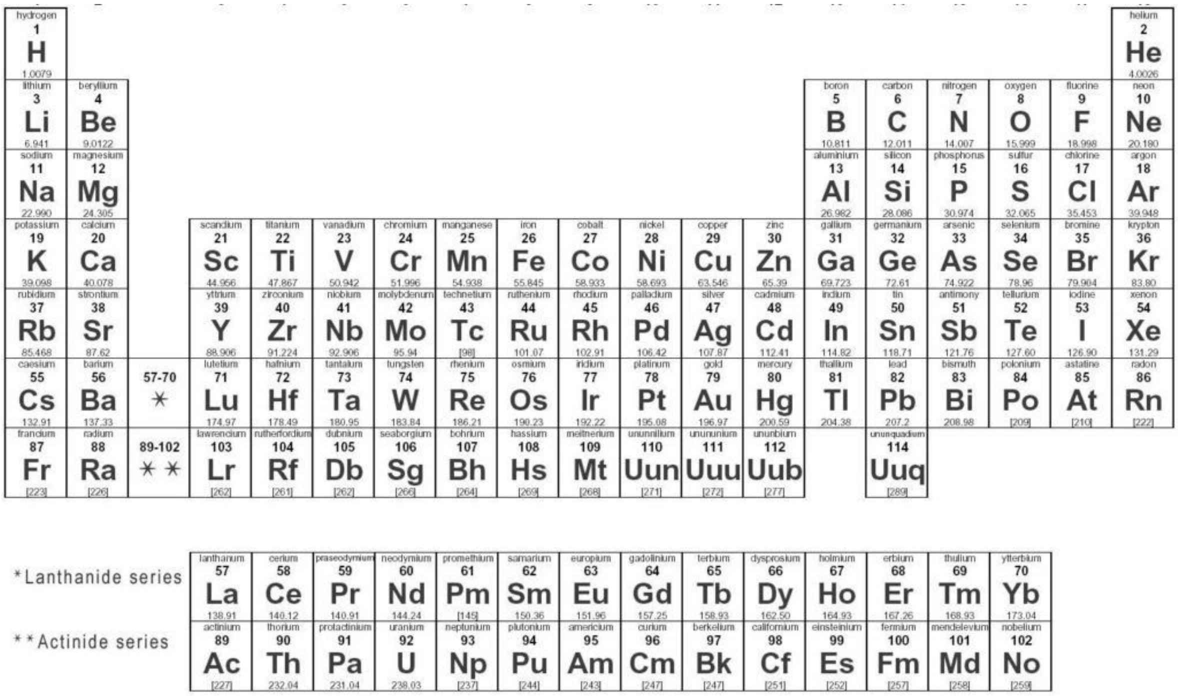
$\Pi = C\ R\ T = (n_2/V)\ R\ T$

where, Π – osmotic pressure, C – molarity, R – gas constant, T – temperature, V – a volume of solution in liters, n – the number of moles of solute.

Since $n_2 = w_2/M_2$, then $\Pi\ V = w_2RT/M_2$ OR $M_2 = w_2RT/\Pi\ V$

NOTE: The measurement of osmotic pressure is widely used to determine the molar masses of polymers, proteins, and other macromolecules.

Determination of Molar Mass



hydrogen 1 H 1.0079																		helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122												boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305												aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078		scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.468	strontium 38 Sr 87.62		yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	89-102 * *	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununnilium 110 Uun [271]	unununium 111 Uuu [272]	ununbium 112 Uub [277]		ununquadium 114 Uuq [289]				

*Lanthanide series	lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
**Actinide series	actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

Usually, the measurement of boiling point elevation, freezing point depression or osmotic pressure, is used to calculate the molar mass or the molecular weight of a solute in a solution.

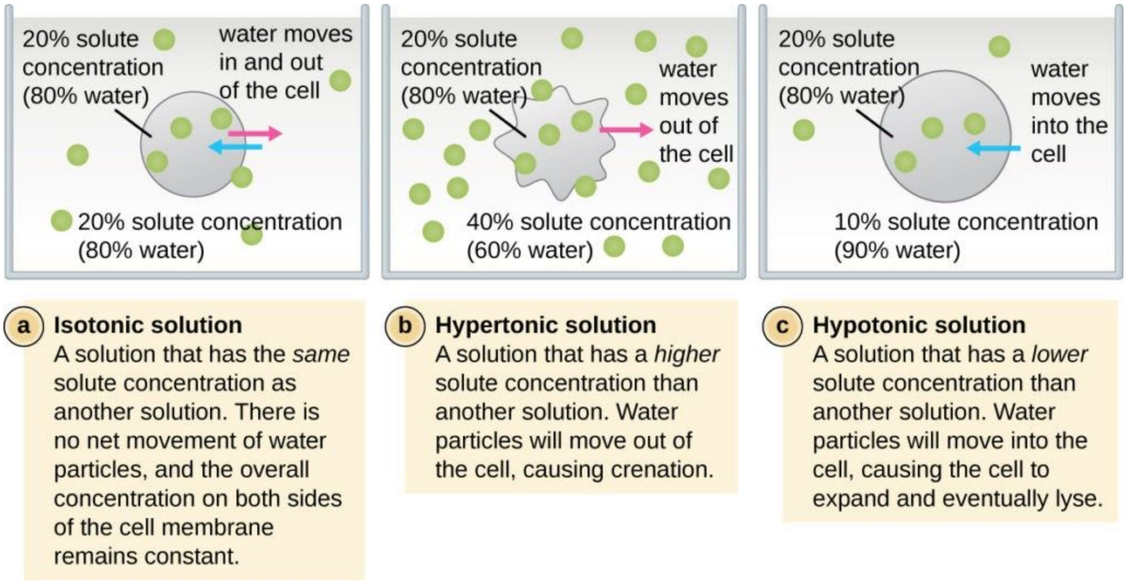
Video on Strength of Solution

Some Important Terms

Isotonic solutions are solutions that have the same osmotic pressure at a given temperature.

Hypotonic solutions are those that have a lower osmotic pressure than other solutions.

Hypertonic solutions are those that have a higher osmotic pressure than other other solutions.


20% solute concentration (80% water)
water moves in and out of the cell
20% solute concentration (80% water)
20% solute concentration (80% water)
water moves out of the cell
40% solute concentration (60% water)
20% solute concentration (80% water)
water moves into the cell
10% solute concentration (90% water)

(a) **Isotonic solution** A solution that has the *same* solute concentration as another solution. There is no net movement of water particles, and the overall concentration on both sides of the cell membrane remains constant.

(b) **Hypertonic solution** A solution that has a *higher* solute concentration than another solution. Water particles will move out of the cell, causing crenation.

(c) **Hypotonic solution** A solution that has a *lower* solute concentration than another solution. Water particles will move into the cell, causing the cell to expand and eventually lyse.

Isotonic, Hypotonic and Hypertonic solutions [Source: Wikimedia Commons]

Solved Question for You

Q: Discuss the formula for the determination of molar mass.

Solution: Different aspects are to be considered for the determination of the molar mass of a solute in a solution. Here, let’s take a look at it now.

1. Firstly, change in boiling point – ΔT = T solution – T pure solvent
2. Secondly, determining the molal concentration – Divide Delta T with constant of boiling point elevation.
3. Finally, determine the molar mass from the mass of an unknown number of moles. Further, for this, divide the mass of unknown with moles of the unknown.

Similarly, the molar mass can be determined from freezing point depression and osmotic point of view. You can determine the moles of the unknown, from the molality of the solution. For this, multiply the molality with the mass of the solvent to determine the same. The same would also be followed in case of freezing point depression and osmotic pressure. Thus, the molar mass can be determined.

Expressing Concentration of Solutions

You know what is concentration, right? But, do you know how to express it? When there is too much salt in your lemonade, you say that it is "too salty". But in chemistry, there is nothing like "too". We have to define it. That is why we are going to study all about the concentration of solutions in this chapter. We will look at the various methods of calculating the concentration of solutions. So, let us start!

Concentration of Solutions

We can calculate the concentration of solutions by various methods. Let's study each method and determine the formulas for this method.

1) Mass/Weight Percentage or Percentage by Mass/Weight

It is the amount of solute in grams present in 100 grams of the solution. Therefore, the formula will be:

$$Mass\ Percentage = \frac{Mass\ of\ Solute}{Mass\ of\ Solution} \times 100$$

$$= \frac{Mass\ of\ Solute}{Mass\ of\ Solute + Mass\ of\ Solvent} \times 100$$

$$= \frac{Mass\ of\ Solute}{Volume\ of\ Solution + Density\ of\ Solution} \times 100$$

The ratio mass of solute to the mass of the solvent is the mass fraction. Thus, the mass percentage of solute = Mass fraction × 100. 10% solution of sugar by mass means that 10 grams of sugar is present in 100 grams of the solution, i.e., we have dissolved 10 grams of sugar in 90 grams of water.

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2) Volume Percentage

It is the volume of solute in mL present in 100 mL solution. The formula will be:

$$Volume\ Percentage = \frac{Volume\ of\ Solute}{Volume\ of\ Solution} \times 100$$

10% solution of HCl by volume means that 10 mL of liquid HCl is present in 100 mL of the solution.

3) Mass by Volume Percentage

It is the mass of solute present in 100 mL of solution. We can calculate the mass of the solute using the volume percentage. The formula would be:

$$Mass\ by\ Volume\ Percentage = \frac{Mass\ of\ Solute}{Volume\ of\ Solution} \times 100$$

A 10% mass by volume solution means that 10 gm solute is present in 100 mL of solution.

4) Molarity

The molarity of a solution gives the number of gram molecules of the solute present in one litre of the solution.

$$Molarity(M) = \frac{Number\ of\ moles\ of\ solute}{Volume\ of\ Solution\ in\ L}$$

For example, 1 mol L^{-1} solution of KCl means that 1 mol of KCl is dissolved in 1 L of water. Unit of molarity: mol L^{-1}

Watch Videos on Molarity

5) Molality

Molality of a solution is the number of moles of solute dissolved in 1 Kg of the solvent.

$$Molality\ (m) = \frac{Number\ of\ moles\ of\ solute}{Mass\ of\ Solvent\ in\ kg}$$

Thus, if one gram molecule of a solute is present in 1 kg of the solvent, the concentration of solutions is said to be one molal. The unit of molarity is mol kg^{-1}. Molality is the most convenient method to express the concentration of solutions because it involves the mass of liquids rather than their volumes. It is also independent of the variation in temperature.

6) Normality

The normality of a solution gives the number of gram equivalents of the solute present in one litre of the solution.

$$Normality\ (N) = \frac{Number\ of\ gram\ equivalents\ of\ solute}{Volume\ of\ Solution\ in\ L}$$

Thus, if one gram equivalent of a solute is present in one litre of the solution, the concentration of solutions is said to be 1 normal.

- 1N = Normal = One gram equivalent of the solute per litre of solution = Normality is 1
- N/2 = Seminormal = 0.5 g equivalent of the solute per litre of solution = Normality is 0.5
- N/10 = Decinormal = 0.1 g equivalent of the solute per litre of solution = Normality is 0.1
- N/100 = Centinormal = 0.01 g equivalent of the solute per litre of solution = Normality is 0.01
- N/1000 = Millinormal = 0.001 g equivalent of the solute per litre of solution = Normality is 0.001

Watch Videos on Normality

7) Mole Fraction

The mole fraction of any component in a solution is the ratio of the number of moles of that component to the total number of moles of all components. The total mole fraction of all the components of any solution is 1. For a binary solution of A and B

$$\text{Mole Fraction of A } (X_A) = \frac{n_A}{n_A + n_B}$$

$$\text{Mole Fraction of B } (X_B) = \frac{n_B}{n_A + n_B}$$

$$\text{And, } X_A + X_B = 1$$

8) Parts per million (ppm)

When a solute is present in trace quantities, it is convenient to express the concentration of solutions in parts per million (ppm). The formula is as follows:

$$ppm = \frac{Number\ of\ parts\ of\ the\ component}{Total\ number\ of\ parts\ of\ the\ components\ in\ the\ solution} \times 10^6$$

In case of mass, we may express it as: (Mass of solute/Mass of solution)× 106

In case of volume, we may express it as: (Volume of solute/Volume of solution) × 106

So, we can express the concentration of solutions in parts per million as mass to mass, volume to volume and mass to volume form. Atmospheric pollution in cities is also expressed in ppm by volume. It refers to the volume of the pollutant in 10^6 units of volume. 10 ppm of SO_2 in the air means 10 mL of SO_2 is present in 10^6 mL of air.

9) Formality

It is the number of mass in grams present per litre of solution. In case, formula mass is equal to molecular mass, formality is equal to molarity. Like molarity and normality, the formality is also dependent on temperature. It is used for ionic compounds in which there is no existence of a molecule. A mole of ionic compounds is called formal and molarity as the formality.

$$Formality = \frac{Weight\ of\ solute(gm)}{Formula\ weight\ of\ solute} \times \frac{1}{Volume\ of\ solutions(L)}$$

$$F = \frac{w}{f} \times \frac{1}{V\ (L)}.(i)$$

$$F = \frac{w}{f} \times \frac{100}{V\ (mL)}.(ii)$$

$$F = n_f \times \frac{1}{V\ (L)}.(iii)$$

Where,

- w = weight of solute,
- f = formula weight of solute
- V= volume of solution
- n_f = no. of gram formula weight

A Solved Example For You

Q: What is the weight percentage of urea solution in which 10 gm of urea is dissolved in 90 gm water.

Solution: Weight percentage of urea = (weight of urea/ weight of solution)× 100

= 10/(90+10) × 100 = 10% urea solution (w/W)

Ideal and Non-ideal Solutions

Too often, you would hear your parents telling you to be an ‘ideal’ kid. What do they mean by that? You better know that! But, when we say ideal and non-ideal solutions, what do we mean? In this chapter, we will study all about ideal and non-ideal solutions. We will look at their properties and examples.

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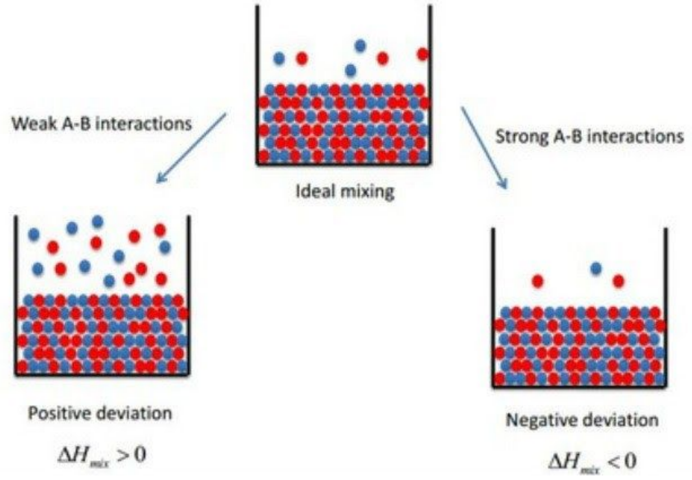
Raoult’s Law

In 1986, it was a French Chemist, Francois Marte Raoult who proposed a relationship between partial pressure and mole fraction of volatile liquids. According to the law, ‘the mole fraction of the solute component is directly proportional to its partial pressure’.


Weak A-B interactions
Ideal mixing
Strong A-B interactions
Positive deviation
$\Delta H_{mix} > 0$
Negative deviation
$\Delta H_{mix} < 0$

On the basis of Raoult's Law, liquid-liquid solutions can be of two types. They are:

- Ideal Solutions
- Non-ideal Solutions

Ideal Solutions

The solutions which obey Raoult's Law at every range of concentration and at all temperatures are Ideal Solutions. We can obtain ideal solutions by mixing two ideal components that are, solute and a solvent having similar molecular size and structure.

For Example, consider two liquids A and B, and mix them. The formed solution will experience several intermolecular forces of attractions inside it, which will be:

- A – A intermolecular forces of attraction
- B – B intermolecular forces of attraction
- A – B intermolecular forces of attraction

The solution is said to be an ideal solution, only when the intermolecular forces of attraction between A – A, B – B and A – B are nearly equal.

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Characteristics of Ideal Solutions

Ideal Solutions generally have characteristics as follows:

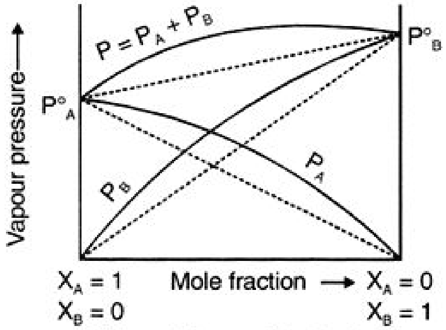
- They follow Raoult's Law. This implies that the partial pressure of components A and B in a solution will be $P_A = P_{A0} x_A$ and $P_B = P_{B0} x_B$. P_{A0} and P_{B0} are respective vapour pressure in pure form. On the other hand, x_A and x_B are respective mole fractions of components A and B
- The enthalpy of mixing of two components should be zero, that is, $\Delta_{mix} H = 0$. This signifies that no heat is released or absorbed during mixing of two pure components to form an ideal solution
- The volume of the mixing is equal to zero that is, $\Delta_{mix} V = 0$. This means that total volume of solution is exactly same as the sum of the volume of solute and solution. Adding further, it also signifies that there will be contraction or expansion of the volume while the mixing of two components is taking place.
- The solute-solute interaction and solvent-solvent interaction is almost similar to the solute-solvent interaction.

Examples of Ideal Solutions

- n-hexane and n-heptane
- Bromoethane and Chloroethane
- Benzene and Toluene
- CCl_4 and $SiCl_4$
- Chlorobenzene and Bromobenzene
- Ethyl Bromide and Ethyl Iodide
- n-Butyl Chloride and n-Butyl Bromide

Non-Ideal Solutions

The solutions which don’t obey Raoult’s law at every range of concentration and at all temperatures are Non-Ideal Solutions. Non-ideal solutions deviate from ideal solutions and are also known as Non-Ideal Solutions.



P-X graph for non-ideal solution showing +ve deviation

Characteristics of Non-ideal Solutions

Non-ideal solutions depict characteristics as follows:

- The solute-solute and solvent-solvent interaction is different from that of solute-solvent interaction
- The enthalpy of mixing that is, $\Delta_{mix} H \neq 0$, which means that heat might have released if enthalpy of mixing is negative ($\Delta_{mix} H < 0$) or the heat might have observed if enthalpy of mixing is positive ($\Delta_{mix} H > 0$)
- The volume of mixing that is, $\Delta_{mix} V \neq 0$, which depicts that there will be some expansion or contraction in the dissolution of liquids

Non-ideal solutions are of two types:

- Non-ideal solutions showing positive deviation from Raoult's Law
- Non-ideal solutions showing negative deviation from Raoult's Law

i) Positive Deviation from Raoult's Law

Positive Deviation from Raoult's Law occurs when the vapour pressure of the component is greater than what is expected in Raoult's Law. For Example, consider two components A and B to form non-ideal solutions. Let the vapour pressure, pure vapour pressure and mole fraction of component A be P_A , P_{A0} and x_A respectively and that of component B be P_B , P_{B0} and x_B respectively. These liquids will show positive deviation when Raoult's Law when:

- $P_A > P_{A0}\ x_A$ and $P_B > P_{0B}\ x_B$, as the total vapour pressure ($P_{A0}\ x_A + P_{0B}\ x_B$) is greater than what it should be according to Raoult's Law.
- The solute-solvent forces of attraction is weaker than solute-solute and solvent-solvent interaction that is, A – B < A – A or B – B
- The enthalpy of mixing is positive that is, $\Delta_{mix}\ H > 0$ because the heat absorbed to form new molecular interaction is less than the heat released on breaking of original molecular interaction
- The volume of mixing is positive that is, $\Delta_{mix}\ V > 0$ as the volume expands on the dissolution of components A and B

Examples of Positive Deviation

Following are examples of solutions showing positive deviation from Raoult's Law:

- Acetone and Carbon disulphide
- Acetone and Benzene
- Carbon Tetrachloride and Toluene or Chloroform
- Methyl Alcohol and Water
- Acetone and Ethanol
- Ethanol and Water

Negative Deviation from Raoult's Law

Negative Deviation occurs when the total vapour pressure is less than what it should be according to Raoult's Law. Considering the same A and B components to form a non-ideal solution, it will show negative deviation from Raoult's Law only when:

- $P_A < P_{A0}\, x_A$ and $P_B < P_{0B}\, x_B$ as the total vapour pressure ($P_{A0}\, x_A + P_{0B}\, x_B$) is less than what it should be with respect to Raoult's Law
- The solute-solvent interaction is stronger than solute-solute and solvent-solvent interaction that is, A – B > A – A or B – B

- The enthalpy of mixing is negative that is, $\Delta_{mix} H < 0$ because more heat is released when new molecular interactions are formed
- The volume of mixing is negative that is, $\Delta_{mix} V < 0$ as the volume decreases on the dissolution of components A and B

A Solved Question for You

Q: Give some examples of solutions showing negative deviation from Raoult's Law.

Solution: Following are examples of solutions showing negative deviation from Raoult's Law

- Chloroform and Benzene
- Chloroform and Diether
- Acetone and Aniline
- Nitric Acid (HNO_3) and water
- Acetic Acid and pyridine
- Hydrochloric Acid (HCl) and water

Osmosis and Osmotic Pressure

You have studied the principle of osmosis. You have possibly done some experiments with salt water as well. Haven't you seen pickles being made at home? That is all the magic of osmosis. But, how does osmosis work? Do you know that osmosis is one major reason for the survival of many species? In this chapter, we will study all about osmosis and osmotic pressure.

What is Osmotic Pressure?

Osmotic pressure is the pressure that we need to apply to stop the flow of solvent molecules from a dilute solution to a concentrated solution through a semi-permeable membrane. Now, the above statement has many terms that need a thorough explanation. We will look at them one by one.

Let us consider the semi-permeable membrane. It is a membrane that selectively allows the movement of particles through it. At some point or the other, we all have seen shrivelling of raw mango when it is pickled in salt water. Blood cells collapse when exposed to saline water. What causes these phenomena? Let us learn about it.

Browse more Topics under Solutions

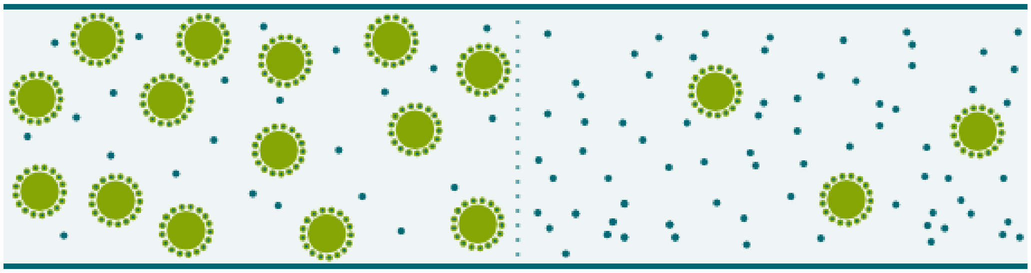
- Abnormal Molar Masses

- Colligative Properties and determination of Molar Mass
- Expressing Concentration of Solutions
- Ideal and Non-ideal Solutions
- Solubility
- Types of Solutions
- Vapour Pressure of Liquid Solutions

What is Osmosis?

We have observed that when we separate a dilute solution from a concentrated solution of the same type by a membrane, the solvent molecules flow from the dilute solution to the concentrated solutions. This movement continues until it reaches an equilibrium. This process of flow of solvent molecules due to the difference in concentration is osmosis.

We can stop the flow of solvent molecules through the membrane by applying external pressure. As we discussed at the beginning, the pressure that just stops the flow of solvent particles is the osmotic pressure.



It is true that osmotic pressure is a colligative property as it only depends on the concentration of the solution. In other terms, osmotic pressure is the extra pressure that we need apply in order to prevent osmosis. Experimental data shows that this pressure is directly proportional to the molarity (number of moles of solute per litre of solution) of the solution at a certain given temperature. Two solutions which have the same osmotic pressures at a given temperature are Isotonic solutions. Learn more about Different Types of Solutions here.

Mathematical Proof

$$\pi = CRT$$

Where,

- π=osmotic pressure

- C=molarity of the solution
- R=Universal Gas constant:
- T=Temperature

Molarity is the number of moles of solute per litre of the solution. Suppose w_2 is the mass of solute having molar mass M_2 in a solution of volume V, then we can write,

$$\pi = w_2RT/M_2V$$

We use the above equation extensively in the determination of the molar mass of complex molecules of proteins, polymers and other macromolecules. Scientists use this preferably for bio-molecules as it shows a significant value even at room temperature.

Learn how to express the Concentration of Solution here.

A Solved Example for You

Q: Is osmosis a reason for cholera?

Ans: Osmosis allows for terrible things to happen, as well. Cholera would not be possible without osmosis. The choleric bacteria populate in our intestines and begin to reverse the intestinal cells' ionic orientation. In other words, it changes the way ions and, subsequently, water transport in our intestines. It means that cholera performs a perfect coup.

First of all, when our ions' orientations are switched, the intestinal cells are no longer able to absorb water into the body. Now osmosis happens in the other direction and water moves from our intestinal cells into our intestines. This is what causes cholera's infamously deadly watery diarrhoea. Second, this compounds the rate at which you get dehydrated. Not only can you not absorb water, you are literally being drained dry. This is why cholera can kill you so quickly because it does not rely on how much water you consume.

Solubility

You know quite a bit about solutions. Your favorite lemonade is a solution! Isn't it? However, do you know what solubility is? What is the solubility of a lemonade? Let us look at the concept of solubility in this chapter. We will look at the solubility of different solutions. Let's begin.

What is Solubility?

Solubility is the maximum amount of solute which dissolves in a specified amount of solvent at a specific temperature. It is the interaction between particles of the solute and the solvent.

Therefore, it depends on the nature of the solute and the solvent. The solubility of solids in liquids is independent of pressure. We will now look at the solubility of solids in liquids.

Browse more Topics under Solutions

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- Vapour Pressure of Liquid Solutions

The Solubility of Solids in Liquids

Two factors determine the solubility of solids in liquids,

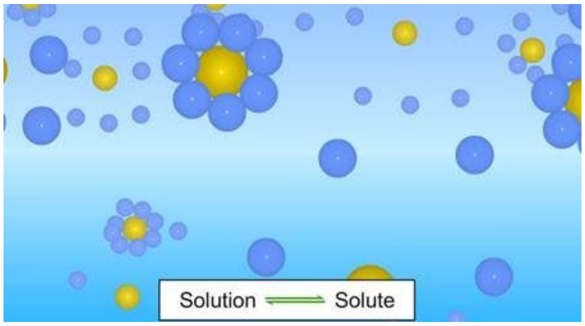
- Nature of the solute and solvent
- The temperature

1) Nature of the Solute and Solvent

In general “like dissolves like”. Thus, a polar solute dissolves in a polar solvent, and a non-polar solute dissolves in a non-polar solvent. Therefore, polar (or) ionic molecules like sugar and sodium chloride dissolve in water molecules as these are polar. On the other hand, non-polar molecules like naphthalene and anthracene dissolve in solvents like benzene and carbon tetrachloride as these are non-polar.

The solubility of ionic compounds is the result of the strong electrostatic interaction between the ions of the solute and the polar molecules of the solvent. On the other hand, the solubility of non-polar solutes is the result of similar solute-solute, solute-solvent, and solvent-solvent interactions.

When there is the addition of solid solute to a solvent, its concentration in the solution increases. This process is known as dissolution. On continuous addition of the solute, there will come a state where no more solute can dissolve in the solvent at a given temperature. Such a solution is known as a saturated solution.



A state of dynamic equilibrium reaches between the solute particles going into the solution and the solute particles separating out. The concentration of the solute in such a solution is its solubility. If any more solute is added to a saturated solution, it will separate out. This is the process of precipitation. A solution in which more solute can be dissolved at a specific temperature is an unsaturated solution.

2) Temperature

We require heat to break the bonds holding the molecules in the solid together. At the same time, the formation of new solute-solvent bonds gives off heat. If the heat liberated in the dissolving process is higher than the heat required to break the solid apart, the net dissolving reaction is exothermic.

The Solubility of a Gas in Liquids

If you thought only solids dissolve in liquids, you are wrong! Even gases dissolve in liquids. One common example of this would be the cold drinks that you enjoy or the aerated drinks. They have carbon dioxide dissolved in them.

Solved Example for You

Q: Explain the Le-Chatelier’s principle.

Solution: As per Le-Chatlier’s principle, for an exothermic dissolution process, an increase in temperature inhibits the dissolving reaction. This is because the reaction already produces the excess heat. If the heat given off in the dissolving reaction is less than the heat we require to break the solid apart, the net dissolving reaction is endothermic.

As per Le-Chatlier’s principle, for an endothermic dissolution reaction, more heat facilitates the dissolving reaction by providing energy to break the bonds in the solid.

Types of Solutions

Solutions are a part of our everyday lives. The soda you enjoy sipping, the deodorant that you put on all important occasions are all examples of solutions. Did you ever wonder how many types of solutions are actually there? Well, in this chapter, we will talk about the different types of solutions and look at what exactly these are.

What is a Solution?

Going by the definition, a binary solution is nothing but a homogeneous mixture of two substances. These two substances or components are the solute and the solvent. The solute is the substance that gets dissolved. It is present in a smaller quantity. On the other hand, the solvent is the substance that dissolves the solute. It is present in a comparatively larger quantity.

There are different types of solutions. But, what is the basis of their differentiation?

Different Types of Solutions

Solutions are of different types, based on a number of criteria, like the difference in the solute or the solvent etc. Let us now look at the different types of solutions, based on different criteria.

On the Basis of Water as Solvent

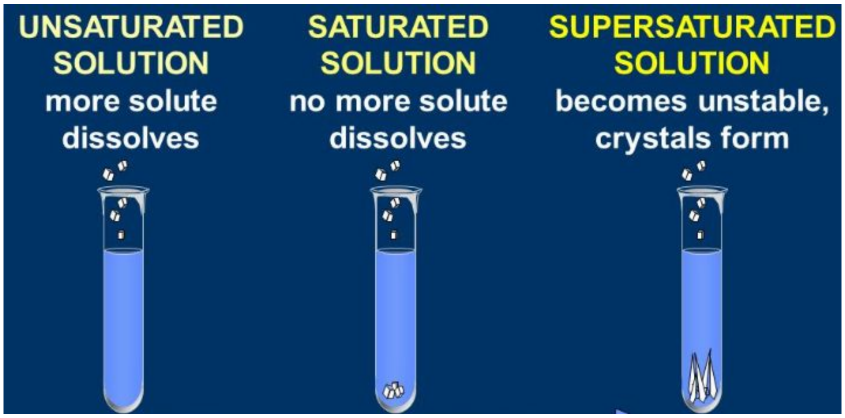
Based on the whether the solvent is water or not, solutions are of two types.

- Aqueous solutions: These solutions have water as the solvent. Examples of such solutions are sugar in water, carbon dioxide in water, etc.
- Non-Aqueous Solutions: These solutions have a solvent that is not water. It could be ether, benzene, petrol, carbon tetrachloride etc. Common examples include sulfur in carbon disulphide, naphthalene in benzene, etc.

On the Basis of the Amount of Solute Added

Based on the amount of solute present in the solution, we can classify them into the following types.

- Unsaturated Solution: An unsaturated is one that can dissolve more solute at a definite temperature. It means that we can still add more solute to the solvent.
- Saturated Solution: A solution is said to be saturated when we can't add any more solute to the solvent. This means that the solution can't dissolve any more solute at a definite temperature.
- Supersaturated Solution: A supersaturated solution is one where the solute is present in an excess amount. This solute is dissolved forcefully by raising the temperature or pressure of the solution. These generally crystal out in the bottom by the method called crystallisation.


UNSATURATED SOLUTION
more solute dissolves
SATURATED SOLUTION
no more solute dissolves
SUPERSATURATED SOLUTION
becomes unstable, crystals form

On the Basis of Amount of Solvent Added

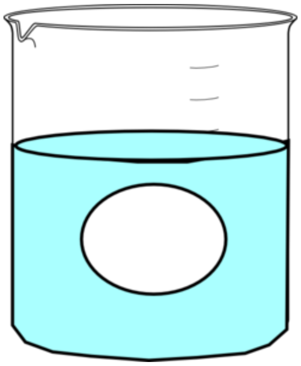
- Concentrated Solution: A concentrated solution has large amounts of solute in the given solvent. Examples include Brine solution, Orange juice, dark colour tea.
- Dilute Solution: A dilute solution has a small amount of solute in a large amount of solvent. Examples include Salt solution, light colour tea.

On the Basis of Concentration of Solute in Two Solutions

Let us consider a cell placed in a solution in a beaker. Based on the concentration of solute in two solvents(in the cell and in the beaker), we can have the following types of solutions:

- Isotonic Solution: These solutions have the same concentration of the solute in it. Therefore, water moves across the cell from the solution in the beaker in both directions.
- Hypertonic Solution: The solution kept in beaker has a higher concentration of solute in it so water comes out of the cell and into the solution in beaker causing the cell to plasmolyze/shrink.

- Hypotonic Solution: The solution kept in beaker has a lower concentration of solute in it so water moves into the cell causing cells to swell up and finally burst.



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Learn more about How to Express Concentration of Solution here.

A Solved Example for You

Q: Give an example of a gas-solid solution.

Answer: Hydrogen gas in palladium metal is an example of a gas-solid solution.

Vapour Pressure of Liquid solutions

Vapour pressure can be defined as pressure formed by the vapor of the liquid (or solid) over the surface of the liquid. This pressure is formed in a thermodynamic equilibrium state in a closed container at a certain temperature. Liquid's evaporation rate is identified by the equilibrium vapor pressure. Vapour pressure increases with the temperature. The boiling point of the liquid is the point when the pressure exerted by surrounding equals to the pressure exerted by vapor. In this chapter, we will study more about the Vapour Pressure on liquids and its characteristics.

What is Vapour Pressure?

You have read about pressure. It is the force that a mass exerts on another. But, do you know vapour also exerts pressure, even if you can't see it? You have of course felt it! Haven't you?

We form a liquid Solution by dissolving a solid, liquid or gas in a specific liquid solvent. Vapour Pressure of liquid solutions is the amount of pressure that the vapours exert on the liquid solvent when they are in equilibrium and a certain temperature.

Vapour pressure changes with the temperature of the surroundings and the nature of the liquid. Let us now have a look a some of the important characteristics of vapour pressure on liquid solutions.

Browse more Topics under Solutions

- Abnormal Molar Masses
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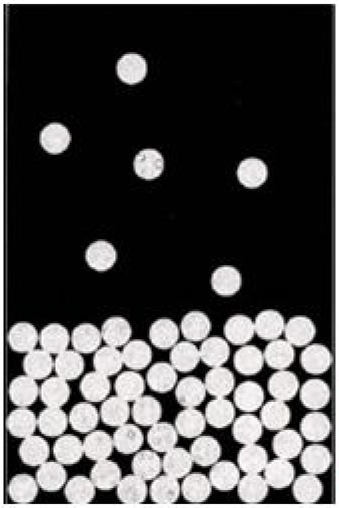
- Types of Solutions

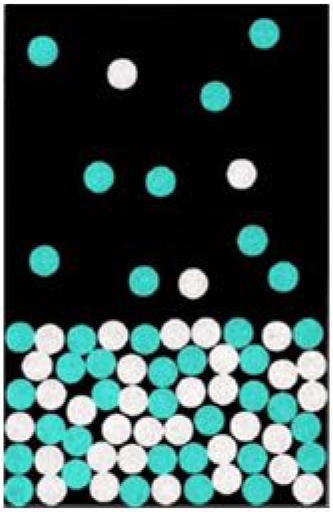
Characteristics of Vapour Pressure

- A pure liquid experiences a greater amount of vapour pressure as against a liquid’s solution.
- It is inversely proportional to the forces of attraction existing between the molecules of a liquid.

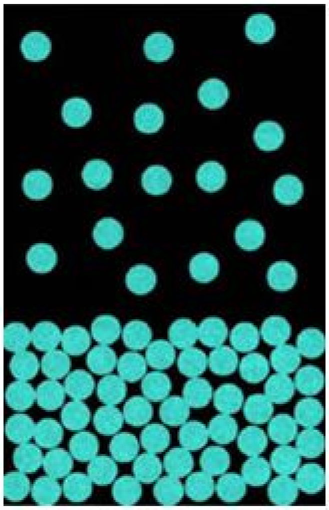
- It increases with a rise in the temperature. This is because the molecules gain kinetic energy and thus, vapourise briskly.



Vapor-liquid equilibria for pure tolune



Vapor-liquid equilibria for equal amounts of pure tolune + benzene



Vapor-liquid equilibria for pure benzene

A liquid solution might have a volatile solute and solvent as well. In the majority of the cases, we can see that the solvent is volatile, while the solute is not. Based on this, we will study it in two instances: Liquid-Liquid Solutions and Solid-Liquid Solutions.

Vapour Pressure of Liquid-Liquid Solutions

To evaluate this, we take two volatile liquid solutions. Let us name their liquid components as A and B. After placing the volatile liquid with their components in a closed vessel, we find that equilibrium establishes between the liquid phase and vapour phase.

Suppose P_{total} is the overall vapour pressure at an equilibrium state and let P_A and P_B be the partial vapour pressures of components A and B respectively. Adding further, the mole fraction of respective components is x_A and x_B respectively. To evaluate vapour pressure of volatile liquids, we use Raoult's Law.

Raoult's Law

The law states that the partial pressure is directly proportional to the mole fraction of the solute component. So, according to Raoult's Law, the partial pressure of A will be

$$P_A \propto x_A$$

$$P_A = P_{A0}\ x_A$$

where P_{A0} is the vapour pressure of pure liquid component A. Similarly partial pressure of B will be

$$P_B \propto x_B$$

$$P_B = P_{B0}\, x_B$$

where P_{B0} is the vapor pressure of pure liquid component B. Now, we will apply Dalton's law of partial pressures. This law tells us that the total pressure (P_{total}) of the solution placed in a container is the sum of partial pressures of its respective components. That is

$$P_{total} = P_A + P_B$$

$$P_{total} = P_{A0}\, x_A + P_{B0}\, x_B$$

Also since, $x_A + x_B = 1$, we can write the relation as:

$$P_{total} = P_{A0} + (P_{B0} – P_{A0})\, x_B$$

Vapour Pressure of Solutions of Solids in Liquids

Let us now look at the other type of solutions i.e. solids in liquid solution. Here we consider a solid as the solute, while the solvent is a liquid. In these cases, the solute is non-volatile in nature. The vapour pressure is less than the pure vapor pressure of the solution. Let us now see how we can find the overall vapour pressure of such a solution.

We consider a solution in which A is the solvent and B is the solute. Applying the Raoult’s Law, we know that partial vapour pressure of individual component (solute/solvent) is directly proportional to its mole fraction.

Now, if we add a non-volatile solute, it is imperative that vapour pressure comes only from the solvent part. This is because they are the only available component in the vapour phase. Hence, if P_A is the vapor pressure of the solvent, x_A is its mole-fraction and P_{A0} is the vapor pressure of the pure solvent, then by Raoult’s law, the relation will come out to be:

$$P_A \propto x_A$$

$$P_A = P_{A0}\, x_A$$

When we plot a graph between mole fraction of solvent and vapour pressure, we find its nature to be linear.

Solved Example For You

Question: Why does the Vapour Pressure decrease when we add a non-volatile solute in the solvent?

Answer: We know that evaporation is a surface phenomenon. The greater the surface area, the more is the evaporation. Hence, the vapour pressure is more. In a pure liquid, we can see that there is more surface area available for the molecules to get evaporated. Therefore, they have more vapour pressure.

On adding a non-volatile solute, we cause the solvent molecules to get less surface to escape. Hence, it decreases.