VAPOUR PRESSURE OF SOLUTION

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Vapor pressure of liquid- When a liquid is placed in a closed vessel, part of the liquid evaporates and fills the available space with the vapours. As the evaporation proceeds, the number of gaseous molecules in the vapour phase increases gradually. These molecules move about at random in a limited space and during their random movement, some of these strike the surface of liquid and get condensed. The process of condensation acts in opposite direction to the process of evaporation.



Thus, both evaporation and condensation processes go on simultaneously. Ultimately a stage is reached when the rate of evaporation becomes equal to the rate of condensation and an equilibrium gets established between liquid and vapor phases. The pressure exerted by the vapor at the equilibrium is called vapor pressure.

"The pressure exerted by the vapors above the liquid surface in equilibrium with the liquid at a given temperature is called vapor pressure"

Factors on which vapor pressure of a liquid depends:

Nature of the liquid: - Each liquid has a characteristic vapor pressure because each liquid has different magnitude of intermolecular forces. The liquids, which have weaker inter-molecular forces, tend to escape readily into vapor phase and therefore, have greater vapor pressure. For example, dimethyl ether and alcohol have higher vapor pressure than water at a given temperature because of weaker intermolecular forces in them as compared to water.

Temperature:- The vapor pressure of a liquid increases with increase in temperature. This is due to the fact that with increase in temperature, more molecules will have larger kinetic energies. Therefore, larger number of molecules will escape from the surface of the liquid to the vapor phase resulting in higher vapor pressure.

Vapor pressure of liquid solutions: Liquid solutions are formed when solvent is a liquid and the solute may be a gas, a liquid or a solid. Let us learn about the solutions of liquids and solids in a liquid. Such solutions may contain one or more volatile components. Generally, the liquid solvent is volatile. The solute may or may not be volatile. We shall mainly concentrate on the properties of binary solution containing only two components.

Vapor pressure of liquid-liquid solution: When a binary solution of two volatile liquid is placed in a closed vessel, both the components would evaporate and eventually an equilibrium would be established between vapor phase and the liquid phase. In the case of binary solutions of volatile liquids, the vapor phase consists of vapor of both the components. The French chemist Raoult (1886) gave a quantitative relationship between the partial pressures and the mole fraction of two components. This relationship is known as Raoult's law which states that "at a given temperature for solution of volatile liquids, the partial vapor pressure of each component in solution is equal to the product of vapor pressure of the pure component and its mole fraction".

Let us consider a binary solution of two volatile liquids and denote the components as A and B having mole fraction x_A and x_B respectively. If P_A and P_B are the vapor pressures of the components in the solution, then according to Raoute's law:

$$P_{A} = p_{A}^{0} x_{A}$$
$$P_{B} = p_{B}^{0} x_{B}$$

Where p^{0}_{A} is the vapor pressure of the component A and p^{0}_{B} is the vapor pressure of pure component B at the same temperature.

According to Dalton law of partial pressures, the total pressure p over the solution phase in the container will be the sum of the partial pressure of the components of the solution. This is given as: $p = p_A + p_B$.

Substituting the values of p_A and p_B , we get $p = p^0_A x_A + p^0_B x_B$

As we know, $x_A + x_B = 1$ or $x_A = 1 - x_B$ $\therefore p = p^0_A (1 - x_B) + p^0_B x_B - (i)$

 $p = p^{0}_{A} + (p^{0}_{B} - p^{0}_{A})x_{B}$ -----(ii)

From equation (i), the following conclusion can be drawn: (i) Total vapor pressure over the solution can be related to the mole fraction of any one component $[x_A \text{ or } x_B=1-x_A]$.

(ii) Total vapor pressure of the solution varies linearly with the mole fraction of component B because p^{0}_{A} and p^{0}_{B} are constant.

(iii) Depending on the vapor pressure of the pure component A and B, total vapour pressure over the solution decreases or increases with the increase of the mole fraction of the component A. The equation (ii) shows that the total vapour pressure (p) is a linear function of the mole fraction x_B or x_A because p^0_A and p^0_B are constant at a particular temperature. this is shown in figure. The dotted lines give the partial pressures of the two components versus composition and the solid line gives the total vapor pressure vs composition. The graph can be easily understood as:

According to Raoute's law, the partial vapor pressures of two components A and B of a solution are given as: $pA = p^{0}AxA$ and $pB = p^{0}BxB$ Therefore, the vapor pressures of the components are linear functions of their mole fractions. Now,

- (i) when $x_A = 1$, i.e., the liquid is pure A $p_A = p_A^0 x \ 1 = p_A^0$
- (ii) when $x_A = 0$, i.e., the liquid is pure B $p_A = p_A^0 x 0 = 0$.

Thus, the plot of p_A against x_A should give a straight line passing through p^o_A (when $x_A = 1$) and 0 (when $x_A = 0$). This is shown by line 1 in figure. It is clear from the curve that when the liquid is pure ($x_A = 1$), its vapor pressure is equal to p^o_A . As component B is added to component A(x_A decreases), the vapour pressure decreases along the line 1 till it becomes zero ($x_A=0$).



Similarly, the variation of partial pressure of component B (p_B) with its mole fraction (x_B) is represented by the plot from $x_B = 0$ (i.e., $p_B = p_B^0 x 0 = 0$) to $x_B = 1$ (i.e., $p_B = p_B^0 x 1 = p_B^0$). It is shown by line II. The total vapor pressure p, exerted by the solution as a whole at any composition is given by the sum of partial pressures according to Dalton's law of partial pressures.

Thus, $p = p_A + p_B = p_A^0 x_A + p_B^0 x_B$

This is shown by line III in figure. Obtained by joining the points $p^{0}A$ and p^{0}_{B} . It is clear from the figures that the vapor pressure of solutions of different compositions, lies between the vapor pressure of the pure components (p^{0}_{A} and p^{0}_{B}) and they lie on the straight line joining p^{0}_{A} and p^{0}_{B} . The minimum value of p (total vapour pressure) is p^{0}_{A} and the maximum value of p^{0}_{B} assuming that the component A is less volatile than component B i.e., $p^{0}_{A} < p^{0}_{B}$.

Vapor pressure of solution of solid in liquid: This is a most common class of solution formed by the dissolution of solids in liquids such as sodium chloride, glucose, urea, sugar in water and Iodine and sulphur in carbon disulphide. Some physical properties such as vapour pressure are quite different from those of pure solvents. Let us add a small amount of non-volatile solute to the solvent. (e.g. sugar in water) to form the solution. When evaporation of this solution takes place, the vapor phase again consists of vapors of the solvent (i.e., water) because the solute is nonvolatile. However, the vapor pressure of the solution is found to be less than that of pure solvent. This is explained as follows: We know that evaporation is a surface phenomenon. The vapour pressure depends on the escape of solvent molecules from the surface of the liquid. In the case of solution, the non-volatile sugar molecules as shown by small black spheres in the figure, also occupy a certain surface area. As a result, lesser number of solvent molecules will escape into

vapours. In other words, vapour pressure of the solution will be less than that of pure solvent or there will be a lowering in vapour pressure. The increase in the concentration of sugar in the solution will further lower the vapour pressure of the solution.



Raoult's law for liquid solutions containing non–volatile solutes: According to Raoult's law the partial vapour pressure of volatile component in the solution is directly proportional to the mole fraction in it. When the solute is non volatile, only the solvent molecules are present in vapour phase. Therefore, the vapour pressure of the solution will be the vapour pressure of due to solvent only.

Vapour pressure of the solution = vapour pressure of the solvent in the solution

If p_A is the vapour pressure of the solvent over a solution containing nonvolatile solute and x_A is its mole fraction, then according to Raoult's law, the vapour pressure of solvent in solution, $p_A = p_{AA}^0 x_A \quad p = p_{AA}^0 x_A = p$ (pure solvent) x mole fraction of solvent. This relationship is known as Raoult's law.

Thus, for solution containing nonvolatile solutes, the Raoult's law may be stated as at a given temperature, the vapour pressure of a solution containing nonvolatile solute is directly proportional to the mole fraction of the solvent. If vapour pressure of the solution containing a non-volatile solute is plotted against the mole fraction of the solvent, a straight-line plot will be obtained.



The above relationship may also be put forward in different ways as shown by rearranging the above equation, $\frac{p}{r_0} = x$

$$p_A = x_A$$

Subtracting each side of the equation from 1, we have

$$\frac{1 - \frac{p}{p_A^o}}{p_A^o} = 1 - x_A \quad \text{or } \frac{p_A - p}{p_A^o} = x_B \quad (x_A + x_B = 1 \text{ or } 1 - x_A = x_B)$$

$$\frac{p_{solvent}^o - p_{solution}}{p_{solvent}^o} = x_{solute}$$

Here, $p_{A}^{0}-p_{A}$ (difference in vapour pressure of pure solvent and solution) represents the lowering in vapour pressure on the formation of solution. Now, by dividing the lowering in vapour pressure with the vapour pressure of the pure solvent, we get the relative lowering in vapour pressure. The above relation also gives alternative statement of Raoult's law. Thus, the Raoult's law in its modified form may be stated as: the relative lowering in vapour pressure of an ideal solution containing the non-volatile solute is equal to the mole fraction of the solute at a given temperature.

Raoult's law is a special case of Henry's law: Raoult's may be regarded as a special case of Henry's law. According to Raoult's law, the vapour pressure of a volatile component is given solution is given by the relation: $p_A = p_A^0 x_A^0$. Here p_A^0 is the vapour pressure of the pure component, p_A^0 is the vapour pressure is the solution having mole fraction x_A^0 . In the case of solution of a gas in a liquid, the gasesous component is volatile component. Its solubility is regarded governed by Henry law which gives the relation: $p = K_H x$.

Here, p is the pressure of the gas above the solution and x is its mole fraction, K_H is a proportionality constant known as Henry's constant.

The comparison of equations for Raoult's law and Henry law shows that the partial pressure of the volatile component or gas is directly proportional to its mole fraction in solution. The only difference in the two expression is the proportionality constant p^{0}_{A} (in Raoult's law) and K_{H} (in Henry's law). Therefore, Raoult's law becomes a special case of Henry law in which KH becomes equal to Vapour pressure of the pure component (p^{0}_{A}). Even the liquid solution, one of the components may sometime obey Henry's law over a range of mole fraction. In that case K_{H} becomes equal to P^{0}_{A} . In practice, in solutions in which solute behaves ideally according to Henry law, the solvent also behaves ideally according to Raoult's law. However, the reverse is not necessary true and the Raoult's law ideality of the solvent does not mean that solute must obey Henry law.

As the solution becomes more and more dilute and approaches a limit of infinite dilution $(x_2 \rightarrow 0)$ its components behave more ideally, the solvent behaves Raoult's Law whereas the solute minor component) obey Henry law for dilute solutions.