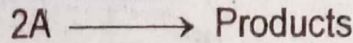


7.8.1 The Collision Theory of Reaction Rates

This theory is based upon two postulates.

- (i) Molecules must collide (تصادم کرنا چاہیے) among themselves to do a chemical reaction
- (ii) The energies of the colliding (تصادم کرنے والے) molecules must be at least equal to the activation energy ' E_a '.

In order to do the mathematical explanation (ریاضیاتی تشریح) of this theory, let us consider a bimolecular reaction with same type of molecules i.e., 'A'.



According to law of mass action, the rate of reaction depends upon the concentration of substance 'A'.

$$-\frac{d[A]}{dt} = k[A]^2 \quad \dots\dots (1)$$

Since, collisions are must for doing a chemical reaction, so we should take into account the number of collisions happening among the molecules of substance 'A'. This is called collision number and is denoted by ' Z_{AA} '. It is the number of collisions between like molecules per unit time per volume.

$$Z_{AA} = \frac{1}{\sqrt{2}} \cdot \pi \sigma^2 n_A^2 \bar{c} \quad \dots\dots (2)$$

' σ ' is the collision diameter (تصادم کے وقت دو ذروں کے سنٹرز کا فاصلہ) of the molecule and it is a quantitative measurement (مقداری پیمائش) of size of the molecules. ' \bar{c} ' is the average velocity (میانگ رفتار) of the gas molecules. ' n_A ' is the number of molecules per unit volume.

According to first assumption (مفروضہ), the rate of this bimolecular reaction should be equal to the collision number.

$$-\frac{d[A]}{dt} = Z_{AA}$$

Moreover, the concentration of the substance 'A' may be replaced by ' n_A ' which is the number of molecules per unit volume.

$$\text{As } -\frac{d[A]}{dt} = k[A]^2$$

$$\text{Hence } -\frac{d[A]}{dt} = kn_A^2$$

In other words,

$$kn_A^2 = Z_{AA}$$

$$k = \frac{Z_{AA}}{n_A^2} \quad \dots\dots (3)$$

According to the equation (3), the rate constant of the reaction is expressed in terms of collision number ' Z_{AA} ' and number of molecules per unit volume.

The units of the rate constant of bimolecular reaction are $\text{dm}^3 \text{mol}^{-1} \text{sec}^{-1}$. The units of R.H.S. of equation (3) should be changed accordingly. Hence equation (3) is converted into

$$\left(\frac{N_A}{10^3} \right) \text{ سے ضرب دی ہے۔}$$

$$k = \left[\frac{N_A}{10^3} \right] \times \frac{Z_{AA}}{n_A^2} \cdot \text{dm}^3 \text{mol}^{-1} \text{sec}^{-1} \quad \dots\dots (4)$$

Let us substitute the value of Z_{AA} from equation (2) in (4) and simplify it.

$$k = \left[\frac{N_A}{10^3} \right] \times \frac{1}{\sqrt{2}} \cdot \pi \sigma^2 \bar{c} \cdot \text{dm}^3 \text{mol}^{-1} \text{sec}^{-1} \quad \dots\dots (5)$$

' \bar{c} ' is the average velocity and has the expression.

$$\bar{c} = \sqrt{\frac{8RT}{\pi M}}$$

Let us put this expression of ' \bar{c} ' in equation (5) and simplify

$$k = 2 \left(\frac{N_A}{10^3} \right) \sigma^2 \sqrt{\frac{\pi RT}{M}} \text{dm}^3 \text{mol}^{-1} \text{sec}^{-1} \quad \dots\dots (6)$$

If we compare equation (4) and (6) then,

$$\left(\frac{N_A}{10^3} \right) \frac{Z_{AA}}{n_A^2} = 2 \left(\frac{N_A}{10^3} \right) \sigma^2 \sqrt{\frac{\pi RT}{M}} \quad \dots\dots (7)$$

Let us now consider that the reaction is taking place at unit concentration Under these circumstances.

$$\left[\frac{N_A}{10^3} \right] \frac{Z_{AA}}{n_A^2} = Z^0$$

' Z^0 ' is the collision number at unit concentration. When we give the units of second order reactions to ' Z^0 ' then

$$Z^0 = \left(\frac{N_A}{1000} \right) \times \frac{Z_{AA}}{n_A^2}$$

Under these circumstances, we can say that

$$k = Z^0 = 2 \left(\frac{N_A}{10^3} \right) \sigma^2 \sqrt{\frac{\pi RT}{M}} \quad \dots\dots (8)$$

Simply, we can say that

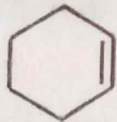
$$k = Z^0 \text{dm}^3 \text{mol}^{-1} \text{sec}^{-1} \quad \dots\dots (9)$$

According to equation (8) and (9), we can calculate the rate constant for this bimolecular reaction, if we know the collision diameter ' σ ' temperature ' T ' and molar mass ' M ' of the reacting substance.

Verification of Equation:

This equation (8) can be verified by two ways.

- (i) By calculating the effect of temperature on rate constant.
(ریٹ کانسنٹ پر درجہ حرارت کا اثر دیکھیں)
- (ii) By comparing the experimental and theoretical rate constants.
(تجرباتی اور غیر تجرباتی k کی قیمتوں کا مقابلہ کریں۔)

(4) $2\text{NO}_2 \longrightarrow 2\text{NO} + \text{O}_2$	9.4×10^9	1.6×10^{11}	6.0×10^{-2}
(5) $\text{C}_2\text{H}_4 + \text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$ \longrightarrow 	3.00×10^7	7.5×10^{11}	4×10^{-3}

نیبل (7.1) کے پہلے دوری ایکشن بتا رہے ہیں کہ ان کا P فیکٹر ایک ہے یعنی orientation کی پرواہ نہیں کر رہے جتنے activated حالت میں کریں ہو رہی ہیں ساری بار آور ہیں۔

Shortcomings (خامیاں) of Collision Theory:

The collision theory in the form of equation (11) is also not applicable to following cases.

- When the complex (پیچیدہ) molecules are involved in the chemical reactions.
- When the chain mechanism (تسلسل والا راستہ) is to be obeyed by the chemical reactions.
- When the reaction is surface catalyzed (سطحی عمل انگیز).

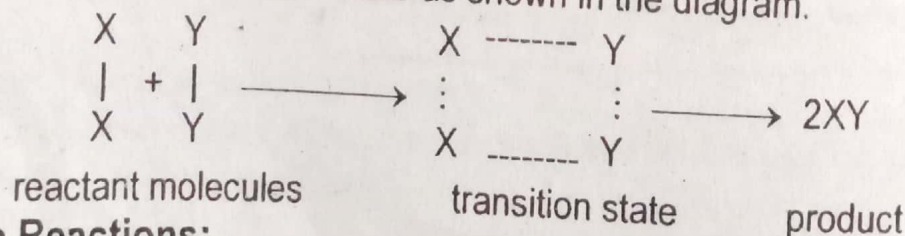
7.9.0 TRANSITION STATE THEORY

7.9.1 Introduction:

Transition state theory tells us the continuous series of changes (تبدیلیوں کا تواتر سے جاری رہنے والا سلسلہ) in bond distances when the reacting molecules approach each other. During these changes in configuration (وضع - ہیئت ترتیب اجزا) of molecules, energy changes also take place. The molecules which are reacting, form a specific configuration (خاص وضع) before getting transformed into products. Such a configuration is called as transition state or activated complex.

The transition state which is formed does not represent an observable substance (ایسی چیز جس کا مشاہدہ ہو سکے). It cannot be isolated (الگ کرنا). It is assumed to possess properties such as bond length, molecular weight, enthalpy along with the rotational and vibrational degrees of freedom. These properties are possessed by real molecules.

The transition state of the reaction corresponds to the highest point on the potential energy diagram (مخفی توانائی کا گراف). The two reacting molecules 'X₂' and 'Y₂' can be visualized (چشم تصور سے دیکھنا) to form the product XY through the transition state as shown in the diagram.



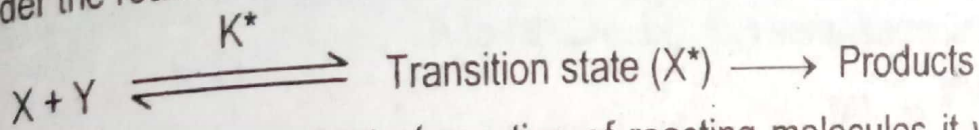
7.9.2 Many Step Reactions:

Some of the reactions take place in a single step but many reactions occur through several steps. Each step passes through a transition state and an intermediate (درمیان میں بننے والا) is formed. The

rate of the reaction is governed by the slowest step. This step is called rate determining step (ریٹ ڈیٹرمیننگ سٹیپ).

Mathematical Equation:

Let us consider the reaction



By using some fundamental (بنیادی) properties of reacting molecules it was shown by Eyring that the rate constant 'k' for any reaction of this type is given by:

$$k = \frac{RT}{N_A h} K^* \quad \dots \dots (1)$$

In equation (1), ' N_A ' is Avogadro's number and ' K^* ' is an equilibrium constant for the formation of activated complex from the reacting molecules.

$$K^* = \frac{X^*}{[X][Y]}$$

The equilibrium constant ' K^* ' is related with free energy change ' ΔG^* ' by well known equation from thermodynamics.

$$\Delta G^* = -RT \ln K^*$$

$$\ln K^* = -\Delta G^* / RT$$

Taking antilog on both sides

$$K^* = e^{-\Delta G^* / RT} \quad \dots \dots (2)$$

ΔG^* is the free energy for activation. Putting equation (2) in equation (1)

$$k = \frac{RT}{N_A h} e^{-\Delta G^* / RT} \quad \dots \dots (3)$$

7.9.4 Significance of Equation of Transition State Theory:

Equation (3) gives us the information about the effect of temperature and free energy change on the rate constant of chemical reaction. This equation has two factors i.e. $RT / N_A h$ and $e^{-\Delta G^* / RT}$. If the temperature is constant then the first factor is constant and so the rate constant depends upon the second factor which involves the free energy change. If ' ΔG^* ' has a negative value then the second factor is greater than unity and the rate constant k is favourable for the chemical reaction. Greater the negative value of ' ΔG^* ', greater the rate constant of the chemical reaction.

7.9.5 Advantages of Transition State Theory Over Collision Theory:

- (i) In collision theory of reaction rates, we have a probability factor ' P ' which is introduced arbitrarily (بے اصولی کے ساتھ). But in transition state theory the introduction of the entropy of activation ' ΔS^* ' has been justified.
- (ii) In collision theory of reaction rates, we simply assume that the molecules of the reactants collide together and change into products, but in transition state theory, we introduce the concept of formation of activated complex which is more appropriate (مناسب).

7.10.0 COLLISION THEORY OF UNIMOLECULAR REACTIONS

8.1.0 INTRODUCTION

"A solution is a homogeneous mixture of two or more substances existing in one or more states." That solution which is consisted of two components is called a binary (دو چیزوں پر مشتمل) solution. That component (ترکیبی جز) which has the same physical state (وہی طبعی حالت) as that of solution is called solvent. Mostly it is thought that the substance in greater quantity is called solvent and the other component is called solute.

In a dilute solution, the quantity of the solute is very small as compared to that of solvent.

There are various types of solutions depending upon the fact that out of three states of matter which is solute and which of them is the solvent.

8.1.1 Concentration Units of Solutions

The concentration (تکثیف) of a solution tells us quantity of solute dissolved in a given quantity of solvent or solution. The various units are as follows:

1. **Strength of solution:** It is the number of grams of solute present in one dm^3 of solution.

2. **% age of Solution:**
The % age of solution can be (a) weight / weight (b) weight / volume (c) volume / weight (d) volume / volume.

It is the % age by mass or by volume per 100 parts of the solution.

3. Molarity (M)

It is the number of moles of the solute dm^{-3} of solution.

4. Molality (m)

It is the number of moles of the solute per 1000 grams of solvent.

5. Normality:

It is the number of gram equivalents of the solute dm^{-3} of solution.

6. Mole Fraction:

It is the number of moles of any component divided by total number of moles of all the components of the solution. It is always less than unity.

7. Parts per Million:

It is the number of parts of a component per million parts of the solution. It is abbreviated as ppm

$$\text{ppm of a component} = \frac{\text{Mass of the component}}{\text{Total mass}} \times 10^6$$

This unit is used for those solutions in which the quantity of the solute is extremely small.

8.1.2 Formulas for Various Concentration Units of Solutions:

(1) % age composition:

(a) **Weight/weight % age:**

5 grams of glucose is dissolved in 100 grams of solutions. (5 g of solute + 95 g of solvent)

(b) **Weight/volume % age:**

5 grams of glucose is dissolved in 100 cm³ of solution.

(c) **Volume/weight % age:**

5 cm³ of ethyl alcohol is dissolved in 100 g of solution.

(d) **Volume / volume % age:**

5 cm³ of ethyl alcohol is dissolved in 100 cm³ of solution.

It means that the total volume or weight of the solution is 100 units. It may be mass in gram or volume in cm³.

(2) **Molarity:**

Molarity of solution is related with mass of the solute, molar mass of the solute and volume of the total solution:

$$\text{Molarity} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1}{\text{Volume of solution in dm}^3}$$

(3) **Molality:**

Molality of a solution is related with mass of the solute, molar mass of solute and mass of the solvent

$$\text{Molality} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1}{\text{Mass of solvent in kg}}$$

(4) **Normality:**

Normality of a solution is related with mass of the solute, equivalent mass of the solute and volume of the solution in dm³.

$$\text{Normality} = \frac{\text{Mass of solute}}{\text{Equivalent mass of solute}} \times \frac{1}{\text{Volume of solution in dm}^3}$$

(5) **Mole fraction:**

"It is the ratio of number of moles of one component to the total number of moles of all the components of solution."

Suppose, there are three components 'A', 'B' and 'C' having number of moles 'n_A', 'n_B' and 'n_C'. The mole fractions are denoted by 'x_A', 'x_B' and 'x_C'.

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

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

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

The sum of mole fractions is unity

$$x_A + x_B + x_C = 1$$

Now let us discuss
Ideal Solution:

In order to differentiate (فرق کرنا) between ideal (معیاری) and non-ideal (غیر معیاری) solutions, some of the following criteria are taken into consideration.

(i) If the forces of interaction (جوڑنے والا قوتیں) of the components after mixing are same as among the molecules of pure components, then the solutions are ideal.

(ii) If the heat of solution ($\Delta H = 0$) (سولیوشن کے بننے کے دوران حرارت) is zero, then the solution is ideal.

(iii) If there is no change in the volume ($\Delta V = 0$) (جسامت میں کوئی تبدیلی نہ ہو) of the solution, then the solution is ideal.

(iv) If the equation of osmotic pressure (نفوذی دباؤ) is obeyed by the solutions, then they behave as ideal solutions i.e.

$$\pi V = n_2 RT$$

(v) Those solutions which obey the Raoult's law at all concentrations and all the temperatures, then they are called ideal solution.

8.2.3 Best Criteria of Ideality of a Solution:

Raoult's law is one of the best criteria to check, whether a solution is ideal or not. So, in order to understand the difference between an ideal and non-ideal solution, let us thoroughly (مکمل طور پر) understand the Raoult's law.

8.3.0 RAOULT'S LAW

8.3.1 Introduction:

We know that vapour pressure is one of the basic (بنیادی) properties (صفت) of a liquid. It increases with the increase of temperature. When solutes are added into the solvents, then their vapour pressures are lowered. This lowering of vapour pressure is due to the presence of the particles of the solute on the surface of solutions. Raoult has given the quantitative relationship (مقداری تعلق) between vapour pressure of the solution and the quantities of the solutes and the solvents.

8.3.2 Raoult's Law When the Solute is Non-volatile (جو طیران پذیر آسانی سے نہ ہو یا بخارات میں آسانی سے):

Non-electrolyte (نابرق پاش):
Let us consider that, the vapour pressure of the pure solvent is P° , and that of the solution is

Let the mole fraction of solvent and the solute be ' X_1 ' and ' X_2 ' respectively.
According to first definition of Raoult's law, "the vapour pressure of the solution is directly proportional to the mole fraction of the solvent."

$$P \propto X_1 \quad \dots\dots\dots (1)$$

$$\boxed{P = P^\circ X_1}$$

Since,

$$X_1 + X_2 = 1$$

Rearranging

$$X_1 = 1 - X_2$$

Putting the value of 'X₁' in equation (1)

$$P = P^\circ (1 - X_2)$$

Opening brackets

$$P = P^\circ - P^\circ X_2$$

$$P^\circ - P = P^\circ X_2$$

$$\boxed{\Delta P = P^\circ X_2} \quad \dots\dots\dots (3)$$

$$\Delta P \propto X_2$$

ΔP is called lowering of V.P.

So, "the lowering of vapour pressure ' ΔP ' is directly proportional to the mole fraction of the solute". This is, you can say the second definition of Raoult's law.

$$\boxed{\frac{\Delta P}{P^\circ} = X_2} \quad \dots\dots\dots (4)$$

$\frac{\Delta P}{P^\circ}$ is called relative lowering of vapour pressure.

According to third definition of Raoult's law "the relative lowering (مقابلہ تانگی) of vapour pressure is equal to mole fraction of the solute".

8.3.3 Importance of Relative Lowering of Vapour Pressure:

According to third definition of Raoult's law, given in equation (4), we feel it would be better that $\frac{\Delta P}{P^\circ}$ should be reported in the literature (درجہ حرارت کی تبدیلی سے آزاد), rather than lowering of vapour pressure. Relative lowering of vapour pressure is

- Independent of temperature.
- Proportional to the concentration of the solute.
- Is a constant quantity, when equimolecular proportions (موازنے کے لحاظ سے برابر نسبت) different solutes are dissolved in same mass of the same solvent.

Born	10 May 1830
Nationality	French
Fields	Chemistry
Known for	Raoult's law
Died	1 April 1901



François-Marie Raoult

فلاسک میں واپس آنے والے مائع میں B کی مقدار زیادہ ہوتی ہے۔ وہ بخارات جو اوپر جاتے ہیں اور مگلی فلاسک میں وصول ہو جاتے ہیں ان کی مقدار زیادہ ہوتی ہے۔ کیونکہ A کم B.P والا مائع ہے۔ اس کا بخاراتی دباؤ B سے زیادہ ہے۔

8.4.2 Non-ideal Solutions:

No doubt, there are certain pairs of miscible liquids (آپس میں حل ہو جانے والے) which obey Raoult's law throughout the complete range of concentrations (ارتکاز کی مکمل رینج تک) at a given temperature. These pairs are as follows.

- (i) Benzene and bromobenzene
- (ii) Benzene and ethylenedichloride
- (iii) Ethylene dibromide and propylenedibromide

However, there are many systems of pairs of liquids, which do not obey the Raoult's law to greater or lesser extent (کم یا زیادہ حد تک). It depends upon the nature of the liquids and the temperature.

In order to understand the deviations (انحراف) of the solution from Raoult's law, let us understand the graphs between mole fractions and vapour pressures. We observe that there are three types of solutions (سولیوشنز کی تین قسمیں ہیں) which show non-ideal behaviour and they show deviations from Raoult's law.

TYPE-I: Those pairs of liquids, whose total vapour pressures are intermediate between those of pure constituents:

(a) If we plot a graph between compositions (ترکیب) and vapour pressures (بخاراتی دباؤ) for cyclohexane and CCl_4 system, then we observe that the graphs pass above the expected straight line of Raoult's law. Anyhow, the total vapour pressure is all the times intermediate (درمیان) between the vapour pressures of two components. The following diagram (8.6) makes the idea clear.

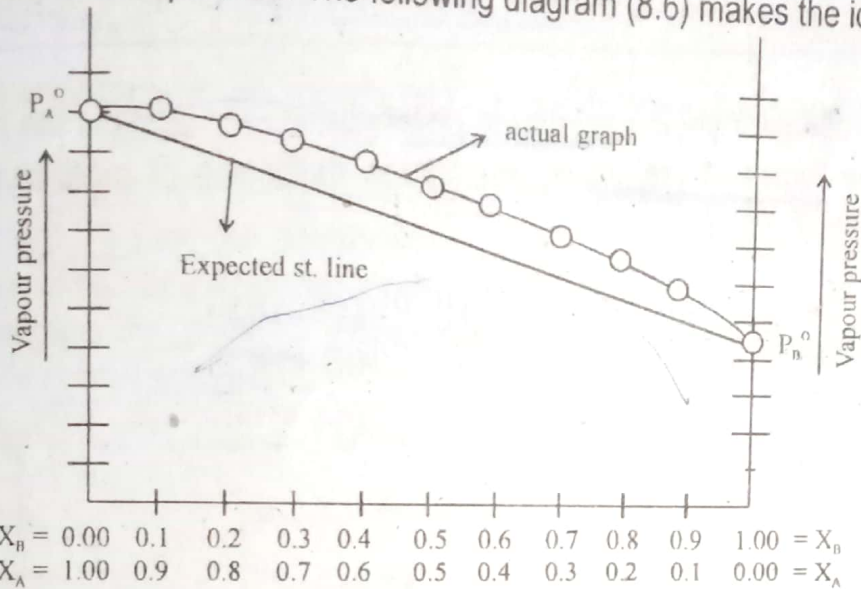


Fig. (8.6) Vapour pressure-composition graph for type-I solutions.

Some other examples in this reference are:

- (i) $\text{CH}_3\text{OH} + \text{H}_2\text{O}$ (ii) $\text{C}_6\text{H}_6 + \text{C}_6\text{H}_5\text{CH}_3$
- (iii) $\text{C}_6\text{H}_6 + \text{CCl}_4$ (iv) $\text{C}_6\text{H}_{12} + \text{CCl}_4$

Such pairs of liquids create the forces of repulsion to some extent, as compared to pure components. This makes the vapour pressure greater than expectations.

TYPE-II: Those pairs of liquids, which show a maximum point (بلندی والا نقطہ) in the total vapour pressure curve, are said to show positive deviation (مثبت انحراف) from Raoult's law. Following graph (8.7) makes the idea clear.

Examples:

- (i) $\text{C}_6\text{H}_6 + \text{C}_6\text{H}_{12}$ (ii) $\text{C}_6\text{H}_6 + \text{C}_2\text{H}_5\text{OH}$ (iii) $\text{C}_2\text{H}_5\text{OH} + \text{CHCl}_3$
- (iv) $\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$ (v) $\text{C}_3\text{H}_7\text{OH} + \text{H}_2\text{O}$ (vi) $\text{CH}_3\text{COCH}_3 + \text{CS}_2$

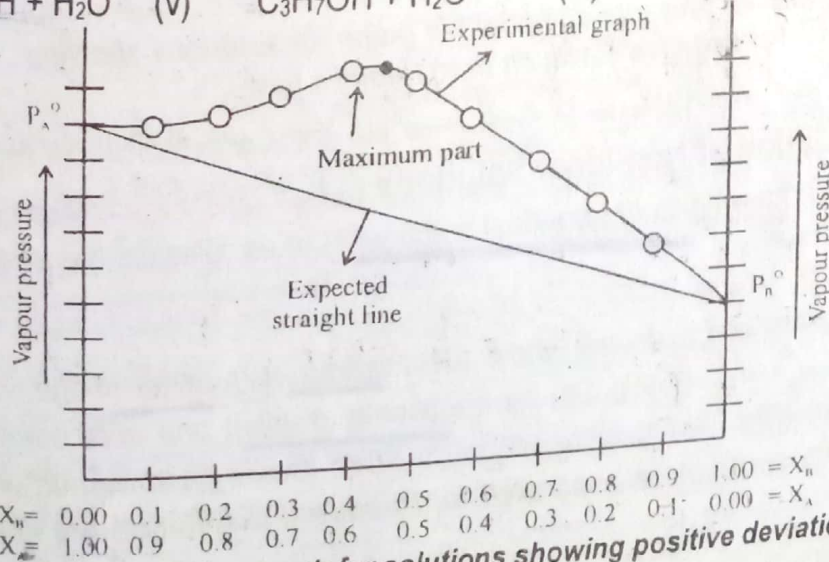


Fig. (8.7) Vapour pressure composition graph for solutions showing positive deviation from Raoult's law.

اس قسم کے سولیوشنز میں دونوں مائع کا بخاراتی دباؤ تھوڑا سا زیادہ ہوتا ہے جتنا ہم امید کر رہے ہوتے ہیں۔ امید تو ہم یہ کرتے ہیں کہ سیدھی لائن ملے گی۔ لیکن کسی بھی سولیوشن کا بخاراتی دباؤ 100% A اور 100% B کے درمیان ہو گا۔ ایسے مائع کے مائیکولز میں ایک دوسرے کو روکنے کی قوت ہوتی ہے۔

یہ ایسا گراف دیتے ہیں کہ امید کردہ سیدھی لائن سے گراف اوپر سے گزرتا ہے۔ یعنی Type I کی طرح۔ پس گراف میں ایک نقطہ بخاراتی دباؤ کا ایسا بھی آتا ہے جس کی قیمت باقی تمام بخارات دباؤ سے کہیں زیادہ ہوتی ہے یعنی گراف میں Maximum پوائنٹ آتا ہے۔

Type-III:

Certain pairs of liquids show a minimum point (کم سے کم قیمت والا نقطہ) in the total vapour pressure curve. They show the forces of attractions among the molecules of pure components. Following diagram (8.8) makes the idea clear.

Examples:

- (i) $\text{CH}_3\text{COCH}_3 + \text{CHCl}_3$
 (iii) $\text{H}_2\text{O} + \text{HCOOH}$
 (v) Pyridine + CH_3COOH .

- (ii) $\text{H}_2\text{O} + \text{HNO}_3$
 (iv) $\text{H}_2\text{O} + \text{HCl}$

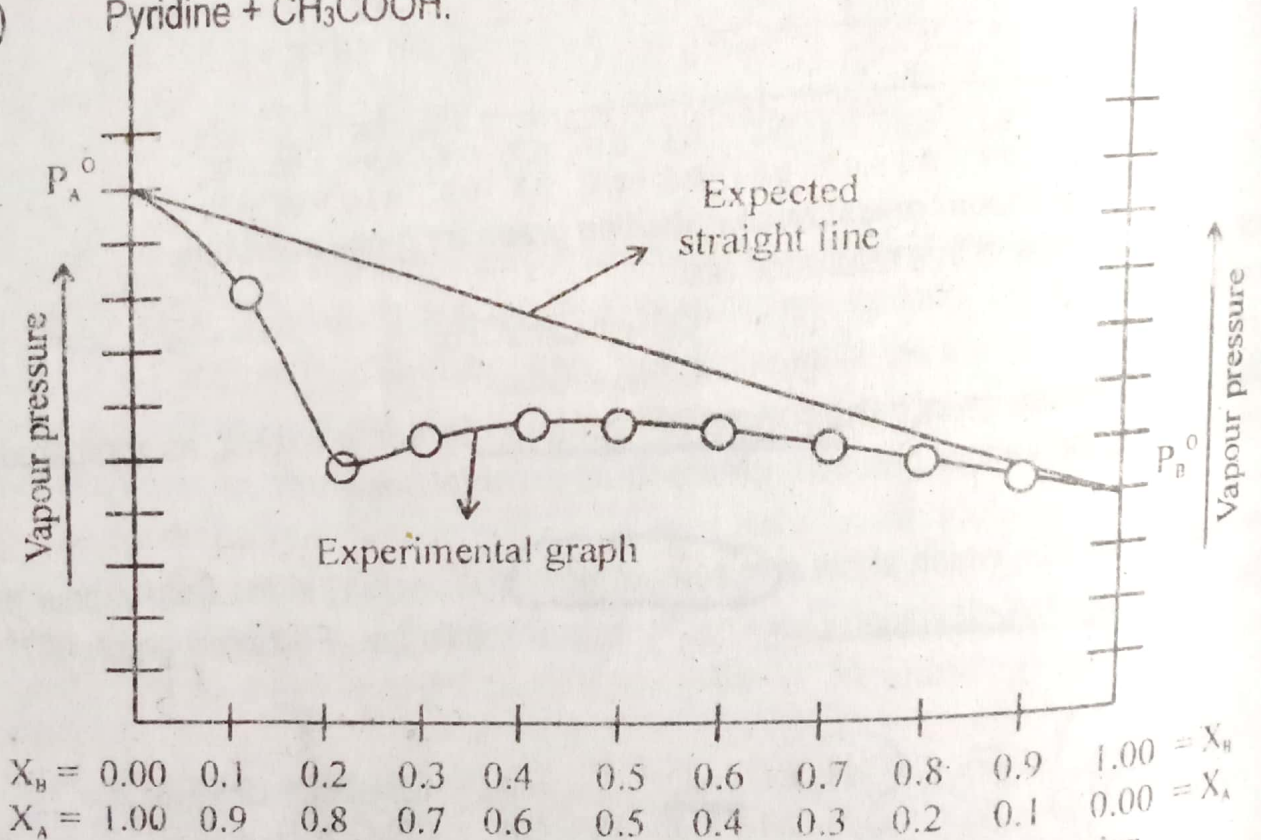


Fig. (8.8) Vapour pressure-composition graph for solutions showing negative deviation from Raoult's Law.

اس قسم کے سولیوشن کا گراف امید کردہ سیدھی لائن سے نیچے سے گزرنے کے دوران ایک کم سے کم قیمت والا نقطہ دیتے ہیں۔

8.4.3

Fractional Distillation of Non-ideal Solutions (فیئر معیاری سولیوشنز کی جزوی عمل کشید)