PHYSICAL CHEMISTRY

CHEMICAL KINETICS
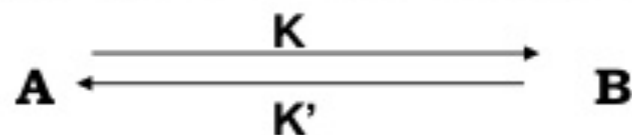
TYPES OF COMPLEX CHEMICAL REACTION

a) Reversible Or Opposing Reaction

b) Consecutive Reaction

c) Parallel Reaction

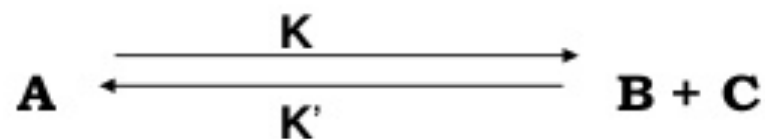# a) OPPOSING REACTION (REVERSIBE)

- The simplest case is, in which both reactions are of first order

$$A \underset{K'}{\overset{K}{\rightleftarrows}} B$$

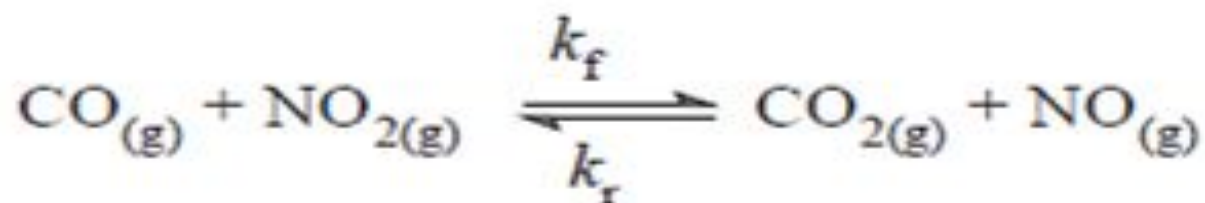- A somewhat more complicated reaction is when forward is first order type and reverse reaction is second order type.
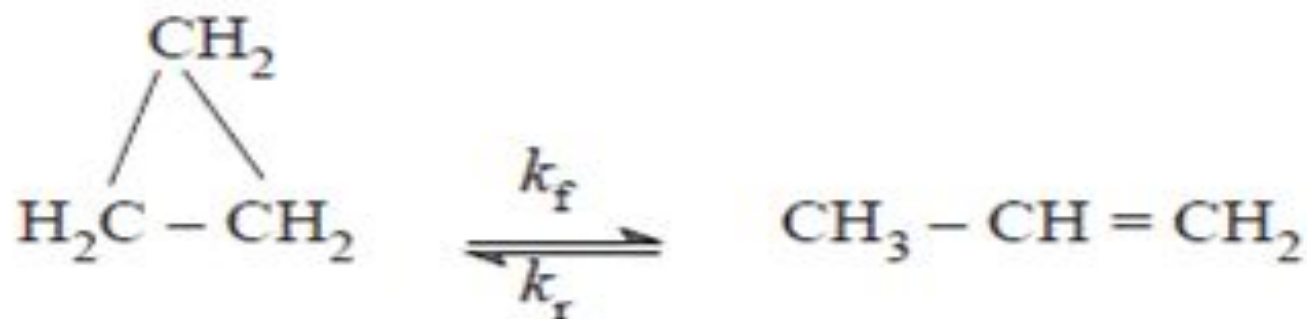
$$A \underset{K'}{\overset{K}{\rightleftarrows}} B + C$$

Example:

Epimerization of tetracycline.

Examples of opposing reactions

(i)   Reaction between CO and NO_2 gases

$$CO_{(g)} + NO_{2(g)} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} CO_{2(g)} + NO_{(g)}$$

(ii)   Isomerisation of cyclopropane to propene

$$\underset{H_2C - CH_2}{\overset{CH_2}{\triangle}} \quad \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \quad CH_3 - CH = CH_2$$

(iii)   Dissociation of hydrogen iodide in gas phase

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

- **What are opposing reactions? Give an example.**

- In opposing reactions **the products formed react back simultaneously to form the reactants**. These reactions are also called as reversible reactions.

- **Example:**

- Dissociation of hydrogen iodide in gas phase

b) CONSECUTIVE REACTIONS

- Simplest is one where both the reaction is of first order.
- If K2 > K1 then B can be considered as unstable intermediate and rate determining step for overall reaction would be conversion of A to B.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

Examples: -
- Radioactive series \ Isotopic decay that follows first order, but it is a consecutive reaction.
- Degradation of chlorbenzodiazepine by hydrolysis to lactam form and further to benzophenone.

What are consecutive reactions? Give an example. Or Write a (brief) note on consecutive reactions.

The reactions in which the **reactant forms an intermediate and the intermediate forms the product** in one or many subsequent reactions are called as consecutive or **sequential reactions**.

In such reactions the **product is not formed directly from the reactant**. Various steps in the consecutive reaction are shown as below :

$k1$ $k2$

$A \rightarrow B \rightarrow C$

A = reactant; B = intermediate; C = product.

Example:

Saponification of a diester in presence of an alkali:

$k1$ $k2$

R'OOC– (CH2)n– COOR $\rightarrow$ R'OOC– (CH2)n– COOH $\rightarrow$ HOOC – (CH2)n – COOH

c) SIDE REACTIONS (PARALLEL)

- Here the reacting substance can be removed by two or more reactions occurring simultaneously, as depicted
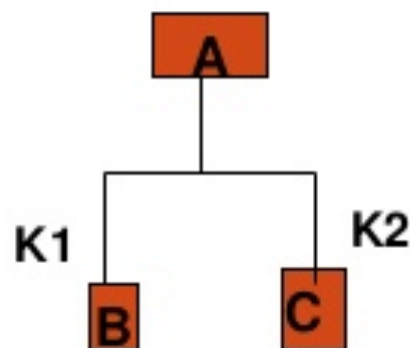
EXAMPLE:

- Purified insulin degrades by two mechanisms- deamidation and polymerization.
- The relative rates of deamidation and polymerization are pH and temperature dependent.

- **What are parallel reactions? Give an example.**

- In these group of reactions, **one or more reactants react simultaneously in two or more pathways to give two or more products**. The parallel reactions are also called as**side reactions**

- **Example:**
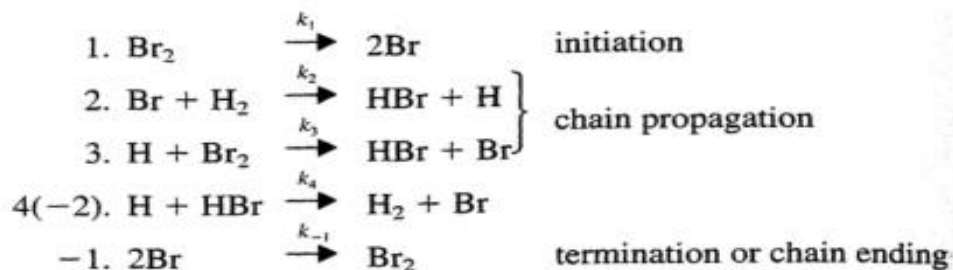
- Bromination of bromobenzene:
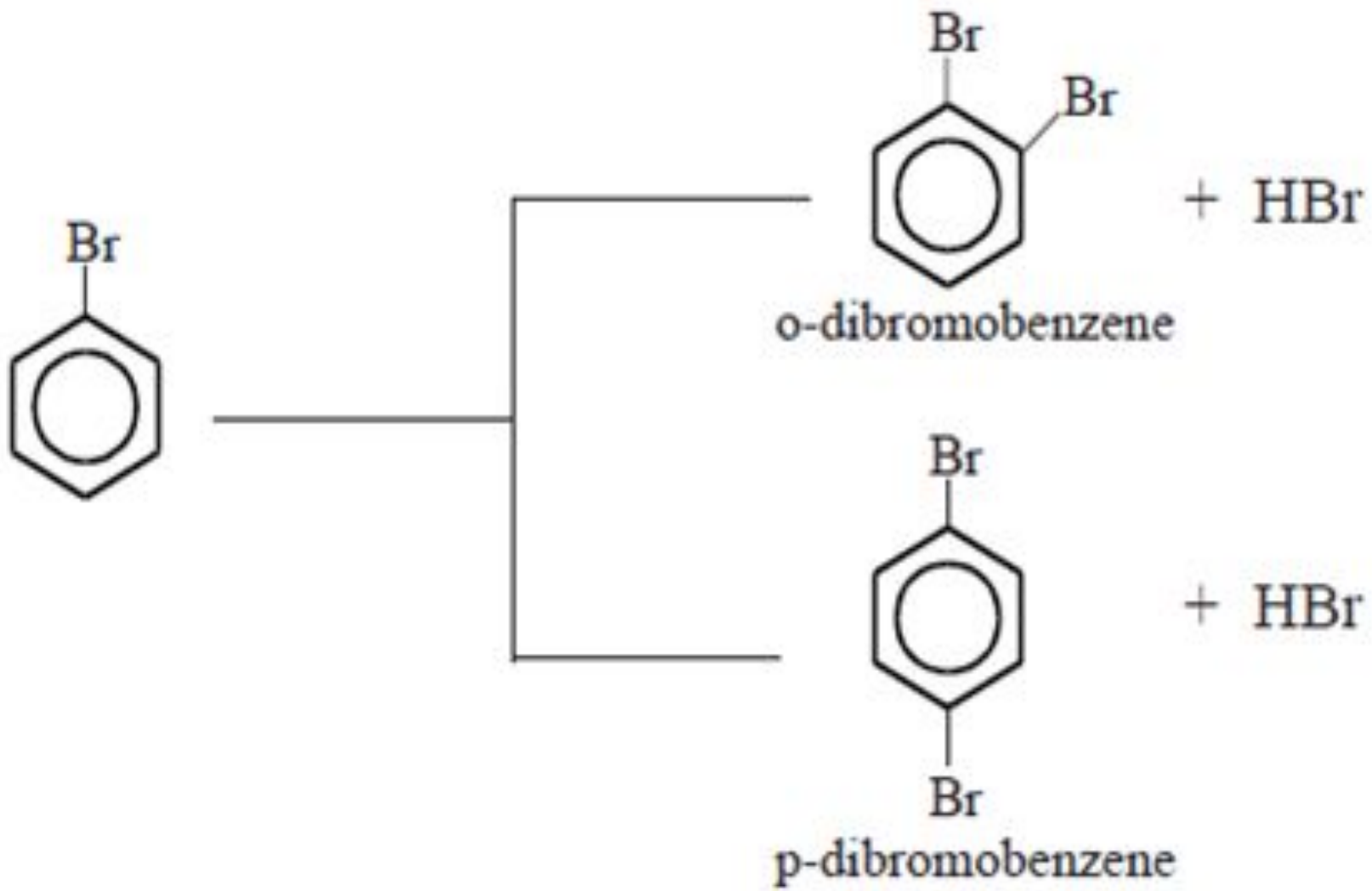
Thermal Chain Reaction

Chain Reactions

Ions play little part in ordinary gas-phase reactions, owing to the difficulty which they are formed in the absence of an ionizing solvent. Atoms and free radicals are produced more easily in the gas phase and, because they enter readily into further reaction, they are important intermediates in reactions.
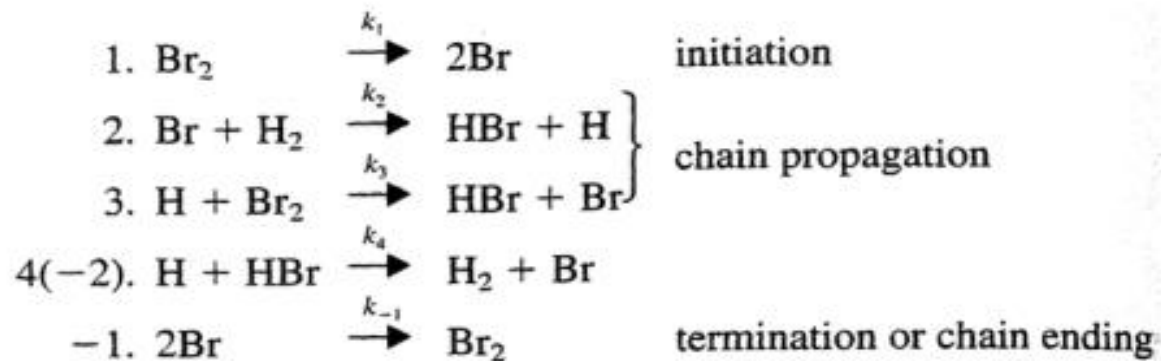
$$H_2 + Br_2 \rightarrow 2HBr \qquad v = \frac{k[H_2][Br_2]^{1/2}}{1+[HBr]/m[Br_2]}$$

This rate equation can be explained by the mechanism

$$
\begin{array}{lll}
1.\ Br_2 & \xrightarrow{k_1} 2Br & \text{initiation} \\
2.\ Br + H_2 & \xrightarrow{k_2} HBr + H \\
3.\ H + Br_2 & \xrightarrow{k_3} HBr + Br \\
4(-2).\ H + HBr & \xrightarrow{k_4} H_2 + Br \\
-1.\ 2Br & \xrightarrow{k_{-1}} Br_2 & \text{termination or chain ending}
\end{array}
$$

chain propagation

A reaction of this type is known as a chain reaction. One essential feature of a chain reaction is that there must be a closed sequence, or cycle, of reactions that certain active intermediates are consumed in one step and are regenerated in another; these active intermediates may be atoms, free radicals, or ions. It is also essential feature that the sequence is, on the average, repeated more than once.

$$1.\ Br_2 \xrightarrow{k_1} 2Br \qquad \text{initiation}$$

$$2.\ Br + H_2 \xrightarrow{k_2} HBr + H \;\Big\}$$

$$3.\ H + Br_2 \xrightarrow{k_3} HBr + Br \Big\} \qquad \text{chain propagation}$$

$$4(-2).\ H + HBr \xrightarrow{k_4} H_2 + Br$$

$$-1.\ 2Br \xrightarrow{k_{-1}} Br_2 \qquad \text{termination or chain ending}$$

~The first reaction, the production of bromine atoms from a bromine molecule is known as the initiation reaction, since it starts the whole process.

~Reaction 2 and 3, the so-called chain~propagation steps, play a very important role in reactions of this type. Bromine atoms disappear in reaction 2 and reappear in reaction 3; hydrogen atoms disappear in reaction 3 and come back again in reaction 2.

~Because of this feature a small number of Br atoms, produced in reaction 1, can bring about a considerable amount of reaction, since after producing two molecules of hydrogen bromide, one in reaction 2 and one in reaction 3, a bromine atom is regenerated.
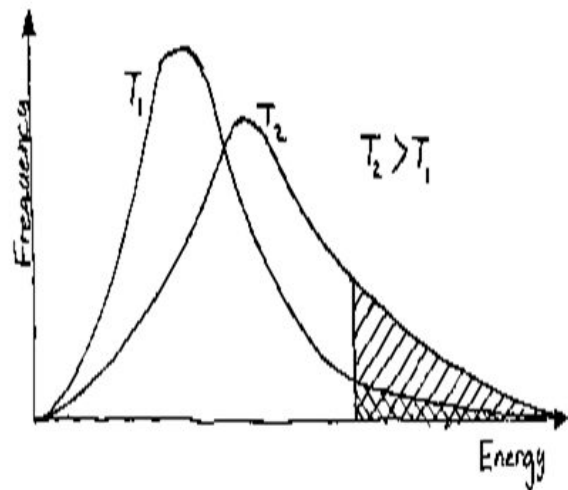
Effect of temperature on rate

Increasing the temperature will make the particles move faster, so there will be more collisions.

At a higher temperature, many more particles will have the necessary activation energy. The ratio of successful collision to unsuccessful collisions will increase.

Which one will contribute more towards increasing the rate of reaction?

$T_2 > T_1$

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Effect of concentration or temperature on the rate of a reaction

If the concentration or temperature of a reactant is increased the reaction goes faster.

When the reactants have a <u>higher</u> temperature, they move faster, thereby <u>increasing</u> the chance of a collision.
When the reactants have a <u>lower</u> temperature, they move slower, thereby <u>decreasing</u> the chance of a collision.
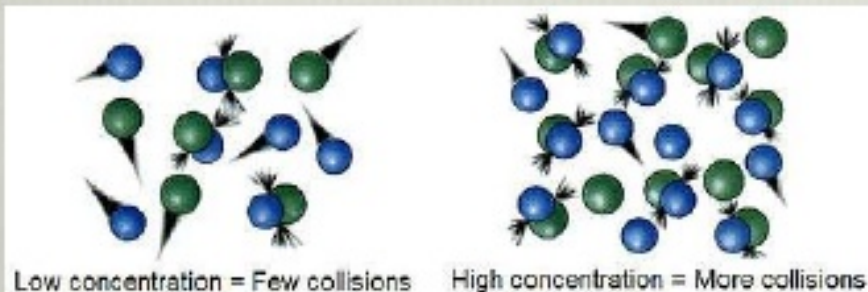
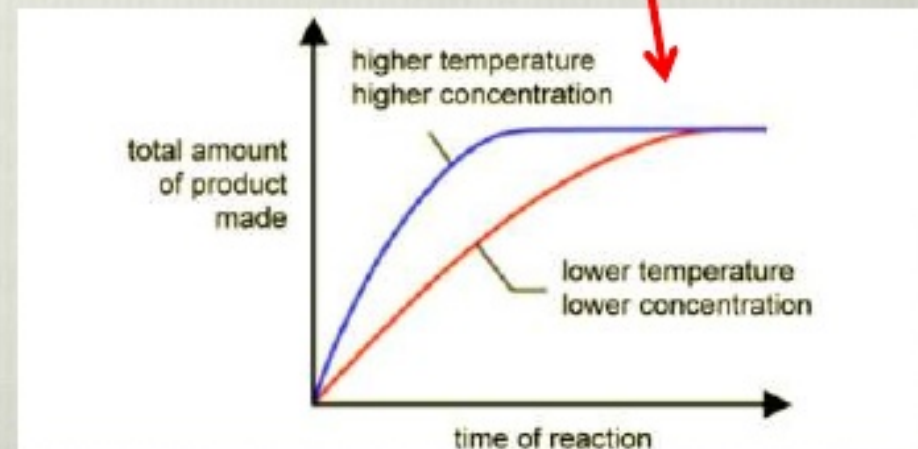When the reactants are <u>less</u> concentrated there is <u>less</u> chance of a collision.
When the reactants are <u>more</u> concentrated there is <u>more</u> chance of a collision.
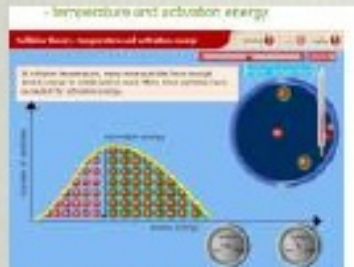
An animation on temperature:
http://www.ltscotland.org.uk/high
ersciences/chemistry/animation
s/collision_theory.asp

Why does this graph have a plateau?

Low concentration = Few collisions   High concentration = More collisions

total amount of product made

higher temperature
higher concentration

lower temperature
lower concentration

time of reaction

Effect of Temperature On the Rate of Reaction

- Arrhenius Equation
- Concept Of Energy of Activation (Ea)

- Arrhenius Equation

- **Write <u>Arrhenius equation</u> and explain the terms.**
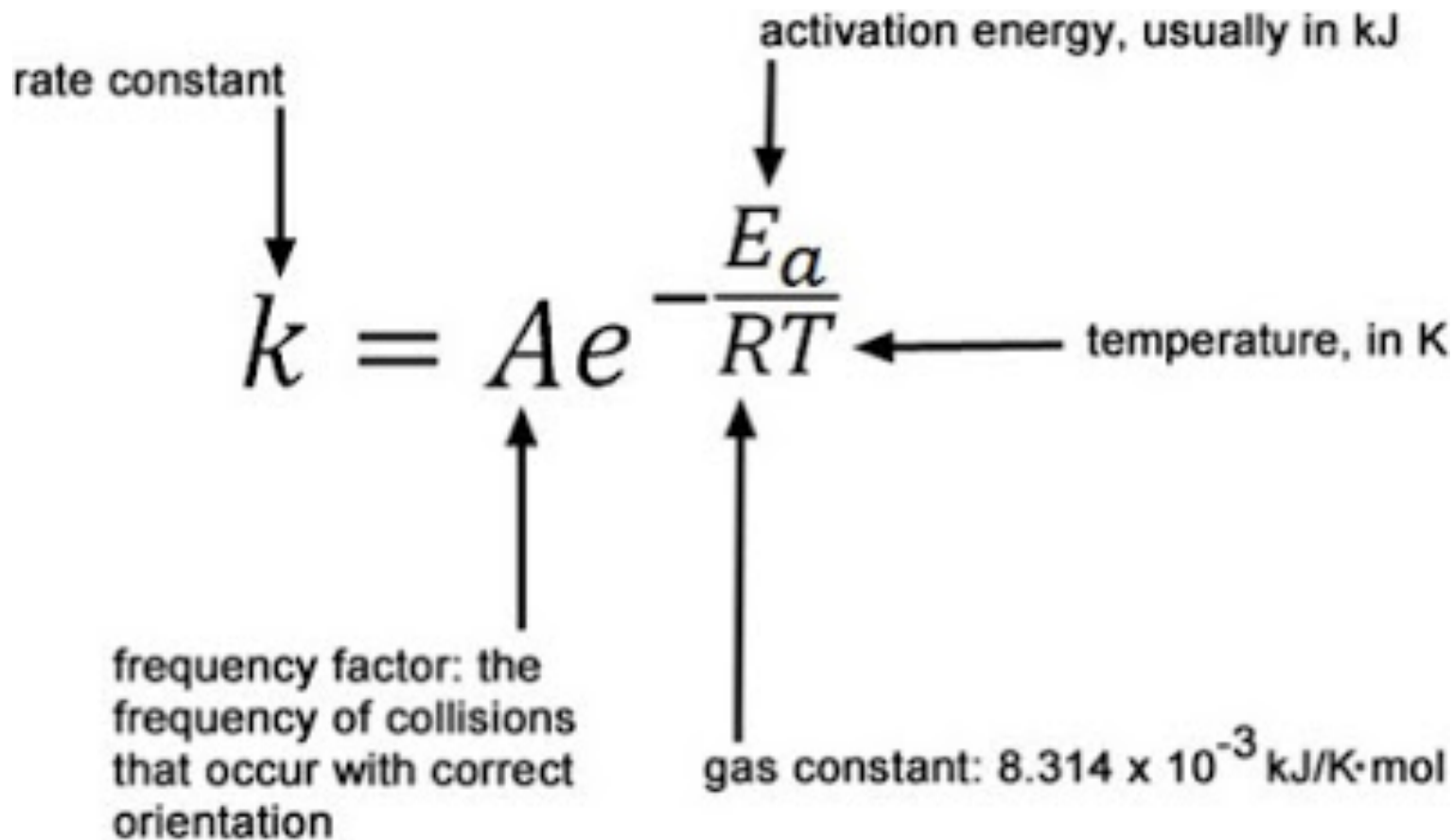
- $k = A\,e^{-E_a/RT}$

- Where,

- k = Rate constant,

- **Ea** = Activation energy,

- **A** = Frequency factor,

- **R** = Gas constant,

- **T** = Temperature in Kelvin.

rate constant

activation energy, usually in kJ

temperature, in K

$$k = Ae^{-\frac{E_a}{RT}}$$

frequency factor: the frequency of collisions that occur with correct orientation

gas constant: 8.314×10^{-3} kJ/K·mol

Energy of Activation (Ea)

ACTIVATION ENERGY

- **Write a note on 'activation energy'.**

- 1. The **additional energy required by the molecules to attain the threshold energy** in addition to the energy of colliding molecules.

- 2. **Activation energy = Threshold energy – Energy of colliding molecules.**

- 3. An **energy barrier that must be crossed by the reactant molecules before getting converted to actual product** molecules.

- 4. The **energy required to form the activated state or the intermediate**, which is necessary to form the products.

- 5. Ea is a **characteristic value of a reaction**.
  6. The **rate, rate constant, and their temperature dependence** are determined by the value of Ea.

- 7. **Higher the value of Ea, slower is the rate** of the reaction.
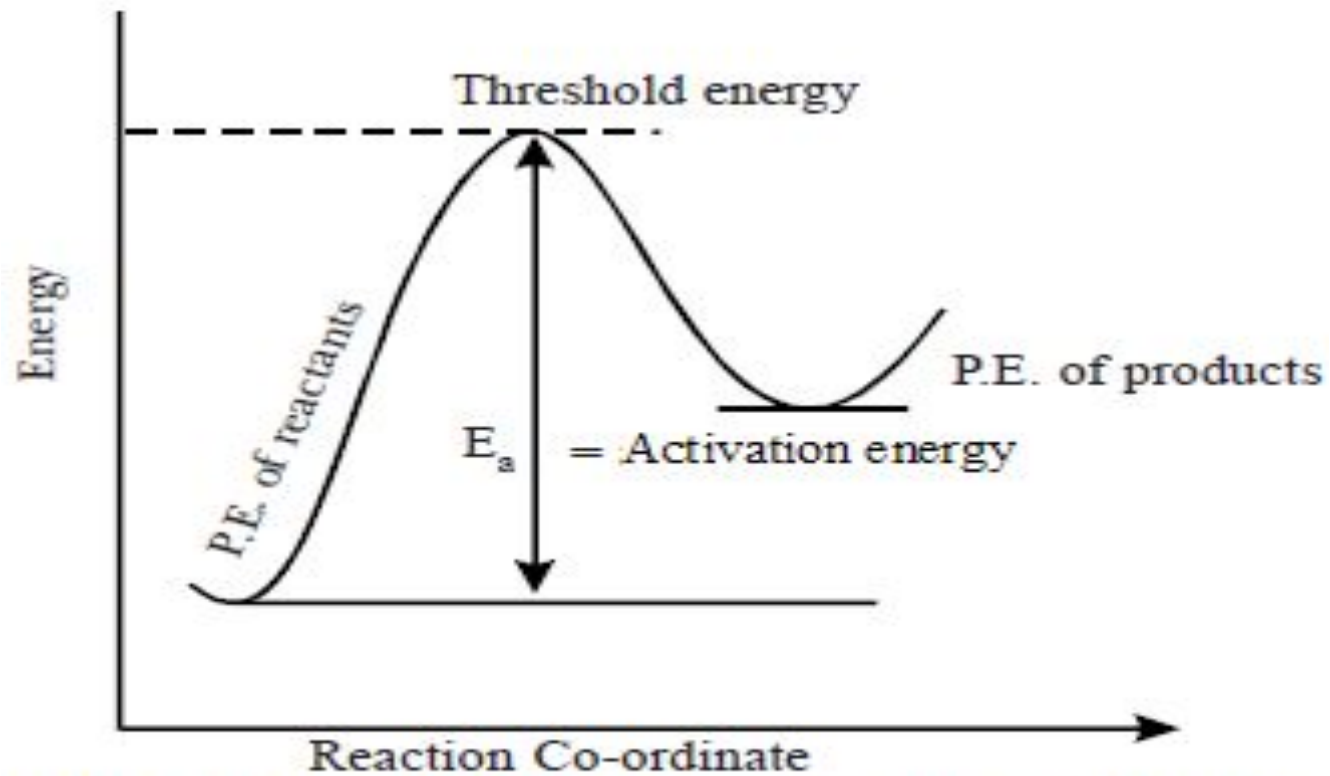
Potential energy diagram of a reaction

Theories Of Temperature on The Rate of Reaction

- Collision Theory
- Activated Complex Theory Of Bimolecular Reaction
- Comparison Between Collision Theory & Activated Complex Theory

Collision Theory

❖ This is the oldest theory based on kinetic theory of collisions.

❖ Originally suggested for gas phase reactions.

❖ This suggests that we can understand the rates of reactions by analysing the molecular collisions.

❖ All assumptions of kinetic theory of gases are applicable

COLLISION THEORY....

- The collision theory states that for a reaction to occur between two particles
  - ❖ The reacting particles must *collide* with each other
  - ❖ The reacting particles must collide with a certain minimum energy known as the *activation energy, E_a.*
  - ❖ The reacting particles collide in *the correct orientation.*
- A collision that results in a reaction is called *effective collision*.
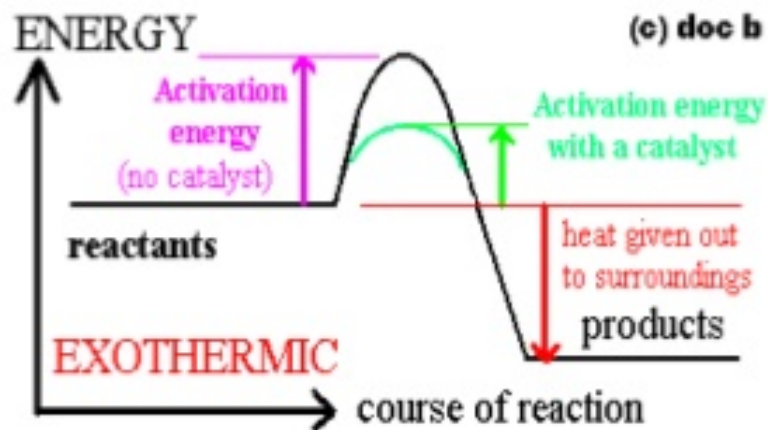- If the frequency of effective collision is high, the rate of reaction is also high.

How Collision theory explain factor of temperature

- The **higher the temperature of reactant solution**, the **higher the kinetic energy of particles**

- **Frequency of Collisions** between particles increase

- **Frequency of Effective collisions** between particles increase
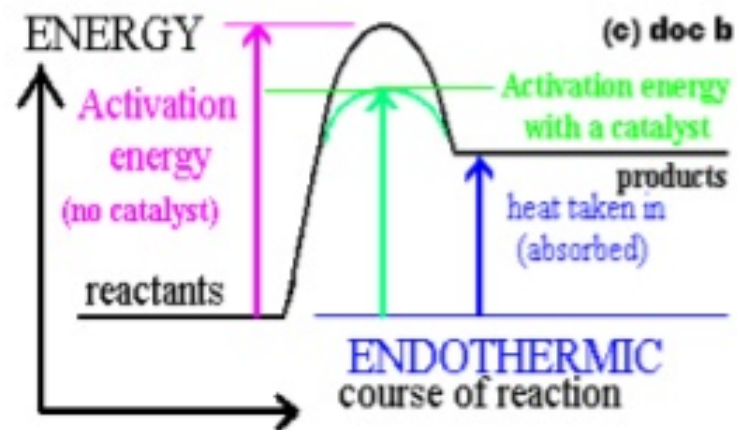
- Therefore **rate of reaction** also increase

COLLISION THEORY....

- ## Use of catalyst

  - ❖ When a catalyst is used in a chemical reaction, it enables the reaction to occur **through an alternative path which requires a lower activation energy**.

ENERGY   (c) doc b

Activation energy (no catalyst)

Activation energy with a catalyst

reactants

heat given out to surroundings

products

EXOTHERMIC

course of reaction

ENERGY   (c) doc b

Activation energy (no catalyst)

Activation energy with a catalyst

products

heat taken in (absorbed)

reactants

ENDOTHERMIC

course of reaction

REACTION: SLOWER
ROR : LOW

REACTION: FASTER
ROR: HIGH

Transition State Theory

- During a chemical reaction, reactants do not *suddenly* convert to products

- The formation of products is a continuous process of chemical bonds breaking and forming

- At some point in a successful collision, a transitional species is formed containing "partial" bonds.

- This species, called the **transition state** or **activated complex**, is highly energetic and normally very short-lived in the reaction.

- The activation energy can be defined as the energy required to form the transition state of a reaction.

- Typically, it decomposes immediately into the products of the reaction or back into the reactants.

Transition State Theory/ Absolute Reaction Rate Theory/ Activated Complex Theory

Suggested by Eyring, Evans and Polyani in 1935

The reactants form some sort of complex with a structure somewhere between the reactant and the product and called as Transition-state or Activated complex
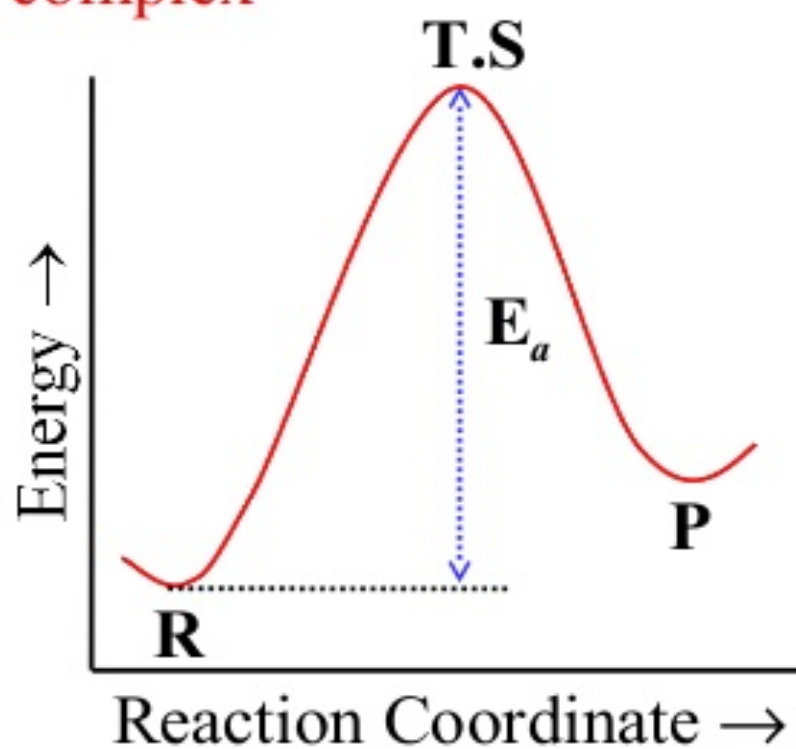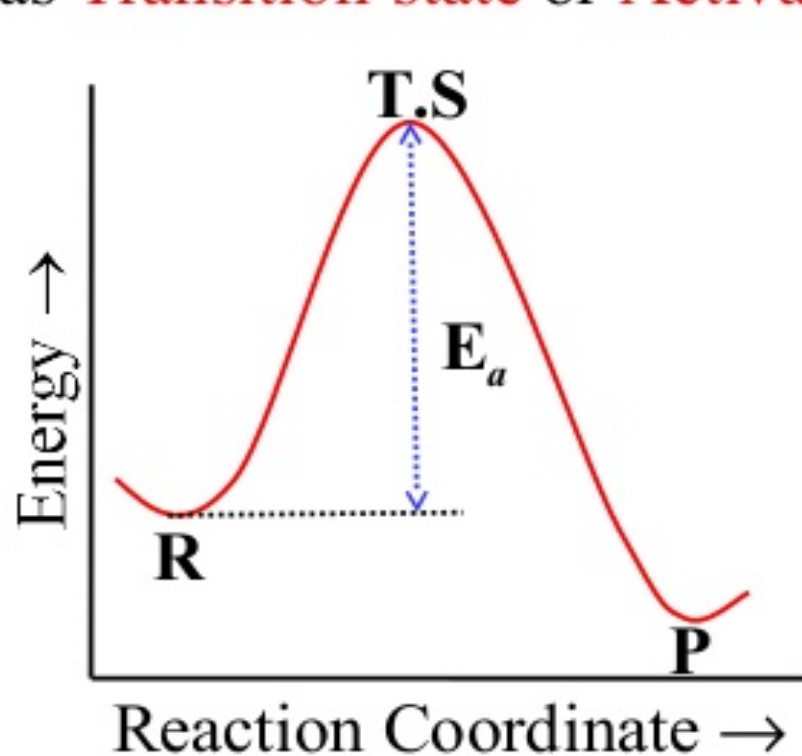
Transition State Theory Differs From Collision Theory In Two Key Ways:

- One can actually make a calculation.

- Collision theory b_{coll} unknown (7.16).

  - Transition state theory replaces b_{coll} with d_{coll}. The distance between reactants at the transition state geometry. d_{coll} can be calculated exactly.

- Transition state theory allows you to consider reactions like reaction (7.27) where only special configurations lead to the desired products.

- Partition function for TST gives many parameters

Raoult's Law

The partial pressure of any volatile component of a solution at any temperature is equal to the vapour pressure of pure component multiply by the mole fraction of that component in the solution.

- In a solution of two miscible liquids (A & B) the partial pressure of component "A" (P_A) in the solution equals the partial pressure of pure "A" (P_A^o) times its mole fraction (x_A)

  Partial Pressure of A in solution $= P_A = (P_A^o) \times (x_A)$

  Partial Pressure of B in solution $= P_B = (P_B^o) \times (x_B)$

- When the **total pressure (sum of the partial pressures) is equal to or greater than the applied pressure, normally Atmospheric Pressure (760 mm Hg), the solution boils**

$$P_{total} = P_A + P_B = P_A^o x_A + P_B^o x_B$$

- If the **sum of the two partial pressures of the two compounds in a mixture is less than the applied pressure, the mixture will not boil.** The solution must be heated until the combined vapor pressure equals the applied pressure.

- Raoult's law is followed by only Ideal solution
- Vapour pressure of ideal binary solution of two components A and B having different mole fractions are shown
  in Fig-1

$$p = p_A + p_B$$

p_A^0

p_B
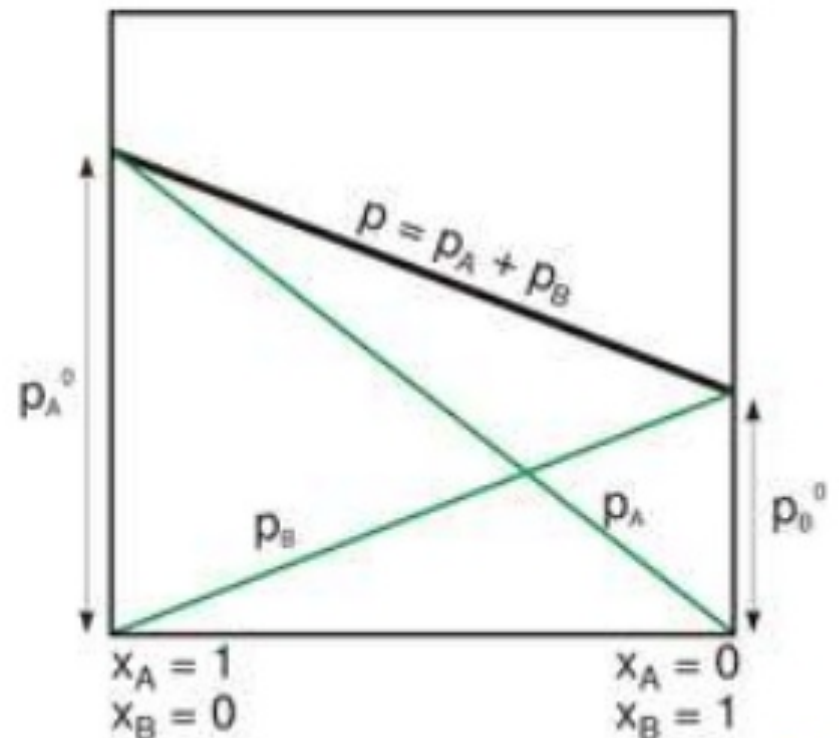
p_A

p_B^0

$x_A = 1$
$x_B = 0$

$x_A = 0$
$x_B = 1$

Fig-1 Vapour Press vs Composition

Ideal Solutions

- Liquid-liquid solutions that obey Raoult's Law are called ideal solutions.
- For solutions that contain volatile solutions a modified Raoult's Law.
- Ptotal = Pa + Pb = XaP°a +XbP°b
- Pa and Pb are the partial pressure of the two liquids in solution.
- P°a and P°b are the partial pressure of the pure solvent.
- X is the mole fraction.

Ideal Solution

...a solution that obeys Raoult's law

$$P_{soln} = \chi_{solvent} P^{\circ}_{solvent}$$

Ideal solutions
- obey Raoult's law exactly
- solute-solute, solvent-solvent, and solute-solvent interactions are identical
- do not exist

Real Solutions
- are nonideal
- may approach ideal behavior if solute and solvent are similar
- Example: sucrose in water

Vapor Pressure of a Solution Containing a Nonvolatile Solute

Vapor pressure of pure solvent

Solution vapor pressure / P_{soln}

Mole fraction of solvent / $\chi_{solvent}$
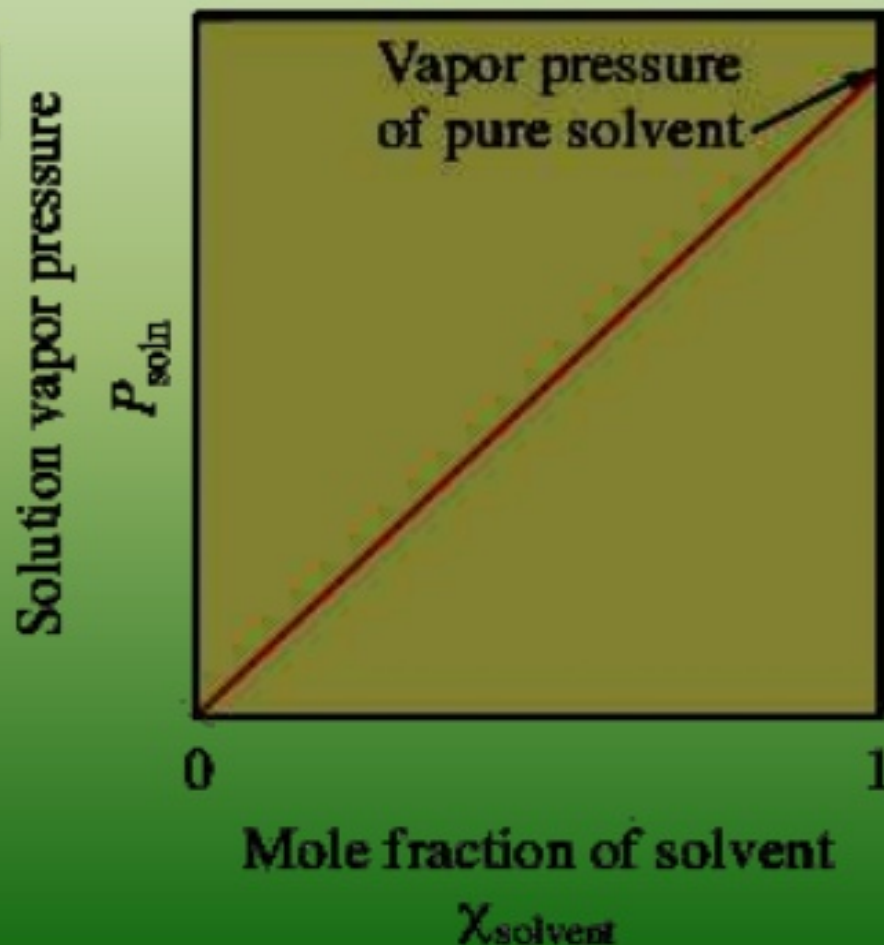
DEVIATIONS FROM RAOULT'S LAW (NON-IDEAL SOLUTIONS)

- There are two types of deviations may possible from Raoult's law

    (i) *Vap. Press curve of liq.pairs showing positive deviation*

    (ii) *Vap. Press curve of liq.pairs showing negative deviation*
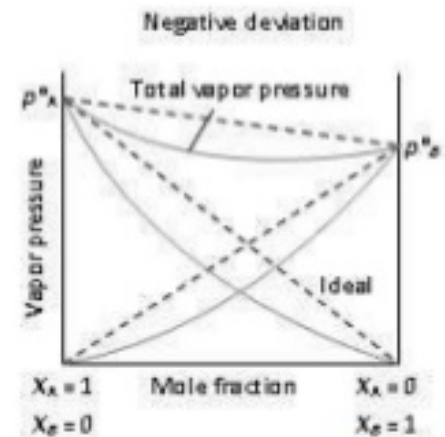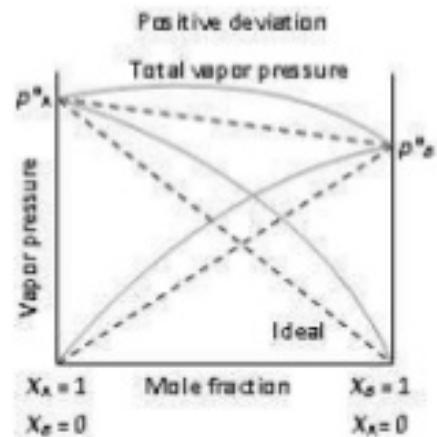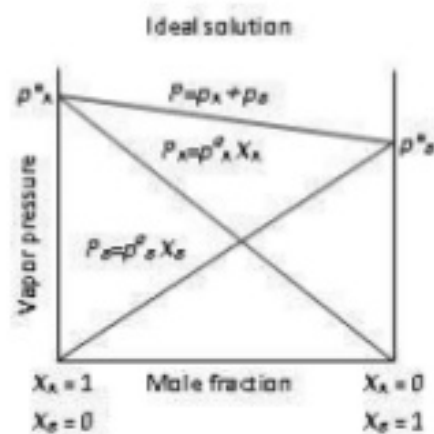
# Deviations from Raoult's law (cont.)

○ **<u>Positive deviation :</u>**

Cohesive (Attraction) forces between unlike   components (say A-B) are weaker than those of the pure liq (say A-A or B-B)

i.e. $P_A > P_A^o x_A$, $P_B > P_B^o x_B$ and $P_{total} > P_A^o x_A + P_B^o x_B$

○ **<u>Negative deviation :</u>**

Attraction forces between unlike molecules in solution (A-B) are stronger than those between like molecules (A-A and B-B)

i.e. $P_A < P_A^o x_A$, $P_B < P_B^o x_B$ and $P_{total} < P_A^o x_A + P_B^o x_B$
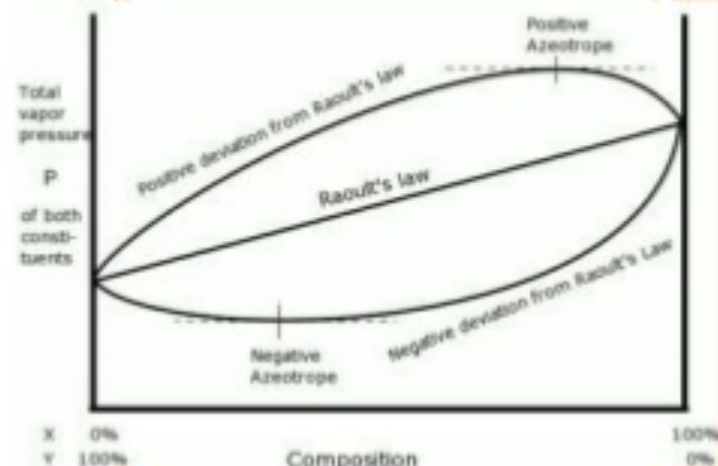
Distillations of Solutions

Temperature-Composition Diagrams

- **Temperature-composition diagram (to discuss fractional distillation) :**
  - **a phase diagram in which** the boundaries show the composition of the phases that are in equilibrium at various temperatures (at a given P [1atm]).

a) The distillation of mixtures:
  - When liq composition a_1 is **heated**, its boils when reach T_2 (so, **Liq has comp a_2 same as a_1 & vapour has comp a'_2**) – vapour is reacher at in the > volatile component A (the component with lower boiling point)

  - From the location of a_2, we can state the vapour comp at the boiling point and from the location of tie line joining a_2 to a'_2 we can read off the boiling temp, T_2 of the original liq mixture.
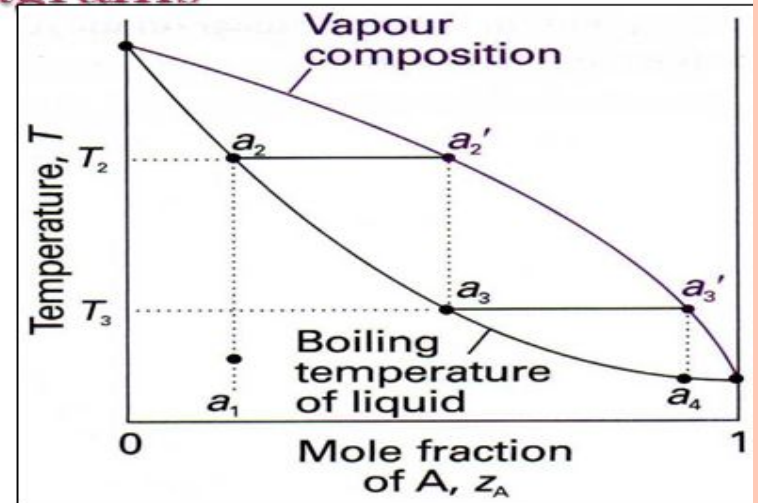
Fig. 6.14 The temperature–composition diagram corresponding to an ideal mixture with the component A more volatile than component B. Successive boilings and condensations of a liquid originally of composition a_1 lead to a condensate that is pure A. The separation technique is called fractional distillation.

THE LEVER RULE

- The lever rule To find the relative amounts of two phases in equilibrium, we measure the distances $l\alpha$ and $l\beta$ along the horizontal tie line and then use the lever rule:

Azeotrope

- An azeotropic mixture is a mixture of two liquids having same boiling point.
- These mixture can't be separated by simple fractional distillation because no change in composition of these mixture on boiling i.e. same boiling point.
- These mixture is called Constant Boiling Point mixture.
- These mixtures are formed by non-ideal solution

Vapor-Liquid Equilibrium 2-Propanol + Water
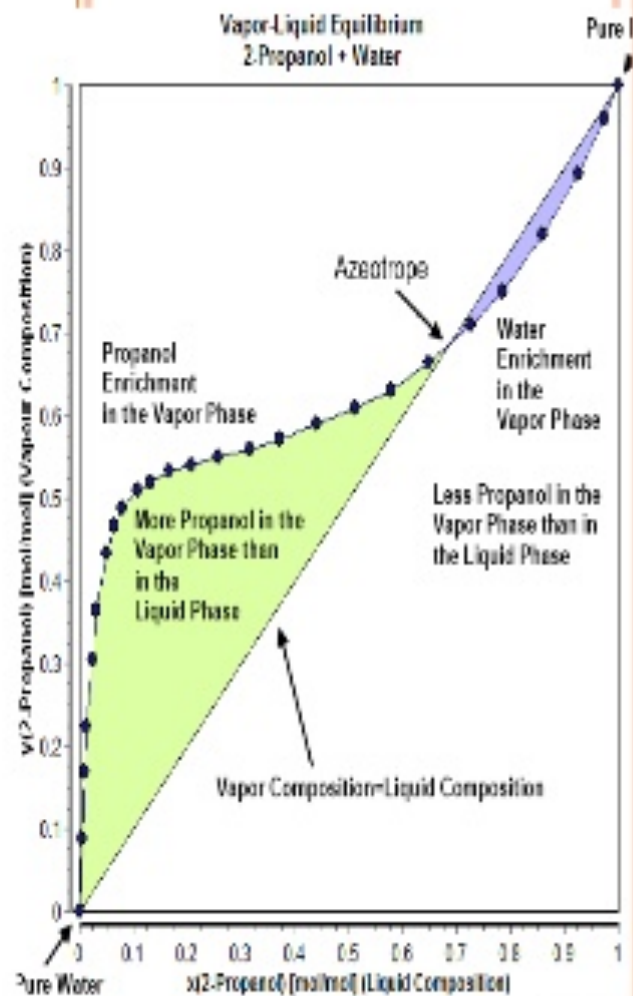
Azeotrope

- Constant boiling mixture
- Non-ideal solution
- Cannot be seperated by simple distillation
- Same composition in distillate and residue at minimum temperature.

TYPES OF AZEOTROPES

Based on the boiling point on temperature-composition or press-composition diagram, Azeotrope can be classified as follows:

❖ Positive azeotrope/ minimum boiling mixture

· When boiling temperature of the azeotrope is less than that of the pure component.-minimum boiling mixture.

· It is shown by those liq.pair which show positive deviation from ideal behavior.

·Example – Ethanol (96%) and Water mixture (4%)

❖ Negative azeotrope/maximum boiling mixture.

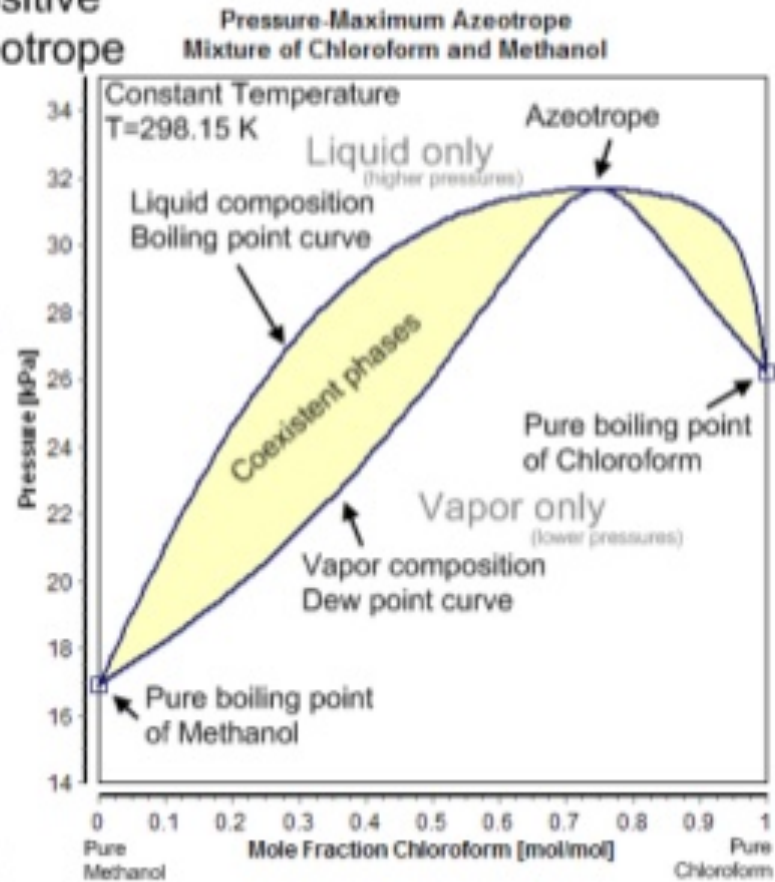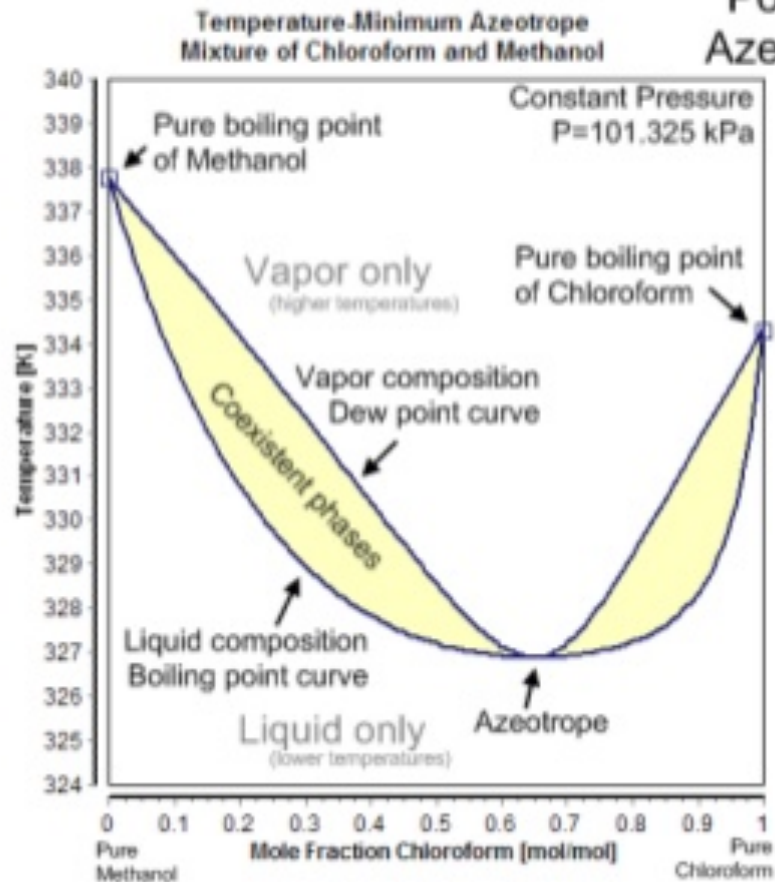· Boiling temperature of the azeotrope is higher than that of pure component

· Liq pair which shows negative deviation

· Example –Water (20.2%) and HCl(79.8%)
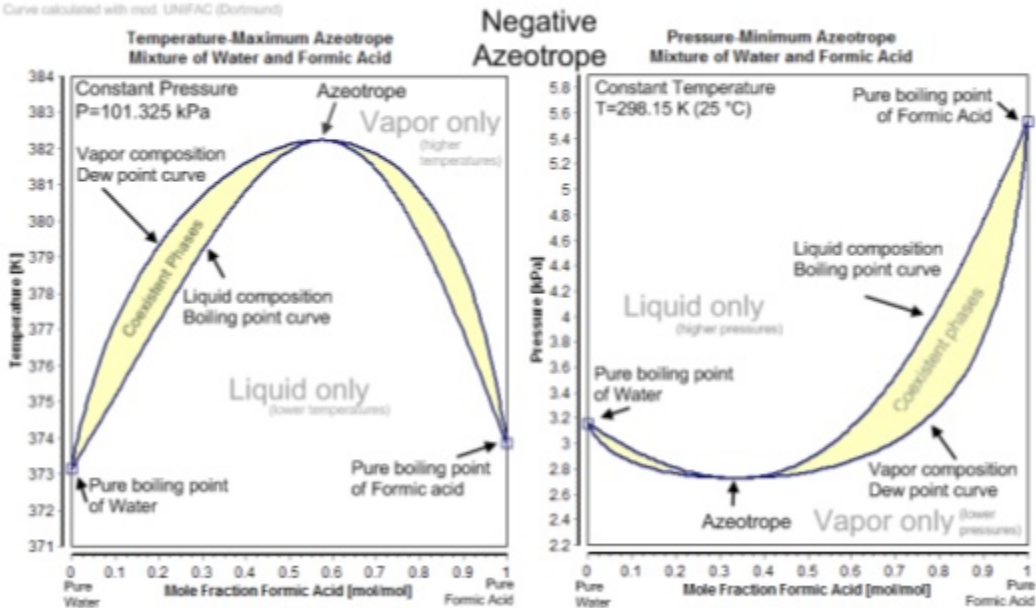
POSITIVE AZEOTROPE / MINIMUM BOILING MIXTURE

NEGATIVE AZEOTROPE /MAXIMUM BOILING MIXTURE

PARTIAL MISCIBILITY OF LIQUIDS

- Critical Solution Temperature
- Effect of Impurity on partial miscibility of liquids with respect to

1) Phenol – Water
2) Triethylamine – Water
3) Nicotine – Water System

CRITICAL SOLUTION TEMPERATURE

When 2 partially miscible liquids are mixed and shaken together, we get 2 solutions of different compositions.

e.g. on shaking phenol and water, we get 2 layers : the upper layer is a solution of water in phenol, and the lower layer is a solution of phenol in water. At a fixed temp, the composition of each solution is fixed, and both the solutions are in equilibrium.

'Above a particular temperature, such solutions are completely miscible in all proportions. Such a temperature is known as the Critical Solution Temperature (CST) or Consolute Temperature.'

The Critical Solution Temperature: CST

- Is the maximum temperature at which the 2-phase region exists (or upper consolute temperature). In the case of the phenol-water system, this is 66.8°C (point h)

- All combinations of phenol and water > CST are completely miscible and yield 1-phase liquid systems.
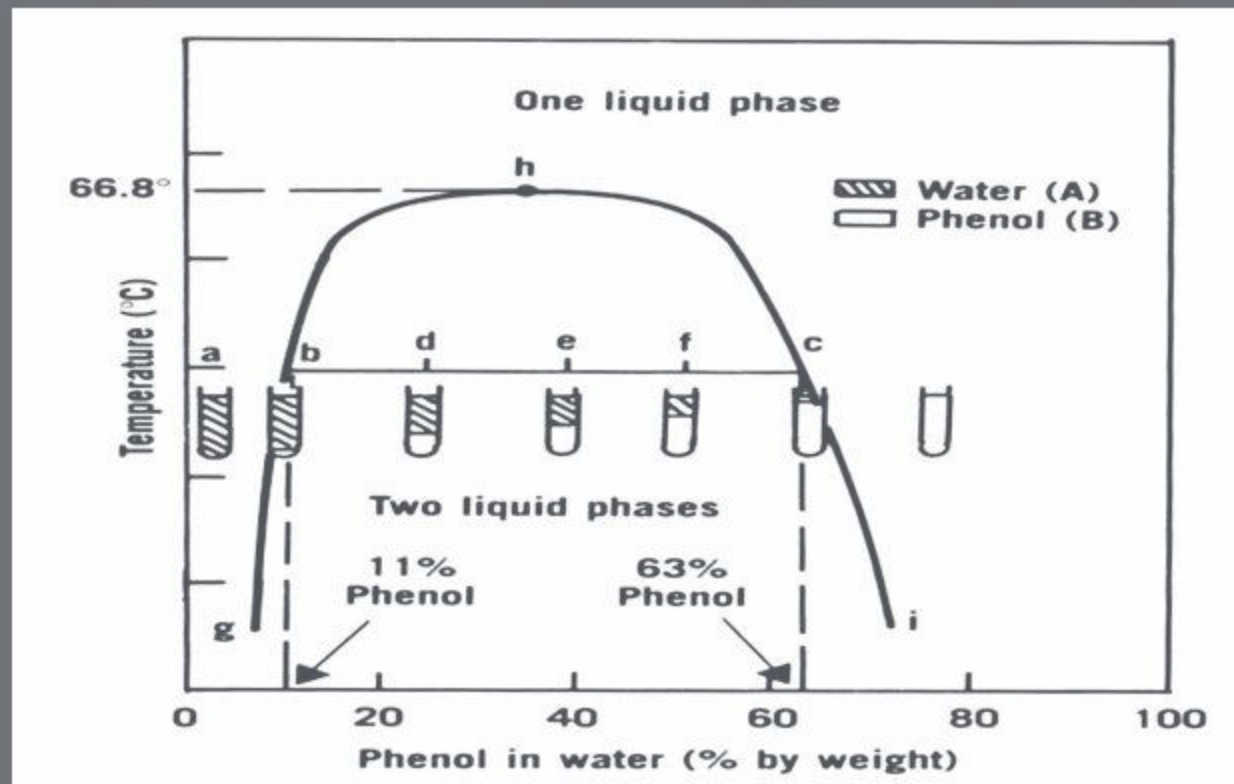
PHASE RULE

theory :- Two liquids when mixed may be(i)completely miscible, (ii) completely immiscible,(iii)partially miscibe . In case (iii) one will have a definite solubility in other . Example of such cases are phenol-water system.if we add phenol to water it will be soluble up to a certain limit and this solubility value will increase with increase in temperature.similarly,if we add water to phenol same phenomena will be observed . The number of homogeneous, mechanically separable and physically distinct parts of a heterogeneous system is known as the number of phases, **P**, of the system. each phase is separated from other phases by a physical boundary. When an equilibrium exists between a number of phases under external controlling conditions such as temperature, pressure, and concentration, the following relationship holds good :

$$F = C-P + 2 \qquad \qquad \text{..........(1)}$$

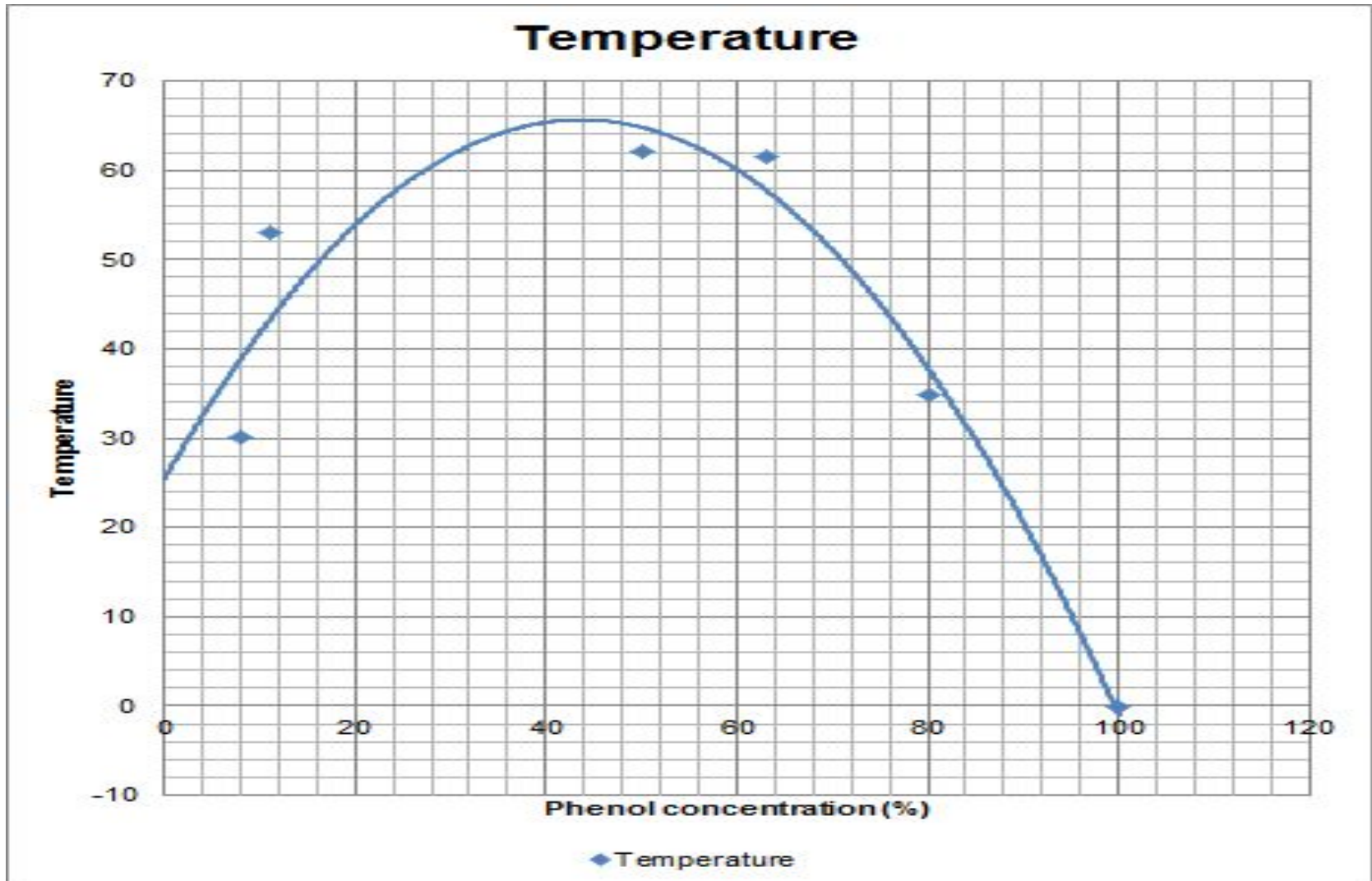where **P = number of Phases in equilibrium,**

C = number of Components in the system, and

F = number of degrees of Freedom.

Equation (1) is called the ***Phase Rule***, which relates the *phases, components and degrees of freedom* of the system.
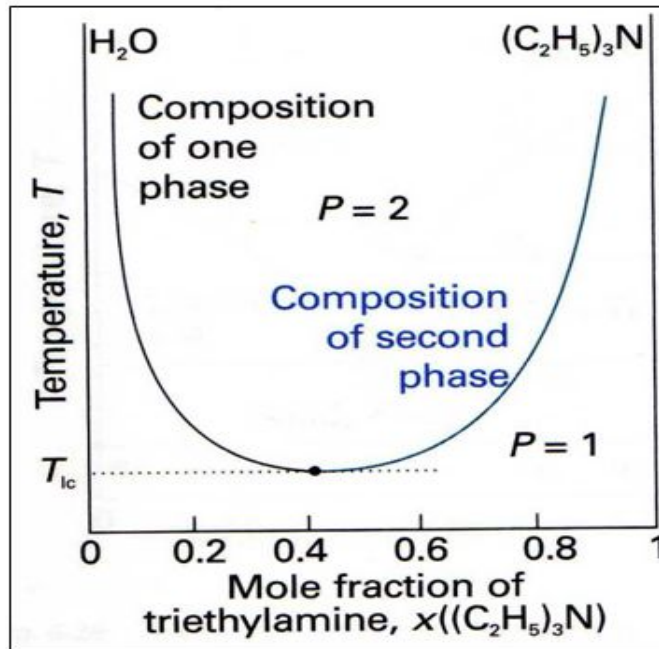
PHENOL- WATER SYSTEM

Lower critical solution temperature

Fig. 6.24 The temperature–composition diagram for water and triethylamine. This system shows a lower critical temperature at 292 K. The labels indicate the interpretation of the boundaries.

- T_{lc}: below which they mix in all proportions and above which they form 2 phases.
- The lowest temp at which phase separation occurs.

- Example: water/triethylamine
- At low temp the two components are more miscible because they form a weak complex,
- at higher temp the complexes break up and the two components are less miscible.

§5-4 Two-component systems

📖 Some system have both upper and lower critical solution temperatures. They occur because, after the weak complexes have been disrupted, leading to partial miscibility, the thermal motion at higher temperature homogenizes the mixture again. just as in the case of ordinary partially miscible liquids.

📖 The most famous example is nicotine and water which are partially miscible between 6 and 210ºC.

water (A) – nicotine (B)

$p=const.$

t

C

l_1+l_2

t_C

C'

l

0

$w_B/\%$

100

A

B
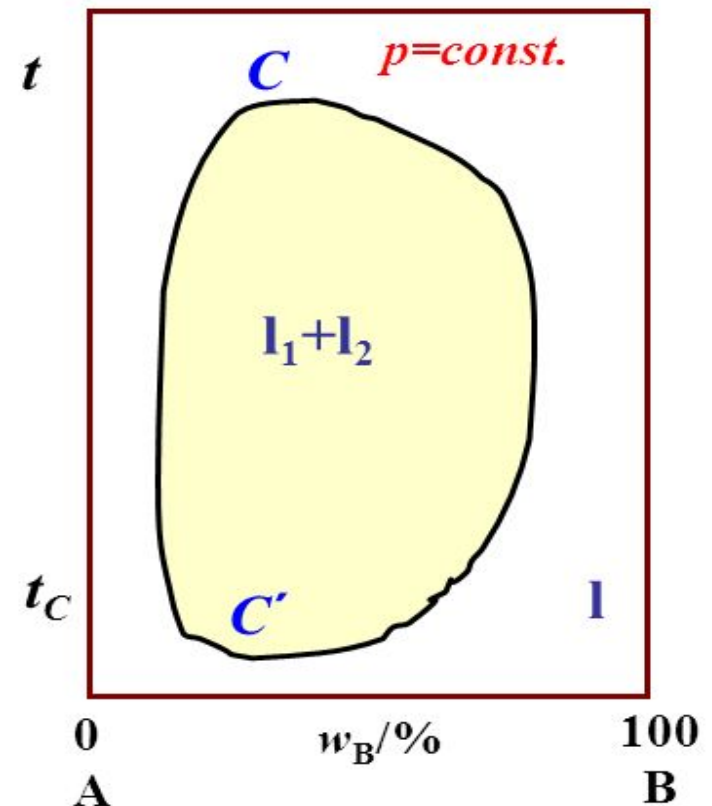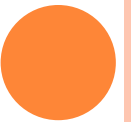
- Immisibility of Liquids
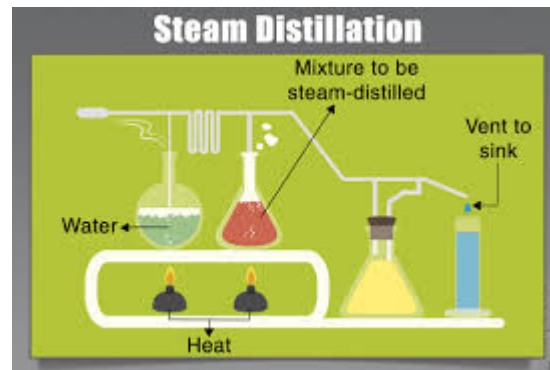- Principle of Steam Distillation

LIQUID MIXTURES
Miscible vs. Immiscible

- **Miscible Mixture:** liquids that mix evenly, forming a homogeneous solution. Example: Soda mixed with Koolaid

- **Immiscible Mixture:** liquids that DO NOT mix evenly, forming a heterogeneous mixture. Example: Oil mixed with Water
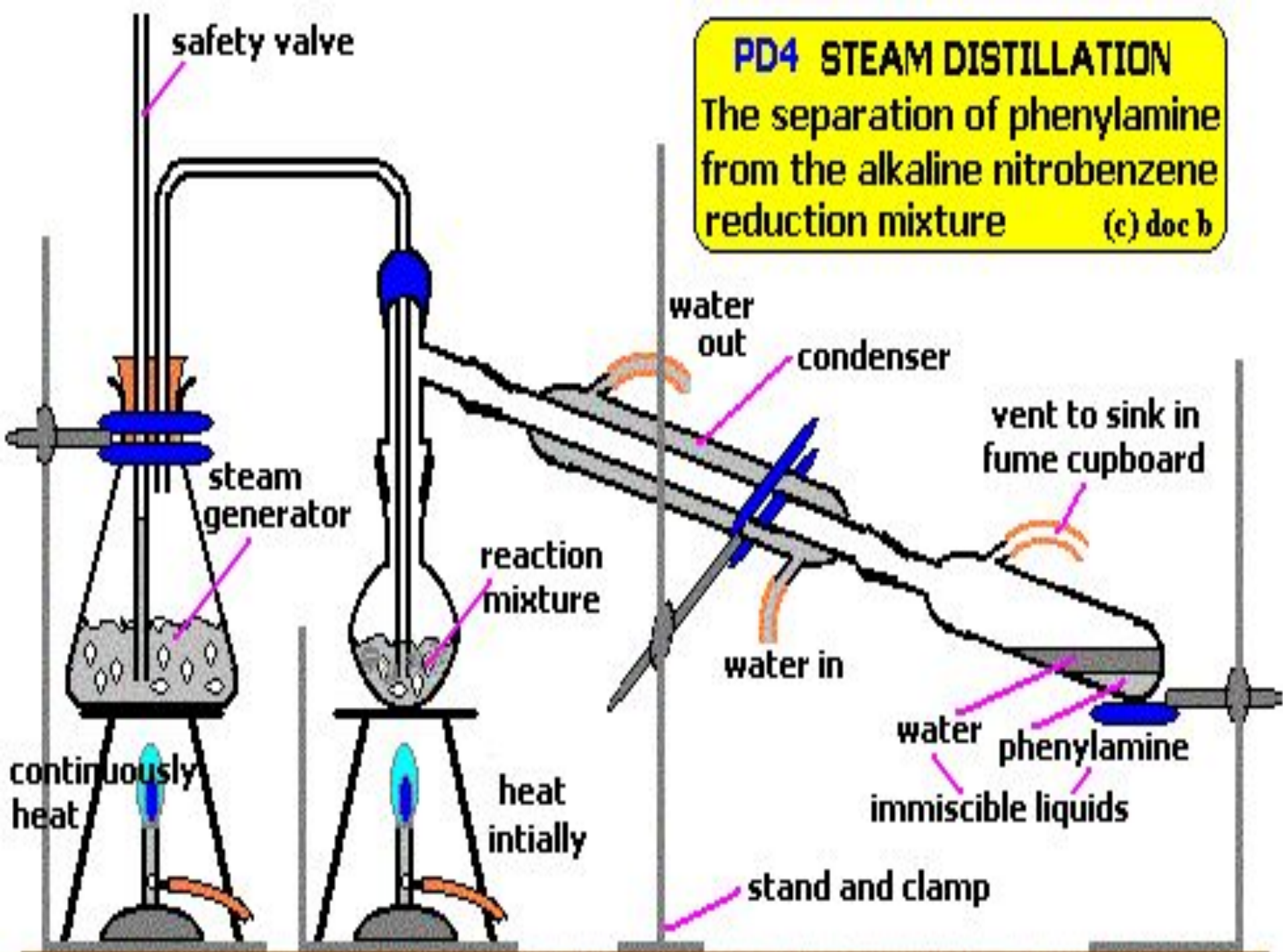
Steam distillation

- Principle - Mixture of immiscible liquids bigin to boil when the sum of there vapour pressure is equal to atmospheric pressure.

- Application Separation of high boiling point liquid from non volatile impurity.

- Ex- to separate toulene / water.

Block Diagram Of Steam Distillation

safety valve

PD4 STEAM DISTILLATION
The separation of phenylamine from the alkaline nitrobenzene reduction mixture (c) doc b

steam generator

water out

condenser

vent to sink in fume cupboard

reaction mixture

water in

water

phenylamine

continuously heat

heat intially

immiscible liquids

stand and clamp

USES OF STEAM DISTILLATION

iv. Steam distillation

- Steam distillation is used as a general term to such products which requires roasting for flavour generation.

- The method includes are:
    1. Wetting the material with moist gas,
    2. Steaming at varying pressure &
    3. Adding hot water.

- Generally used in industries for obtaining coffee flavour.

NERNST DISTRIBUTION LAW & ITS APPLICATIONS

Principle of Nernst Distribution Law

- Nernst's distribution law states that when the added substance is insufficient to saturate the immiscible liquids, the solute distributes between the liquids in such a way that at equilibrium the ratio of concentrations of the solute in the two liquids is constant, at constant temperature.

- Partition(P) or distribution coefficient(D) is the ratio of concentration of a compound in the two phases of a mixture of two immiscible solvents at equilibrium

- Hence these coefficients are a measure of differential solubility of the compound between two solvents.

- One of the solvents is water and the second one is hydrophobic such as octanol. It is useful in estimating the distribution of drugs within the body.

- **It is the ratio of concentration of a substance in organic phase to the concentration of substance in aqueous phase at constant temperature.**

It is given as: **Equilibrium constant,** $K = \dfrac{Co}{Cw}$

Where, K= Partition coefficient/ distribution coefficient/ distribution ratio.

C_o= Equilibrium concentration of substance in organic phase.

C_w= Equilibrium concentration of substance in aqueous phase.

Limitations:

- **Dilute solutions:** The conc. of solute must be low in two solvents. This law does not holds good when the concentrations are high.

- **Constant temperature:** Temperature should be kept constant throughout the experiment, since solubility is dependent on temperature.

- **Same molecular state:** Solute must be in the same molecular state in both the solvent. This law does not hold, if there is association or dissociation of solute molecules in one of the solvents.

- **Equilibrium concentration:** This is achieved by shaking the mixture for longer time.

- **Non-miscibility of solvents**: So, the solvents are to be allowed for separation for a sufficient time.

Applications:

- **Solubility** of drugs in water and other solvents and in mixture of solvents can be predicted.

- **Drug absorption** in vivo can be predicted.

- The oil-water partition coefficients are indicative of lipophilic hydrophilic character of drug molecules.

- Structure activity relationship (SAR) for a series of drugs can be studied.