

Phase Rule, Part-I, B.Sc. II Year

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This presentation includes

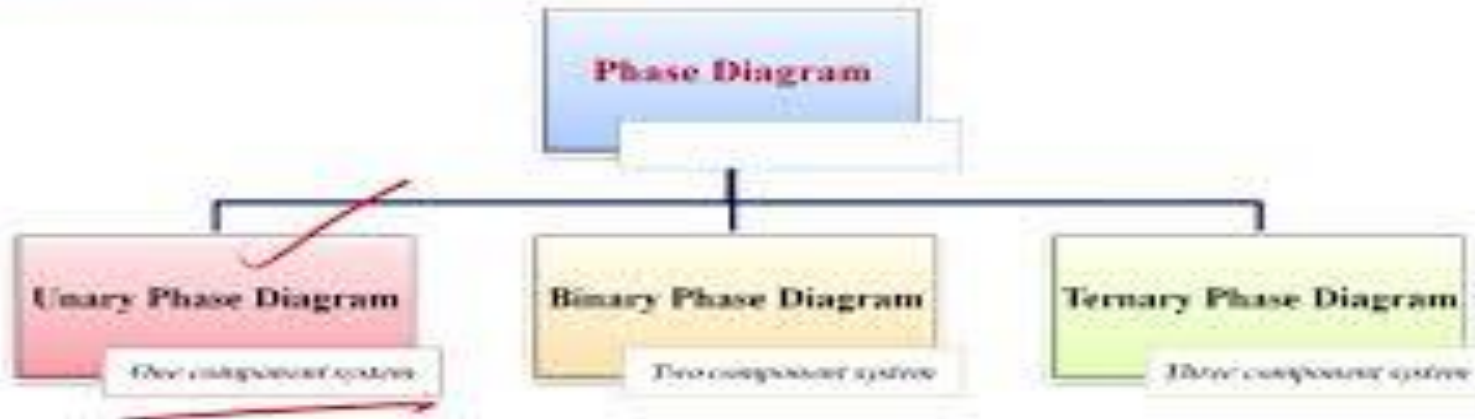
- Phase rule
- Types of phase diagrams
- One component system
- Water system
- Sulfur system
- Carbon di oxide system
- Two component systems
- Lead Silver system
- Bismuth Cadmium system
- Salt water system
- Henry's law
- Raoult's law
- Ideal solution
- Non ideal solution
- Positive and negative deviation from ideal behavior
- Azeotropes
- Positive azeotropes
- Negative azeotropes
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- Phenol water system
- Nicotine water system
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Phase Rule

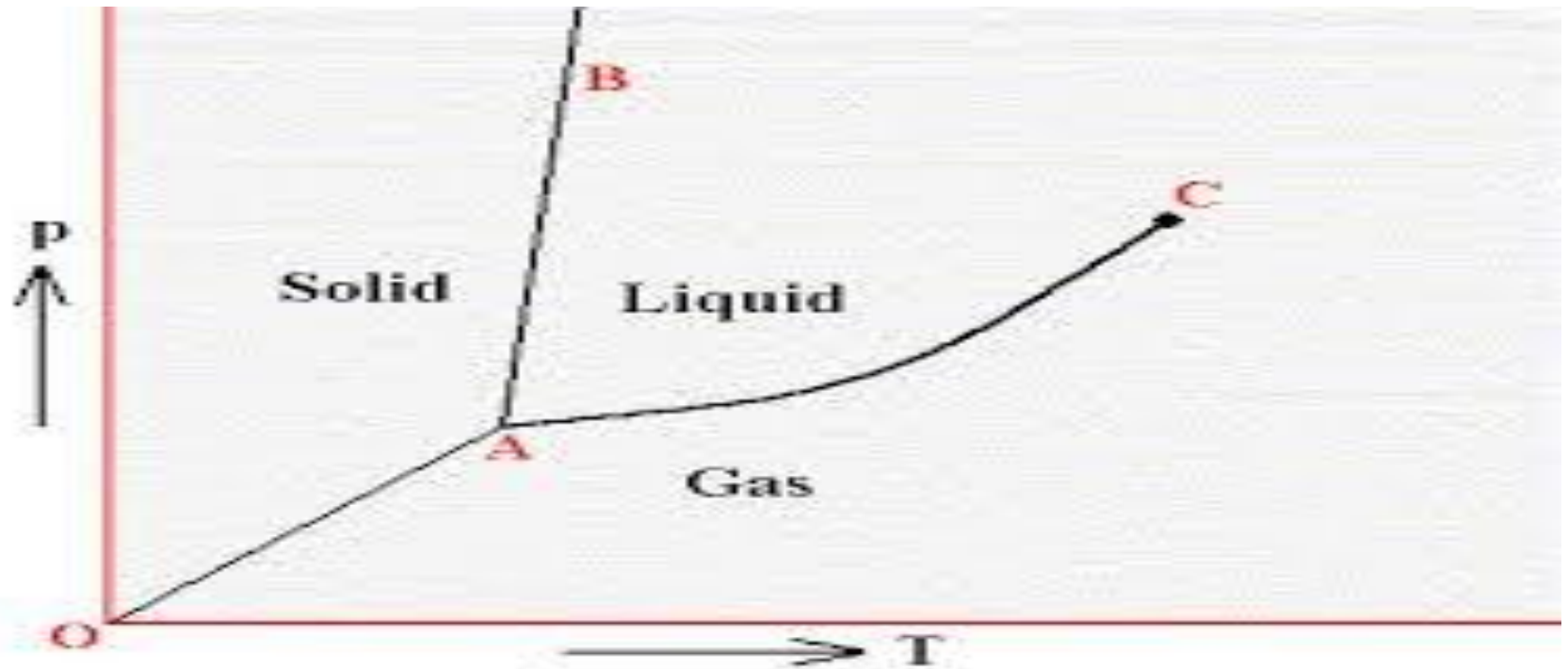
- The **phase rule** is a general principle governing systems in thermodynamic equilibrium. If F is the number of degrees of freedom, C is the number of components and P is the number of phases, then
 - $F = C - P + 2$
- It was derived by Josiah Willard Gibbs in his landmark paper titled *On the Equilibrium of Heterogeneous Substances*, published in parts between 1875 and 1878. The rule assumes the components do not react with each other.

Phase Diagrams

Classification of Phase Diagram:



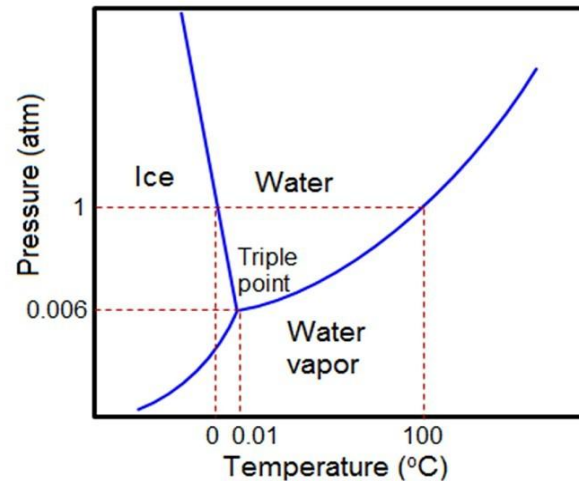
General Phase diagram for one component system



Phase Diagrams

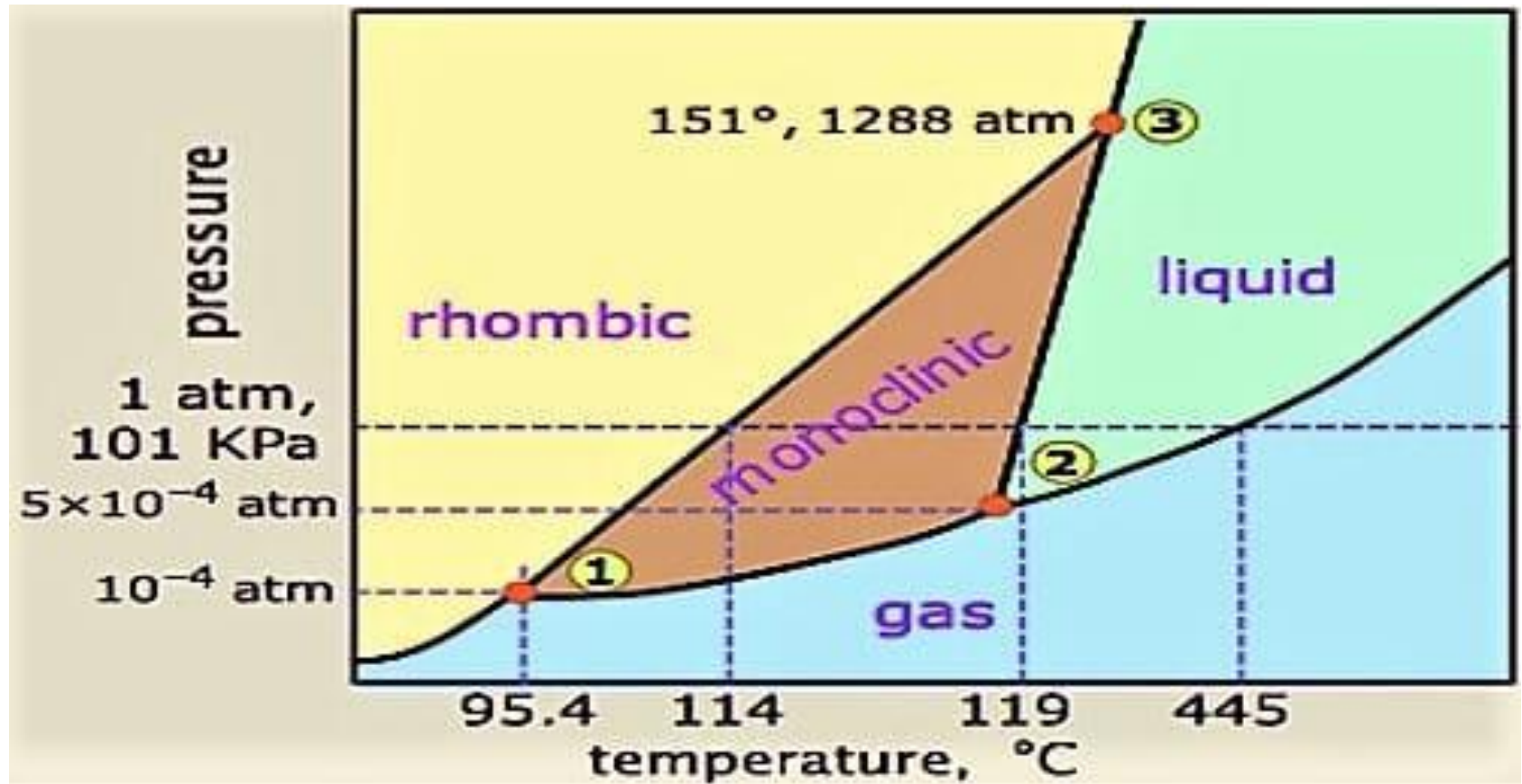
One component system

The simplest phase diagram is the water which is a one component system. It is also known as pressure-temperature or P-T diagram. Two phases exist along each of the three phase boundaries. At low pressure (0.006 atm) and temperature (0.01 °C) all the three phases coexist at a point called triple point.

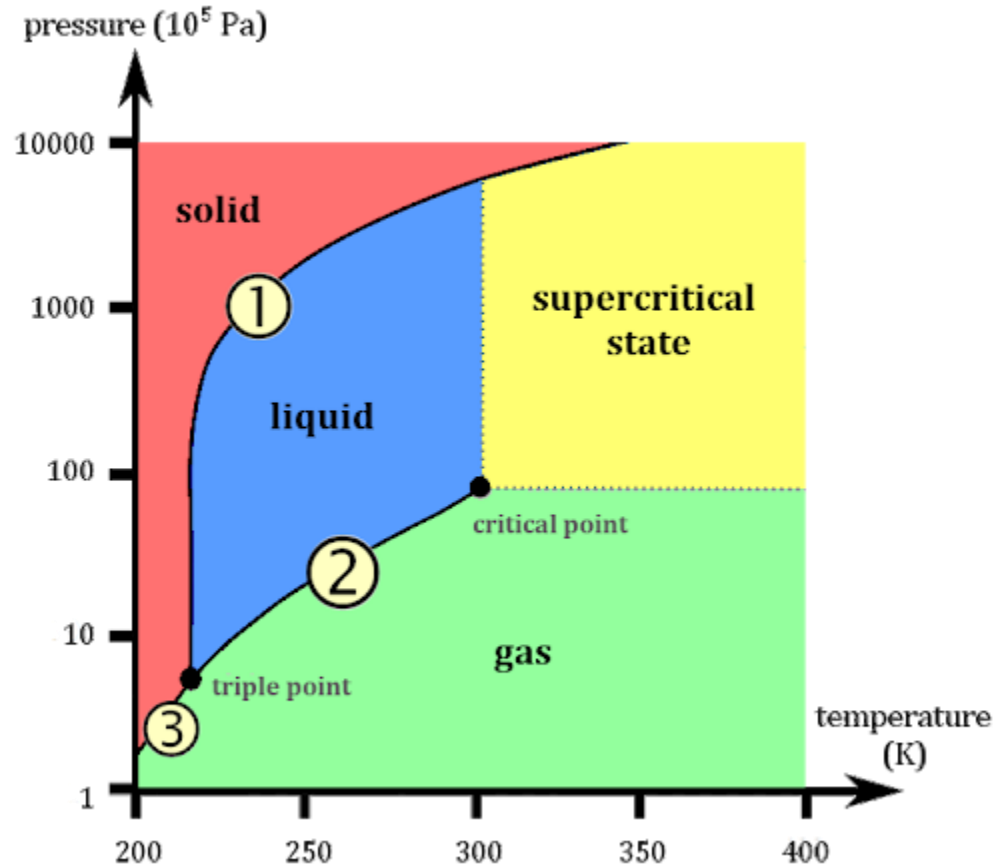


Water phase diagram

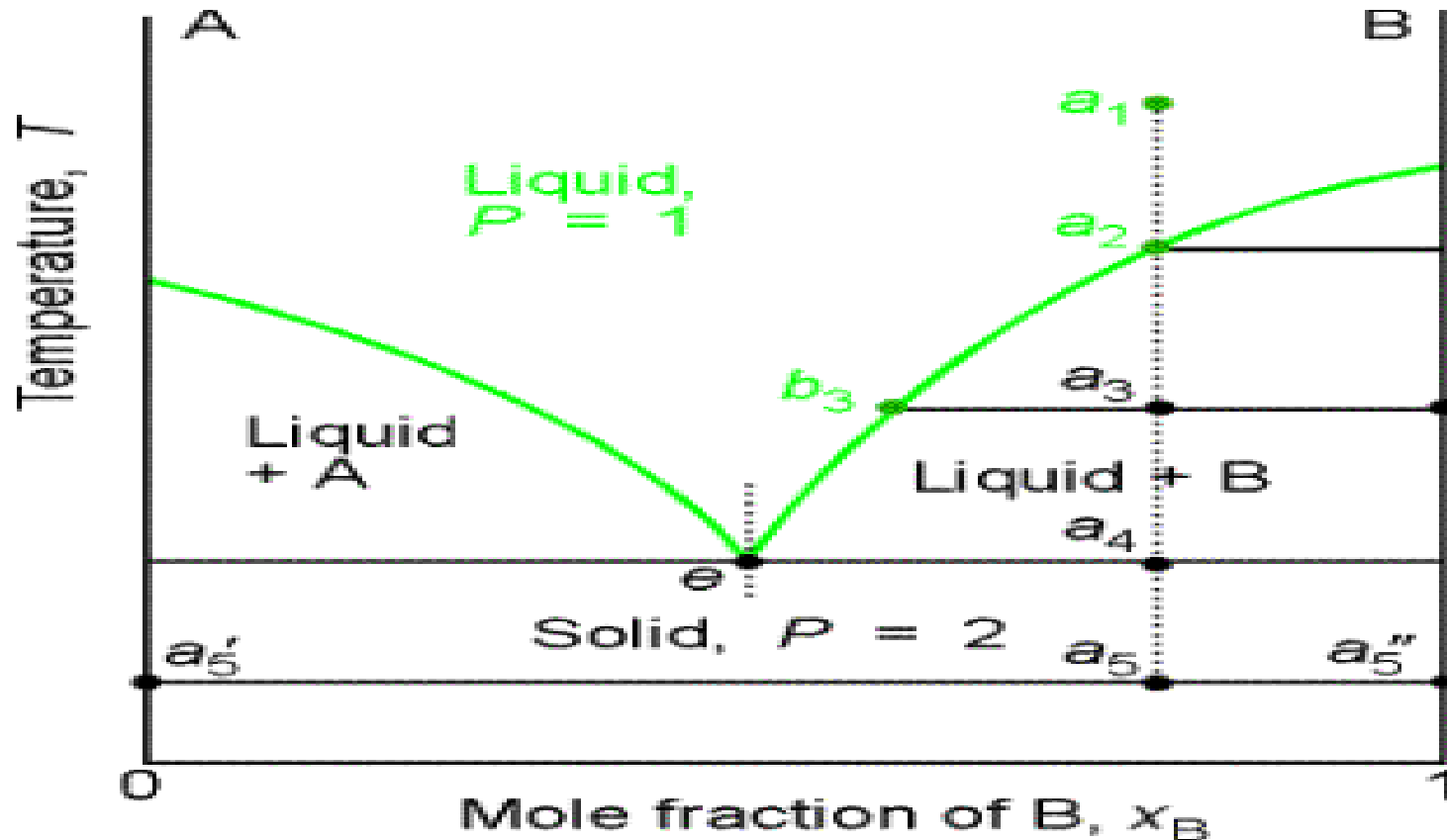
Phase diagram of Sulfur System



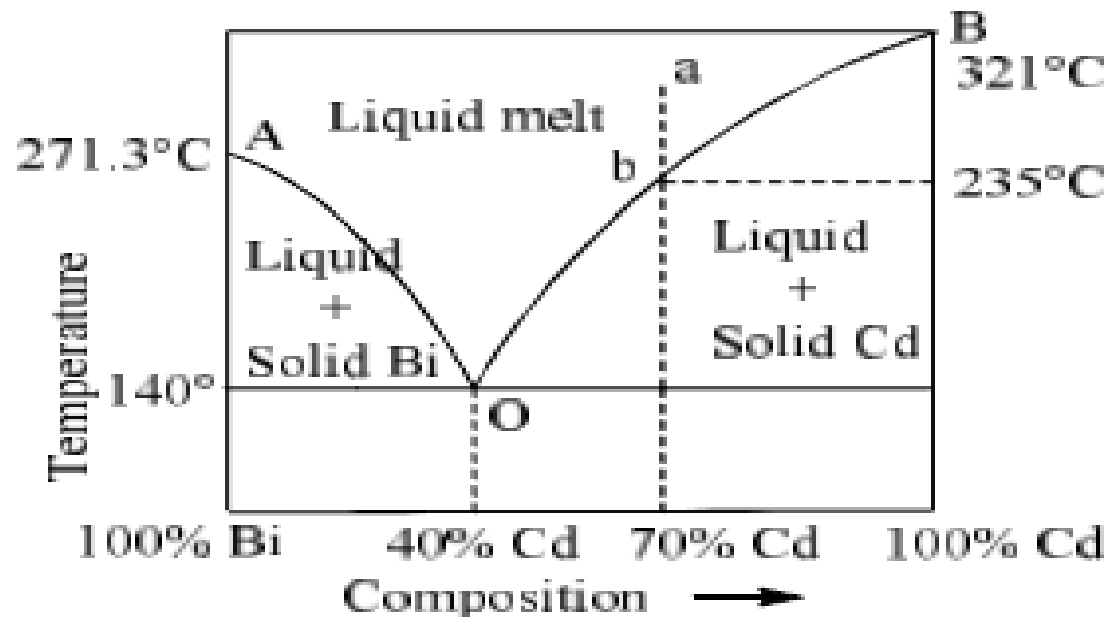
Phase diagram of Carbon di oxide



Phase diagram for 2 component System

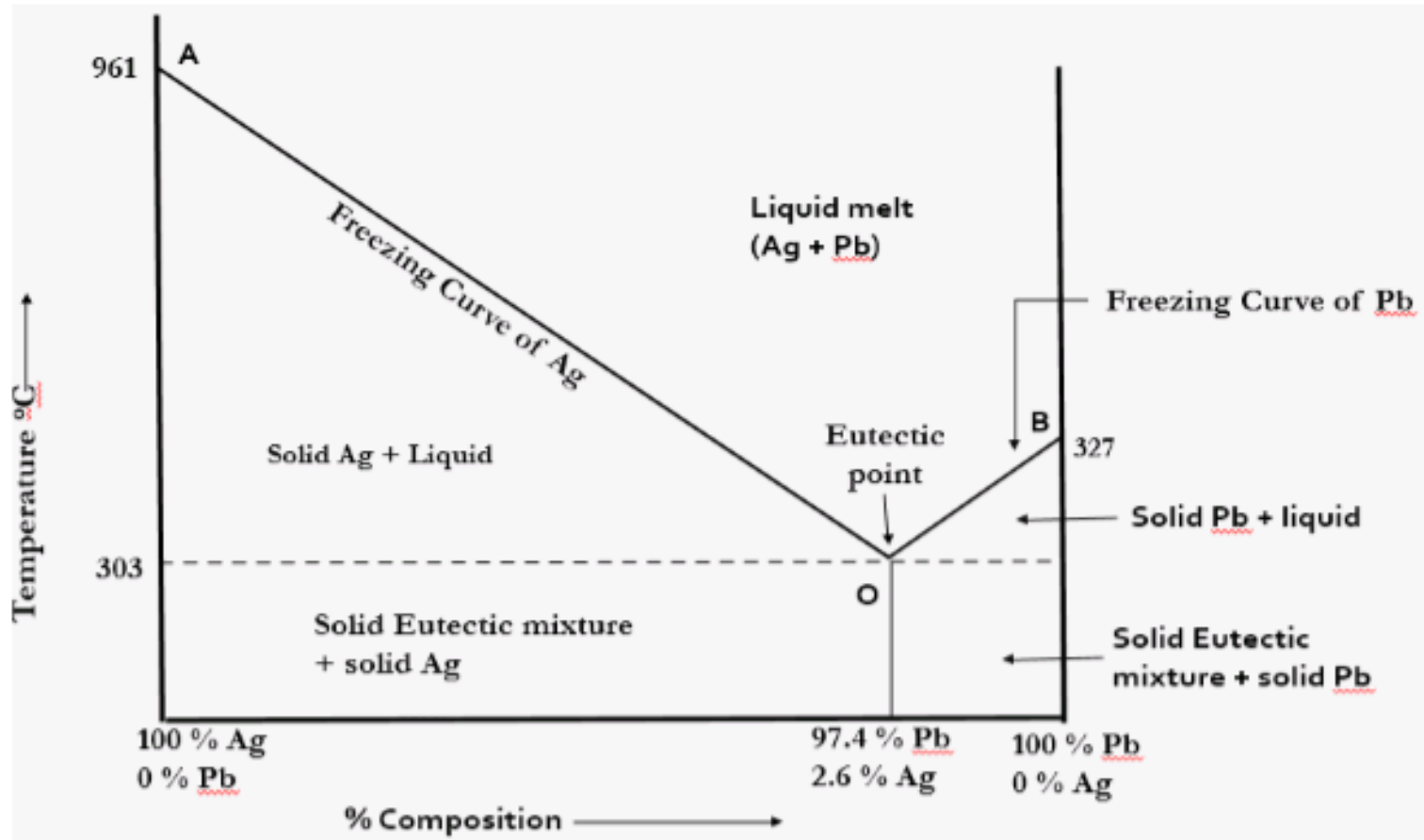


Phase Diagram for Bi-Cd system

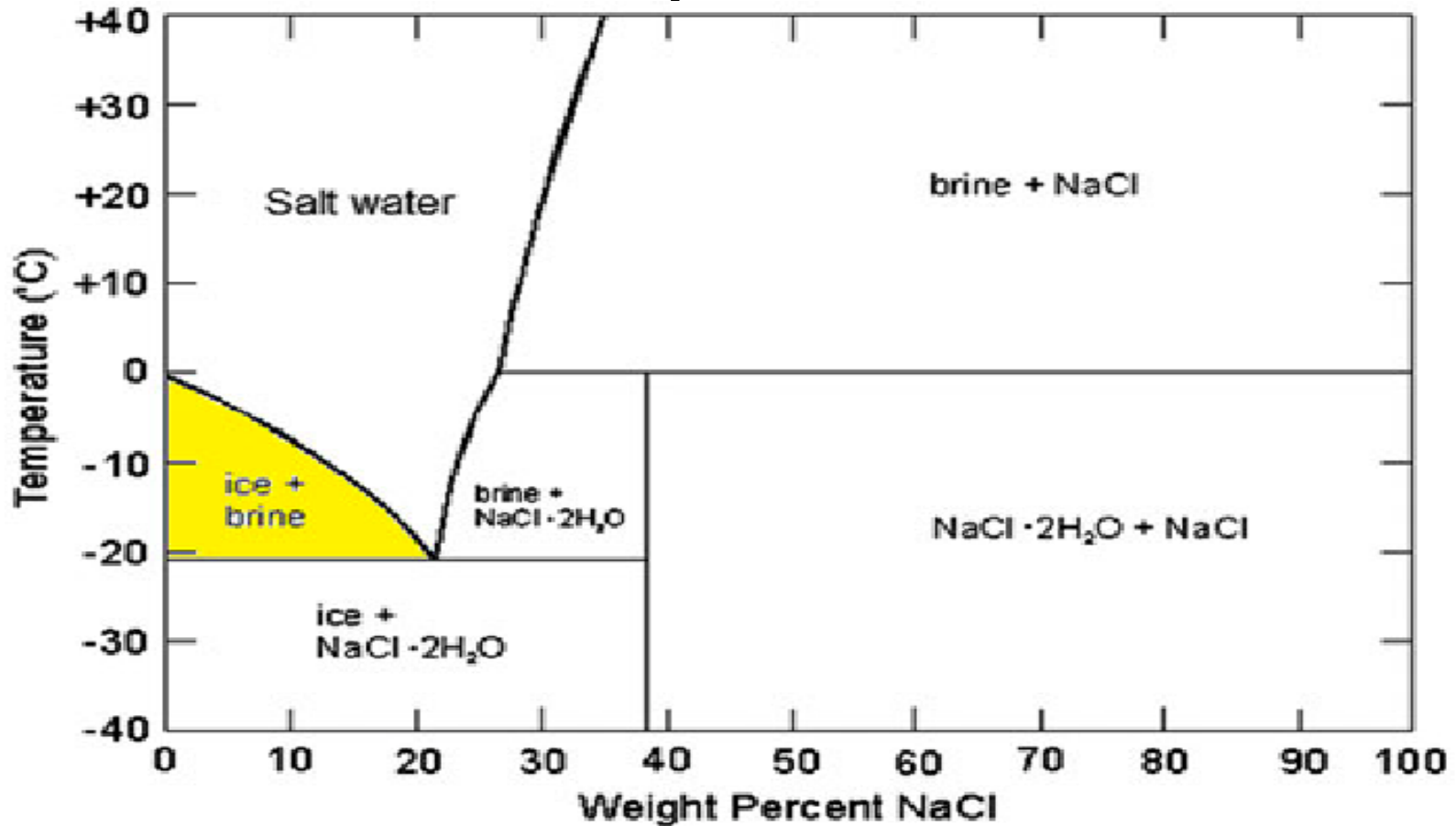


Graphical representation of Bismuth Cadmium system.

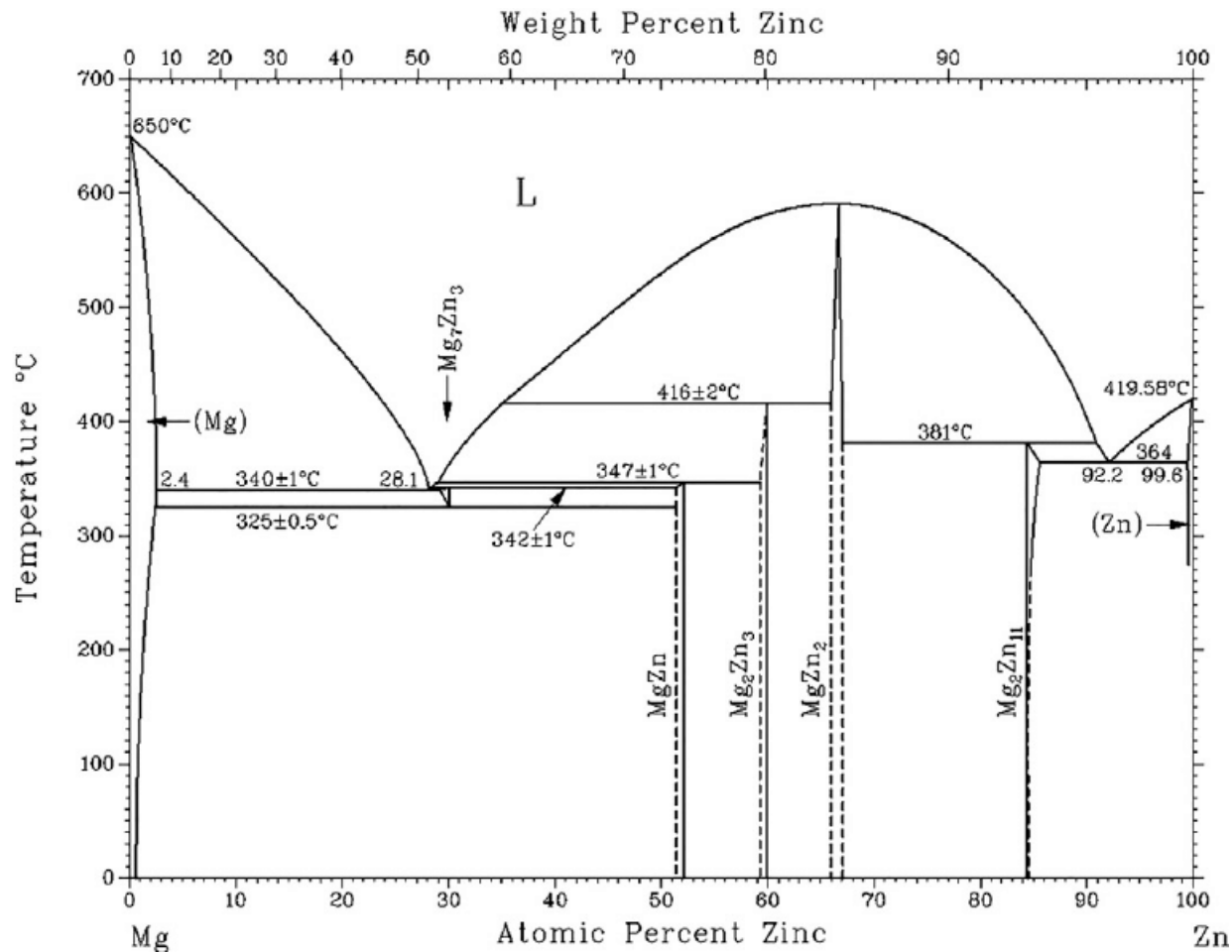
Phase diagram for Pb- Ag system



Phase diagram for Salt and water system



Phase diagram for zinc and magnesium system



Henry's Law

- In physical [chemistry](#), **Henry's law** is a [gas law](#) that states that the amount of dissolved gas in a liquid is proportional to its [partial pressure](#) above the liquid. The proportionality factor is called Henry's law constant. It was formulated by the English chemist [William Henry](#), who studied the topic in the early 19th century. In his publication about the quantity of gases absorbed by water, he described the results of his experiments:
- ... water takes up, of gas condensed by one, two, or more additional atmospheres, a quantity which, ordinarily compressed, would be equal to twice, thrice, &c. the volume absorbed under the common pressure of the atmosphere.
- An example where Henry's law is at play is in the depth-dependent dissolution of oxygen and nitrogen in the blood of [underwater divers](#) that changes during [decompression](#), leading to [decompression sickness](#). An everyday example is given by one's experience with [carbonated soft drinks](#), which contain dissolved carbon dioxide. Before opening, the gas above the drink in its container is almost pure [carbon dioxide](#), at a pressure higher than [atmospheric pressure](#). After the bottle is opened, this gas escapes, moving the partial pressure of carbon dioxide above the liquid to be much lower, resulting in degassing as the dissolved carbon dioxide comes out of solution.

Raoult's Law

The presence of a nonvolatile solute lowers the vapor pressure of the solvent.

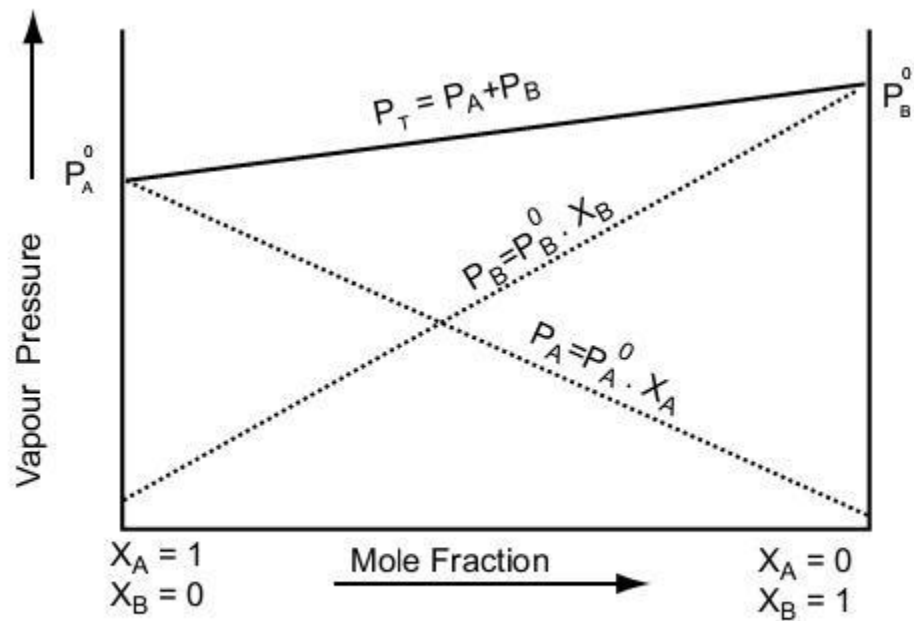
$$P_{\text{solution}} = \chi_{\text{solvent}} P_{\text{solvent}}^0$$

P_{solution} = Observed Vapor pressure of the solution

χ_{solvent} = Mole fraction of the solvent

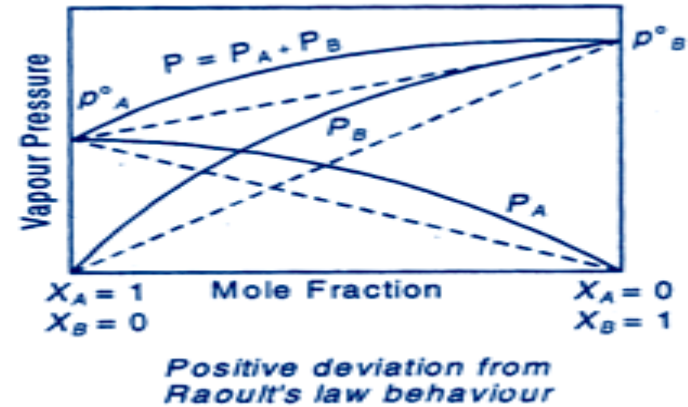
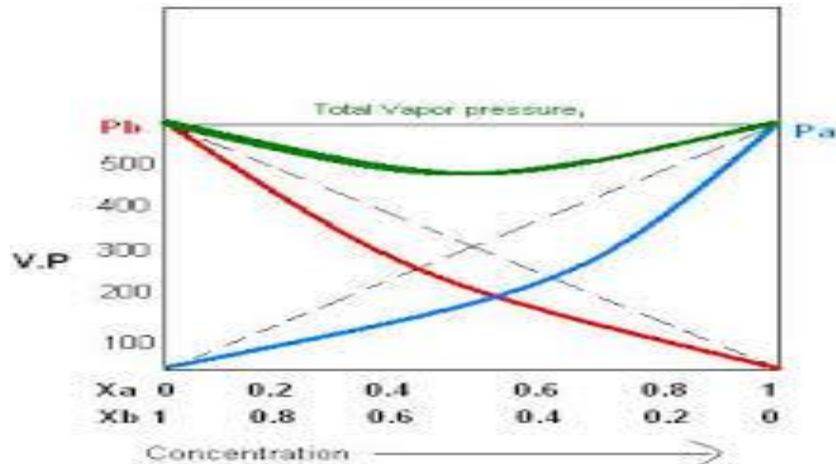
P_{solvent}^0 = Vapor pressure of the pure solvent

Vapor Pressure diagram for ideal solution



Vapour Pressure Diagram for Ideal Solution

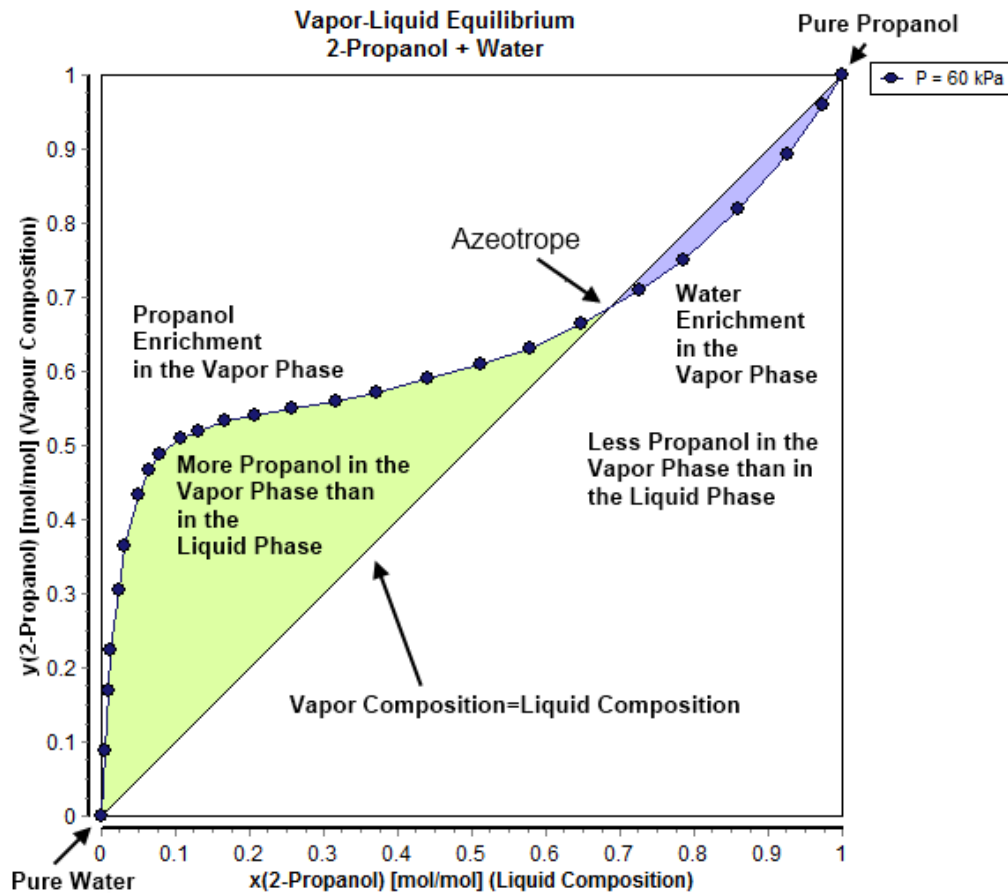
Non Ideal Solutions (With negative and positive deviations)



Azeotropes

- An **azeotrope** or a **constant boiling point mixture** is a mixture of two or more liquids whose proportions cannot be altered or changed by simple distillation. This happens because when an azeotrope is boiled, the vapour has the same proportions of constituents as the unboiled mixture. Because their composition is unchanged by distillation, azeotropes are also called (especially in older texts) constant boiling point mixtures.
- Some azeotropic mixtures of pairs of compounds are known, and many azeotropes of three or more compounds are also known.

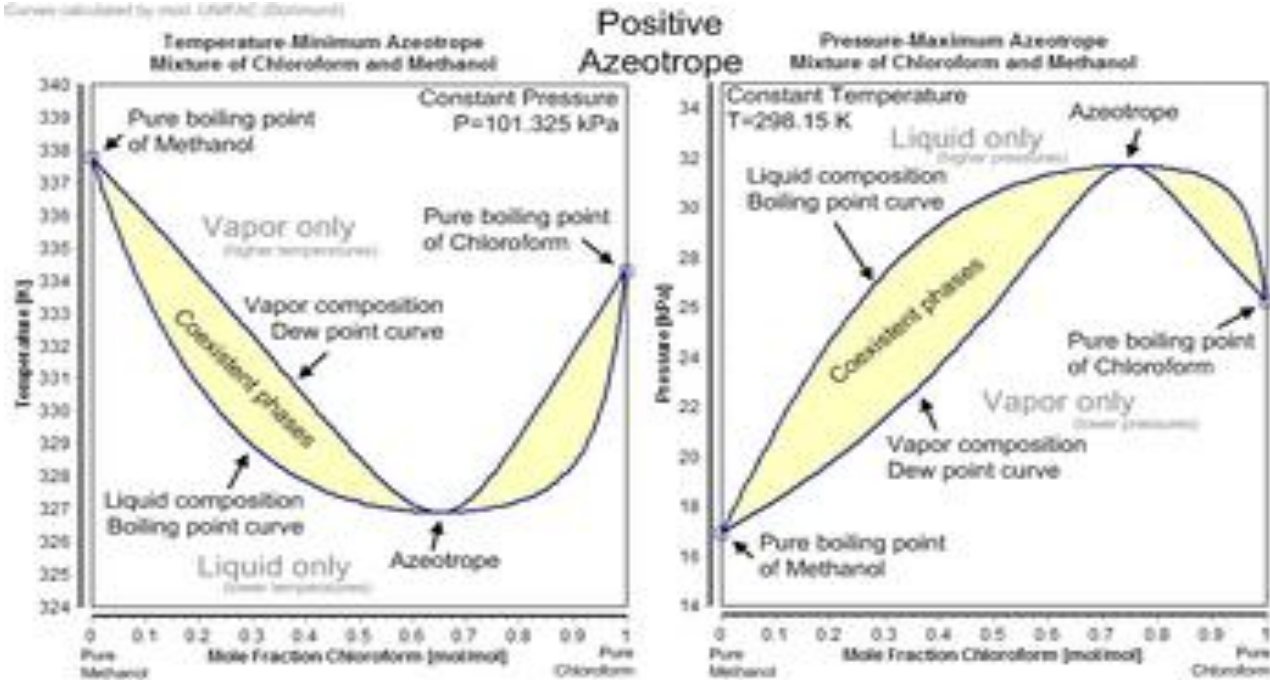
Azeotropes - Example



Data taken from Dortmund Data Bank
Original Source: Marzal P., Monton J.B., Rodrigo M.A., J.Chem.Eng.Data, 41(3), 608-611, 1996

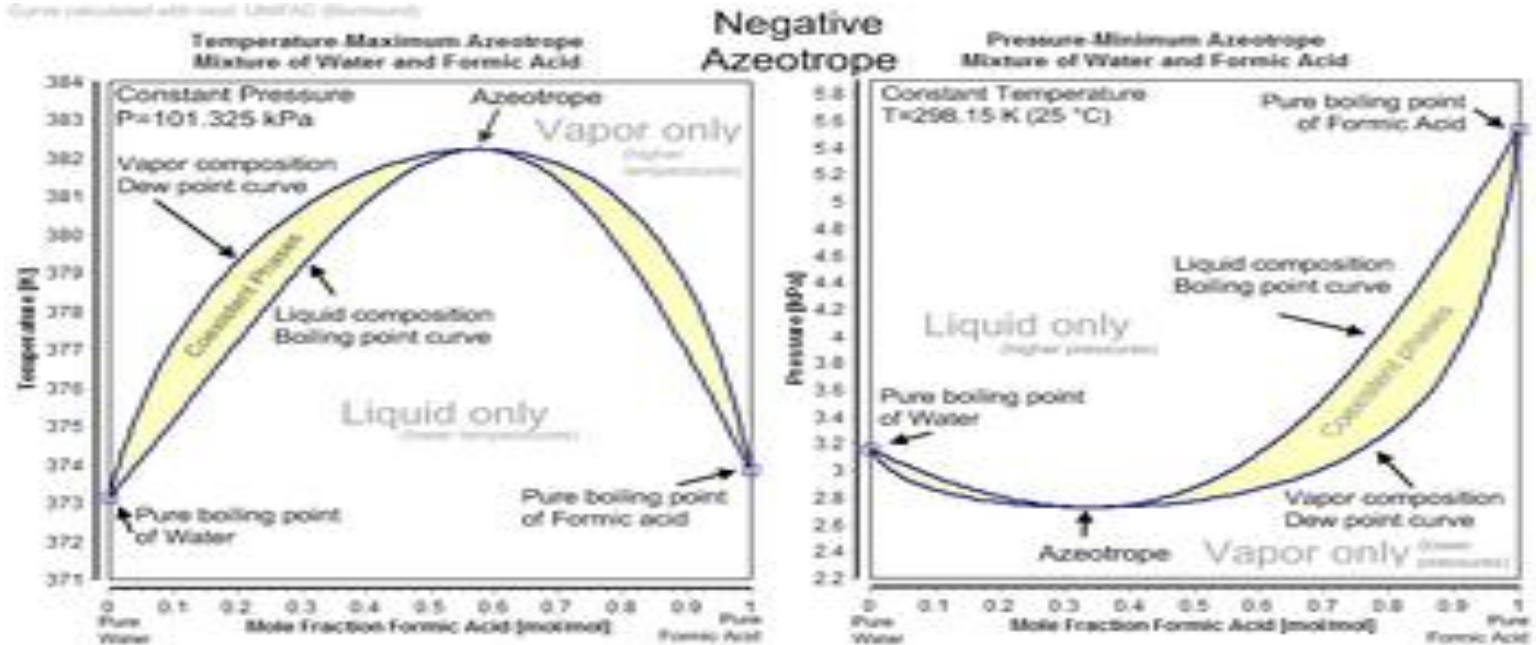
Positive azeotropes

Curves calculated by molal LUFAC (Bostrom)



Negative azeotropes

Curves calculated with tool: UNIFAC (Bismarck)





Phenol and water system phase diagram.

Temperature fixed at 50 °C

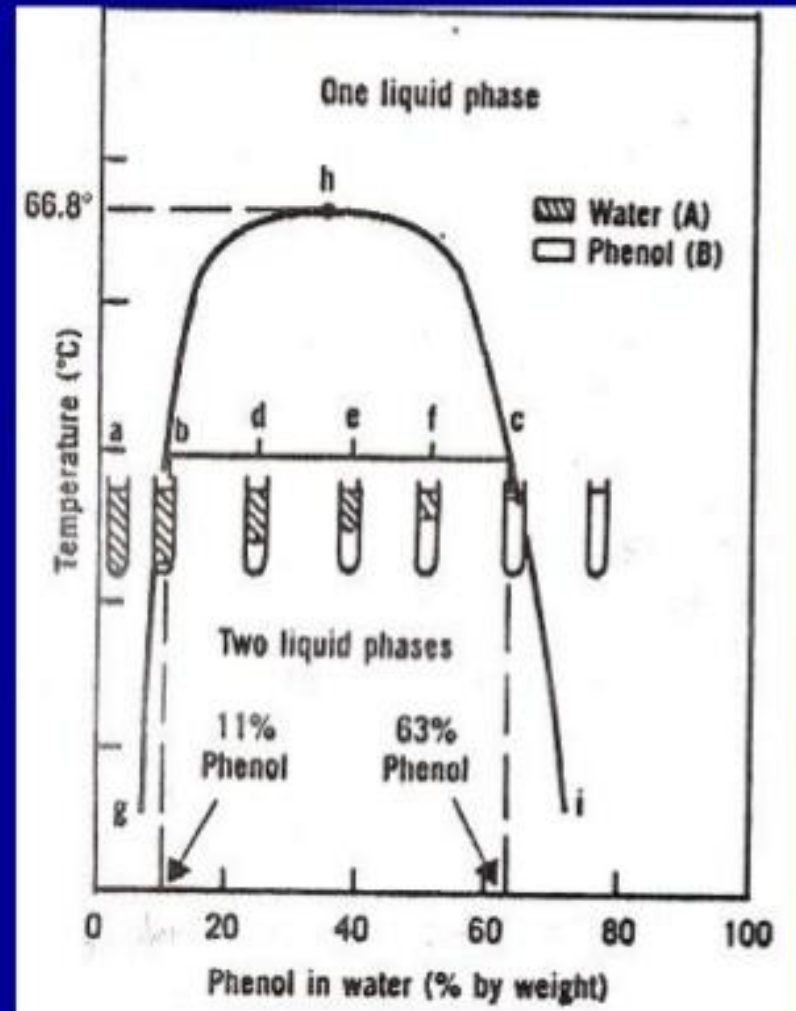
*Point **a**, system containing 100% pure water.

Addition of phenol to water will result in the formation of a single liquid phase until the point **b** is reached.

*At point **b**, appears a second phase.

Phase A: water rich phase containing 11% phenol

Phase B: phenol rich phase containing 63% phenol



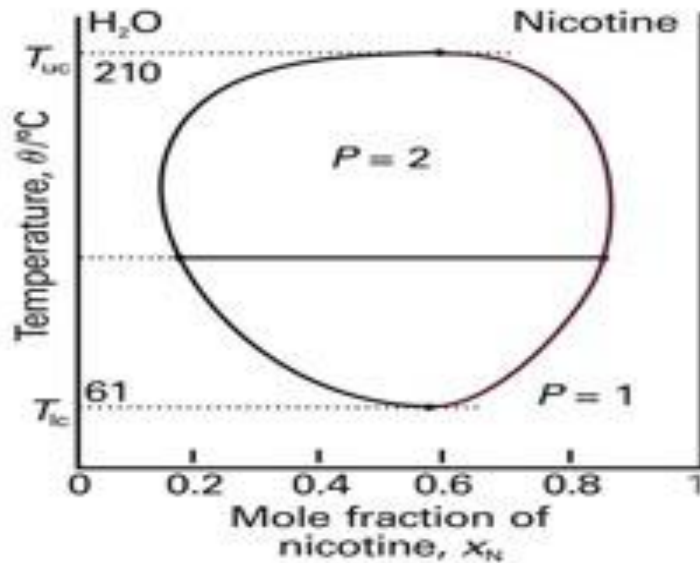
CST for phenol water system

- The consolute **temperature** for **phenol/water system** is 68.5°C. **Phenol** is partial miscible with **water** and at certain **temperature** and certain concentration, one liquid phase will obtain.

Nicotine water system

- The **nicotine-water system** has an LCST of 61 °C, and also a UCST of 210 °C at pressures high enough for liquid **water** to exist at that **temperature**. The components are therefore miscible in all proportions below 61 °C and above 210 °C (at high pressure), and partially miscible in the interval from 61 to 210 °C.

Nicotine water system



The temperature-composition diagram for the water and nicotine, which has both upper and lower critical temperatures.

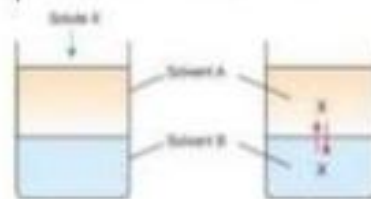
Note the high temperatures for the liquid (especially the water): the diagram corresponds to a sample under pressure.

Nernst's Distribution Law

Nernst gave a generalization governing the distribution of a solute between **two non-miscible solvents**. This is called **Nernst's Distribution law** or **Nernst's Partition law** or simply **Distribution law** or **Partition law**.

Statement of Nernst's distribution law: If a solute **X** distributes itself between two immiscible solvents A and B at constant temperature and X is in the same molecular condition in both solvents,

Then
$$\frac{\text{Concentration of X in A}}{\text{Concentration of X in B}} = K_D$$



If C_1 denotes the concentration of the solute (**X**) in solvent, A and C_2 the concentration in solvent B, then Nernst's Distribution law can be expressed

as
$$\frac{C_1}{C_2} = K_D$$

The constant K_D (or simply K) is called the **Distribution coefficient** or **Partition coefficient** or **Distribution ratio**.

Assignment/ Set of questions

- Q1. write and explain phase rule
- Q2. What do you understand by phase, component and degree of freedom?
- Q3. Draw and explain the phase diagram for water system.
- Q4. Draw and explain the phase diagram for sulfur system.
- Q5. Draw and explain the phase diagram for carbon dioxide system.
- Q6. Draw and explain the phase diagram for Pb-Ag system.
- Q7. Draw and explain the phase diagram for the Bi-Cd system.
- Q8. Draw and explain the phase diagram for salt and water system.
- Q9. Write a note of desilverization of lead.
- Q10. State and explain Henry's law

Assignment/ Set of questions

- Q11. State and explain Raoult's law.
- Q12 What do you understand by ideal and non-ideal solutions?
- Q13. Explain positive and negative deviations from ideal behaviour.
- Q14. What are azeotropes?
- Q15. What are positive and negative azeotropes?
- Q16. What do you understand by critical solution temperature?
- Q17. Draw and explain phase diagram for phenol water system.
- Q18. What are upper and lower CST.?
- Q19. Draw and explain phase diagram for nicotine water system.
- Q20. State and explain Nernst's distribution law.

- Best of luck

Surface Chemistry, B.Sc. II Year, Paper I

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This presentation includes

- Adsorption
- Difference between adsorption and absorption
- Types of adsorption
- Isotherm
- Freundlich adsorption isotherm
- Langmuir Adsorption isotherm
- Adsorption on solid surfaces, Effect of surface area
- Catalyst(Introduction)
- Energy profile (with and without catalyst)
- Type of catalysis
- Applications of catalysts
- Assignment / set of questions

Adsorption

- **Adsorption** is the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface. This process creates a film of the *adsorbate* on the surface of the *adsorbent*. This process differs from absorption, in which a fluid (the *absorbate*) is dissolved by or permeates a liquid or solid (the *absorbent*), respectively. Adsorption is a surface phenomenon, while absorption involves the whole volume of the material. The term sorption encompasses both processes, while desorption is the reverse of it.

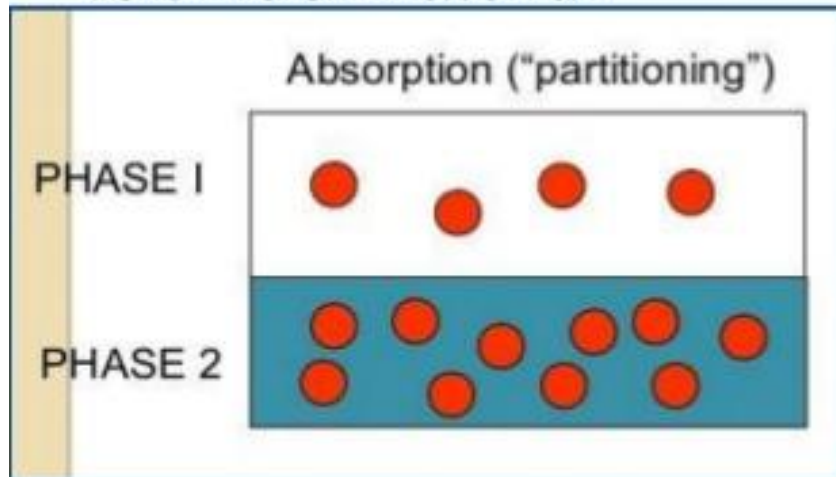
Adsorption

- Similar to [surface tension](#), adsorption is a consequence of [surface energy](#). In a bulk material, all the bonding requirements (be they [ionic](#), [covalent](#) or [metallic](#)) of the constituent [atoms](#) of the material are filled by other atoms in the material. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbates. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as [physisorption](#) (characteristic of weak [van der Waals forces](#)) or [chemisorption](#) (characteristic of covalent bonding). It may also occur due to electrostatic attraction.

DEFINITION

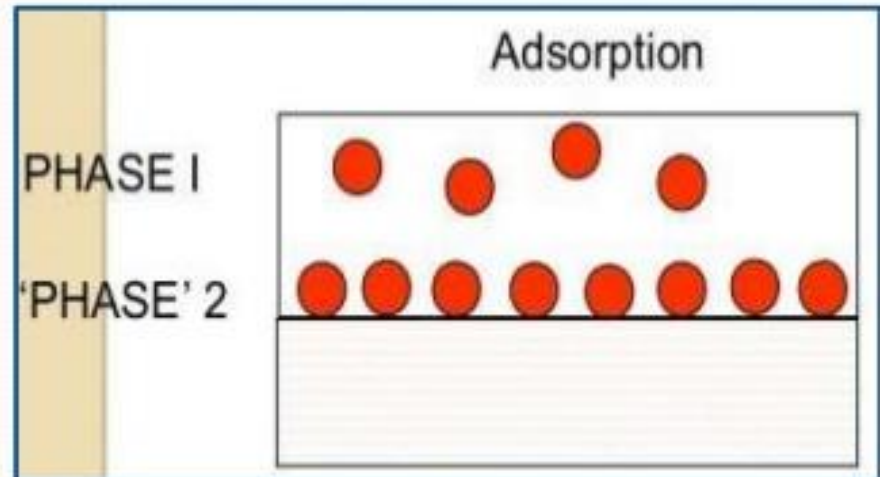
ABSORPTION

- ❖ The process by which one substance takes up another substance through minute pores or spaces between them
- ❖ involves the whole volume of material

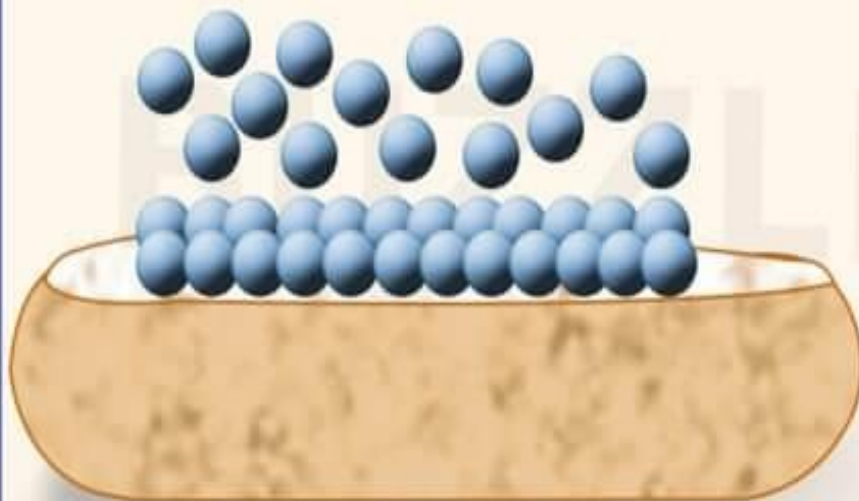


ADSORPTION

- ❖ The process in which there is adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to surface
- ❖ involves the surface area of material

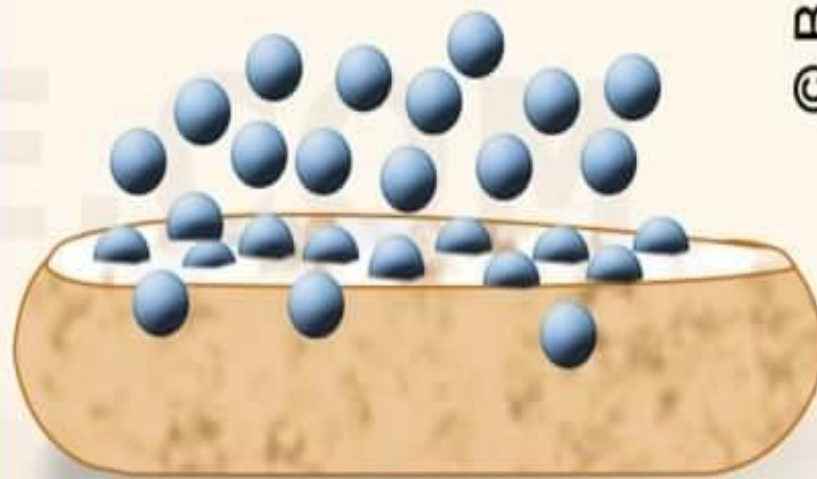


ADSORPTION



Molecules adhere to the surface of the phase.

ABSORPTION



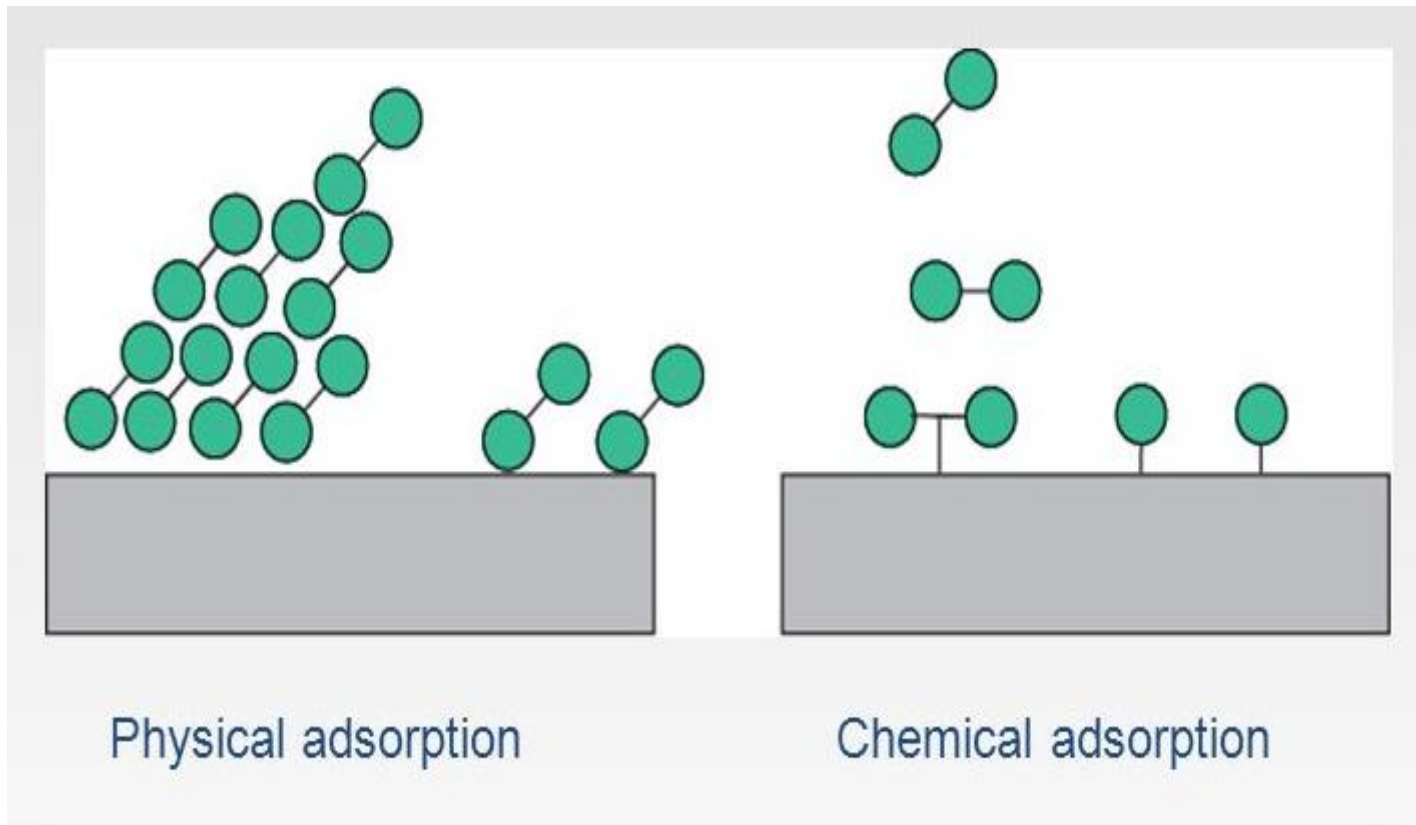
Molecules are drawn into the bulk of the phase.

Absorption	Adsorption
It is the process by which atoms, molecules or ions enters the bulk.	The accumulation of the molecular species at surface not in the bulk.
It is a bulk phenomenon.	It is a surface phenomenon.
It is an endothermic process.	It is an exothermic process.
It is same throughout the material.	In this concentration at the surface is different than that of bulk of adsorbent.
It is not affected by temperature.	It is temperature dependent phenomenon.

Types of Adsorption

Physical adsorption	Chemical adsorption
<ol style="list-style-type: none">1. The forces operating in this case are weak Vander wall's forces.2. The heat of adsorption is low about 20-40 KJ mol⁻¹3. The process is reversible, desorption can be occur by increasing tem. Or decreasing pressure.4. It does not require any activation energy.5. It takes place at the low temperature and decreases with increase in the temperature.6. It is not specific in nature all gases adsorbes on all solids to same extent.7. It increases with the increase insurface area of the adsorbent.8. It forms multimolecular layer.	<ol style="list-style-type: none">1. The Forces operating are chemical bonds (ionic or covalent bond).2. The heat of absorption are high about 40-400 KJ mol⁻¹3. The process is irreversible. Efforts to free the adsorbed gas give different Compounds.4. It requires activation chergy.5. This type of adsorption first increases with increase in temperature6. It is highly specific in nature occurs only by the possibility of formation of chemical bond.7. It also increases with the increases with the increase in surface area of adsorbent.8. It forms unimolecular layer.

Types of Adsorption



Isotherms

- The adsorption of gases and solutes is usually described through isotherms, that is, the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (for liquid phase solutes) at constant temperature. The quantity adsorbed is nearly always normalized by the mass of the adsorbent to allow comparison of different materials.

Freundlich Adsorption Isotherm

freundlich adsorption isotherm:

Freundlich derived an equation for the adsorption of the dissolved solid on the surface of porous substances. The equation is:

$$\frac{X}{m} \propto c^n$$
$$\frac{X}{m} = K c^n$$

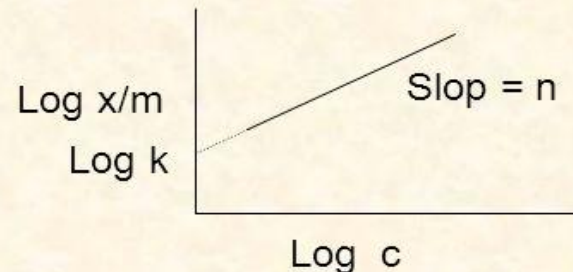
where **X** = weight of material (adsorbate) in grams, adsorbed by **m** grams of adsorbent, **C** = the concentration of solute in g/100.
n and k are constants.

By taking the logarithm of the equation, we obtain:

$$\log x/m = \log K + n \log c$$

According to this equation, a plot of $\log x/m$ versus $\log c$, a straight line is obtained, and the constants may be evaluated.

Intercept = $\log K$. and the slope is n



Langmuir adsorption isotherm

case I $\theta = \frac{C_s}{C_\infty} = \frac{B_0 P}{1 + B_0 P}$

case II $\theta = \frac{C_s}{C_\infty} = \frac{(B_0 P_{AB})^{1/2}}{1 + (B_0 P_{AB})^{1/2}}$

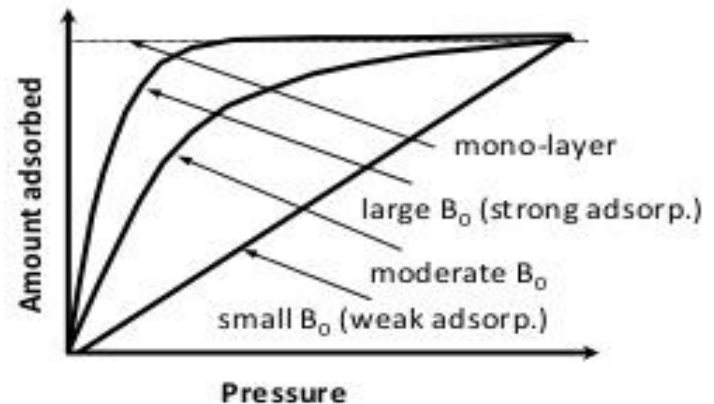
Case III $\theta_A = \frac{C_{s,A}}{C_\infty} = \frac{B_{0,A} P_A}{1 + B_{0,A} P_A + B_{0,B} P_B}$
 $\theta_B = \frac{C_{s,B}}{C_\infty} = \frac{B_{0,B} P_B}{1 + B_{0,A} P_A + B_{0,B} P_B}$

Strong adsorption

$k_{ads} \gg k_{des} \quad \theta = \frac{C_s}{C_\infty} \rightarrow 1$

Weak adsorption

$k_{ads} \ll k_{des} \quad \theta = \frac{C_s}{C_\infty} = B_0 P$



- Langmuir adsorption isotherm established a logic picture of adsorption process
- It fits many adsorption systems but not at all
- The assumptions made by Langmuir do not hold in all situation, that causing error
 - Solid surface is heterogeneous thus the heat of adsorption is not a constant at different θ
 - Physisorption of gas molecules on a solid surface can be more than one layer

Catalysis & Catalysts

Adsorption On Solid Surface

□ Adsorption process

Adsorbent and adsorbate

- **Adsorbent** (also called *substrate*) - The solid that provides surface for adsorption
 - high surface area with proper pore structure and size distribution is essential
 - good mechanical strength and thermal stability are necessary
- **Adsorbate** - The gas or liquid substances which are to be adsorbed on solid

Surface coverage, θ

The solid surface may be completely or partially covered by adsorbed molecules

$$\text{define } \theta = \frac{\text{number of adsorption sites occupied}}{\text{number of adsorption sites available}} \quad \theta = 0 \sim 1$$

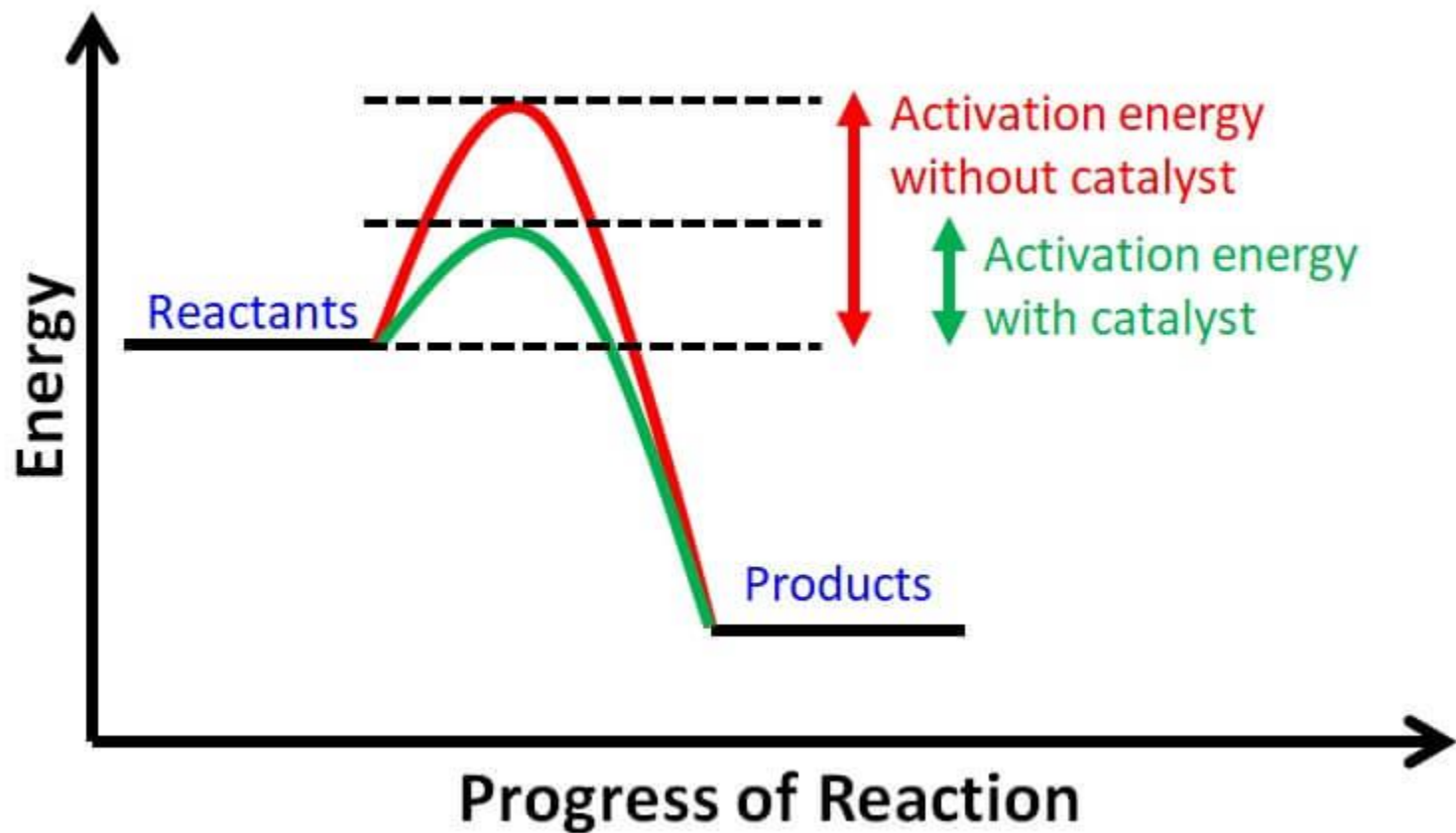
Adsorption heat

- Adsorption is usually exothermic (in special cases *dissociated* adsorption can be endothermic)
- The heat of chemisorption is in the same order of magnitude of reaction heat; the heat of physisorption is in the same order of magnitude of condensation heat.

Catalyst

- **Catalysis** is the process of increasing the rate of a chemical reaction by adding a substance known as a **catalyst**, which is not consumed in the catalyzed reaction and can continue to act repeatedly.
- Because of this, only very small amounts of catalyst are required to alter the reaction rate in most cases.

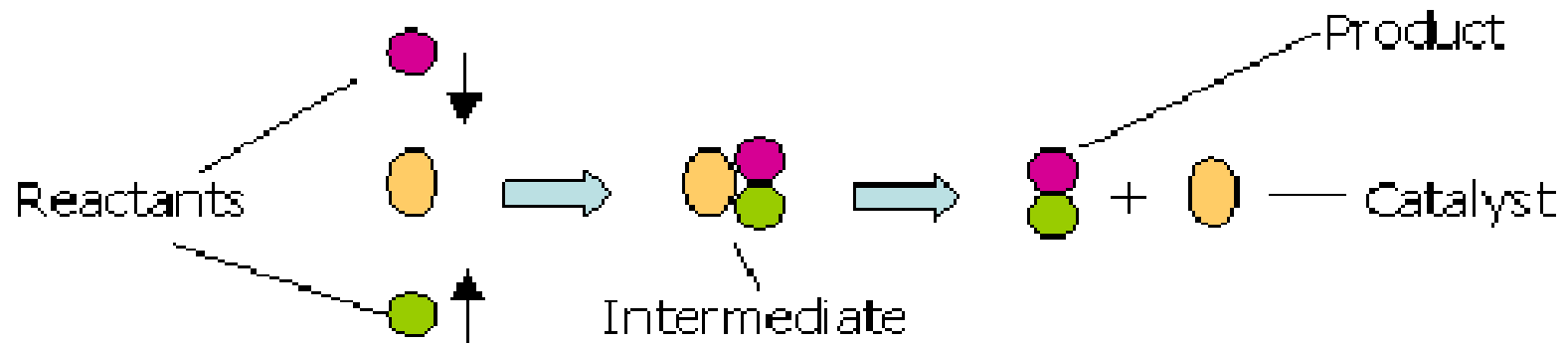
Energy Profile (with and without catalyst)



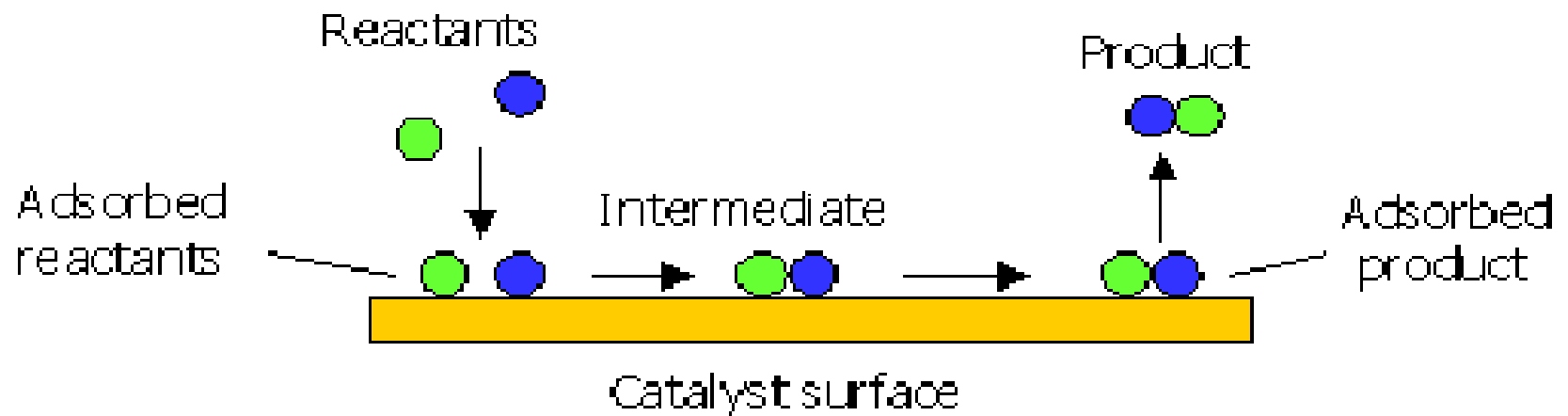
Major differences between homogeneous and heterogeneous catalysts

	Homogeneous	Heterogeneous
Form	Soluble metal complexes, usually mononuclear	Metals, usually supported, or metal oxides
Active site	well-defined, discrete molecules	poorly defined
Phase	Liquid	Gas/solid
Temperature	Low (<250°C)	High (250 – 500°C)
Activity	Moderate	High
Selectivity	High	Low
Diffusion	Facile	Can be very important
Heat transfer	Facile	Can be problematic
Product separation	Generally problematic	Facile
Catalyst recycle	Expensive	Simple
Catalyst modification	Easy	Difficult
Reaction mechanisms	Reasonably well understood	Poorly understood

Homogeneous catalysis



Heterogeneous catalysis



Catalysis & Catalysts

Applications of Catalysis

□ Industrial applications

Almost all chemical industries have one or more steps employing catalysts

- Petroleum, energy sector, fertiliser, pharmaceutical, fine chemicals ...

Advantages of catalytic processes

- Achieving better process economics and productivity
 - Increase reaction rates - fast
 - Simplify the reaction steps - low investment cost
 - Carry out reaction under mild conditions (e.g. low T, P) - low energy consumption
- Reducing wastes
 - Improving selectivity toward desired products - less raw materials required, less unwanted wastes
 - Replacing harmful/toxic materials with readily available ones
- Producing certain products that may not be possible without catalysts
- Having better control of process (safety, flexible etc.)
- Encouraging application and advancement of new technologies and materials
- And many more ...

Assignment/ set of questions

- Q1. What do you understand by adsorption?
- Q2. What are the differences between adsorption and absorption
- Q3. Enlist the differences between physical and chemical adsorption.
- Q4. Write a note on relation of adsorption with surface area.
- Q5. Write a note on Freundlich adsorption isotherm equation.
- Q6. Write a note on Langmuir adsorption isotherm equation.
- Q7. What is a catalyst?
- Q8. Explain energy profile diagram with and without the use of catalyst.
- Q9. Differentiate between homogeneous and heterogeneous catalysts.
- Q10 Write a note on the application of catalyst

- Best of Luck