

CHAPTER 5: SURFACE CHEMISTRY



SURFACE CHEMISTRY

Introduction

Surface Chemistry deals with the study of physical and chemical phenomena occurring at the boundary (interface) separating two bulk phases.

The bulk phase can be a pure compound or a solution.

The bulk phases may be solid – liquid, solid – gas, solid – vacuum, liquid – gas etc.

Let us consider a simple example of a dirty shirt. The dirt stays in the surface of the fabric and the study of phenomena occurring at the interface between the fabric and the dirt is surface chamistry, in simple words

chemistry, in simple words.



Adsorption and Absorption



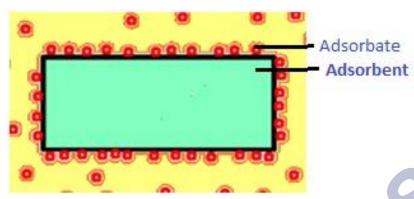
The dirt staying on the surface of the skin as a layer is termed as adsorbtion.

Now consider applying soap solution to the shirt containing dirt. The soap solution is absorbed by the fabric and does not stay on the fabric as a layer. This is called absorption.

Adsorption

Adsorption is the phenomenon of attracting and retaining molecules of a substance on the surface of a solid (or liquid) resulting as a higher concentration of molecules only on the surface.

- Adsorbent- the surface on which adsorption takes place
- Adsorbate- the substance which is adsorbed



Example- Water vapour adsorbed by silica gel

- o Adsorbent-Silica gel
- o Adsorbate- Water vapour
- Differences between Adsorption and Absorption

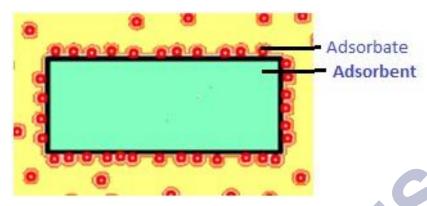
ADSORPTION	ABSORPTION
Surface phenomenon- concentration of the adsorbate increases only on the surface	Bulk phenomenon- concentration is uniform throughout the solid
Exothermic process- heat is released	Endothermic process- heat is absorbed
It is favoured by low temperature	It is not affected by temperature
Eg- Chalk stick dipped in ink adsorbs the colour of the ink but when you break the piece of chalk, its core still remains white	Eg- When anhydrous CaCl ₂ absorbs water vapour, it becomes wet and pasty

Mechanism of Adsorption

Adsorption occurs because the particle on the surface and the particle in the bulk of the adsorbent are not in the same environment. That is, the net force acting on them is not the same.

The particle on the surface has unbalanced forces acting on it which are also called residual attractive forces

Due to these forces, the surface particles of the adsorbent attract the adsorbate particles



During adsorption, there is always a decrease in the residual attractive forces of the surface. That is, the energy of the surface decreases and this appears as heat. This is called the heat of adsorption

The amount of heat evolved when one mole of adsorbate is adsorbed on the adsorbent surface is called enthalpy of adsorption

Adsorption is always exothermic and the enthalpy change, ΔH is always negative When the adsorbate molecules are adsorbed on the surface of the adsorbent, their freedom of movement becomes restricted and hence ΔS the entropy decreases

We know that Gibbs free energy, $\Delta G = \Delta H - T\Delta S$.

For adsorption to be spontaneous, ΔG must be negative. This can happen if ΔH has a significantly high negative value as $-T\Delta S$ is positive.

As the adsorption continues, ΔH becomes less and less negative till it becomes equal to $T\Delta S$ and ΔG becomes zero. At this point, equilibrium is attained.

Factors affecting adsorption of Gases by Solids

- Nature and Surface area of adsorbent:
- The same gas is adsorbed by different solids at different extents even at the same temperature.
- Greater the surface area, greater is the volume of gases adsorbed.
- Nature of the gas being adsorbed:
- Different gases are adsorbed are adsorbed to different extents even by the same solid.
- As the critical temperature of a gas increases, it is easier to liquefy and it is also more readily adsorbed.
- Reason- Higher the critical temperature, the easier it is to liquefy the gas as greater are the
 intermolecular forces to attraction between the molecules of the gas. For such a gas, the
 intermolecular forces of attraction are greater on the surface of the adsorbent and thus,
 the adsorption will be more.
- Temperature: As temperature increases, adsorption decreases
- Pressure: At constant temperature, the adsorption of a gas increases with increase in pressure.
- o Activation of the solid adsorbent: It means increasing the adsorbing power of the

adsorbent.

It can be done by-

Making the surface of the adsorbent rough- It can be done by rubbing the surface or chemical action or by depositing fine metal particles on the surface by electroplating

By dividing the adsorbent into small pieces or grains- It increases the surface area but this method has a practical limitation. If the particles are too fine like powder, the adsorption of the gas will become difficult.

By removing the already adsorbed gases

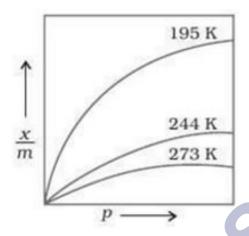
Types of Adsorption

Physisorption	Chemisorption
, ,	
Occurs due van der Waals forces	Caused by chemical bond formation
Not specific in nature that is all gases are adsorbed on the surface to an extent	Highly specific in nature
Reversible	Irreversible
More easily liquefiable gases are adsorbed more readily	Gases which can react with the adsorbent show chemisorption
Enthalpy of adsorption is low(20-40 kJ)	Enthalpy of adsorption is high (80-240 kJ)
It decreases with increase in temperature. Favours low temperature	It increases with increase in temperature. Favours high temperature
It does not need any activation energy	It does require activation energy.
It results into multimolecular layers on adsorbent surface under high pressure	It results into a unimolecular layer.

Adsorption isotherms

The variation in the amount of gas adsorbed by the adsorbent at constant temperature with

change in pressure is shown by a curve called adsorption isotherm.



Freundlich adsorption Isotherm:

Freundlich proposed this relation to show a relation between the extent of adsorption and pressure.

$$\frac{x}{m} = \underline{k}(p)^{1/n} \dots 1$$

$$\underline{\log(\frac{x}{m})} = \log k + \frac{1}{n} \log p \dots 2$$

If there are solutions involved, the above equations become

$$\frac{x}{m} = k (C)^{1/n}$$

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log C$$

Where x -> amount of adsorbate

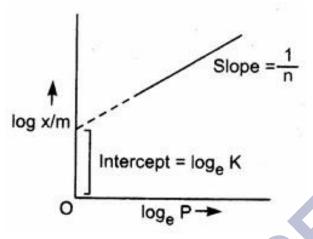
m-> mass of adsorbent

p-> pressure

C-> concentration of adsorbate

K and n->constants, n>1 always

Looking at equation 2, as we plot $\log x/m$ versus $\log p$ on a graph, we get a straight line with slope=1/n and y- intercept= $\log k$.



Applications of adsorption

Production of high vacuum- Remaining traces of air in a vessel already evacuated by vacuum pump can be adsorbed by charcoal to create high vacuum

Control humidity - Silica and aluminium gels can adsorb moisture and remove humidity **Gas masks**- Gas masks consist of activated charcoal or mixture of adsorbents and are used to breathe in coal mines

Removing coloured substances from solutions- This is used in chromatographic analysis. **Separation of inert gases-** Different inert gases are adsorbed to different extents on coconut charcoal

Heterogeneous catalysis- When gaseous reactants are adsorbed on the surface of a solid catalyst, the concentration of the reactants on the surface increases and thus, the rate of reaction also increases (adsorption theory). Eg- Using finely divided Nickel in the hydrogenation of vegetable oils

Adsorption indicators- Many dyes have become useful due to adsorption. These dyes have been introduced as indicators especially in precipitation titrations. Eg- KBr is easily titrated with AgNO3 using eosin as the indicator

Froth floatation process- When sulphide ore is shaken with pine oil and water, the ore particles are adsorbed on the froth that floats and the gangue prticles (like silica, mud) settle down in the tank. This process is used in the concentration of sulphide ores

Chromatographic analysis- The selective adsorption of some substances by a solution helps us separate components of a mixture. Example- All the dyes in ink

Curing Diseases- Some drugs can adsorb the germs on them and hence, kill them saving us from diseases

Properties of Colloids

Physical Properties

- A] Heterogeneous character:
 - 1. Colloidal sols form heterogeneous mixtures which contain particles of the dispersed phaseand the dispersion medium.

2. The heterogeneous character of this sol can be explained more conveniently byphenomena such as the Tyndall effect, electrophoresis and electro-osmosis.

B] Stability:

1. Colloidal sols are stable. The sol which contains larger particle size settles very slowly.

C] Filterability:

- 1. The size of the pores of ordinary filter paper is large and ordinary filter paper cannot be used for the separation of the dispersed phase, because the particle size of colloidal sols isvery small and particles can easily pass through.
- 2. Instead of ordinary filter paper, animal membrane or parchment filter paper can be usedbecause the pore size is very small; hence, the colloidal particles cannot pass through.

D] Visibility and Colour:

- 1. Colloidal particles are very small; hence, they cannot be seen by the naked eye or under anordinary microscope.
- 2. They scatter the light falling on them. The colour of colloidal solutions depends on the wavelength of the light scattered by colloidal particles and on the size and nature of colloidal particles.
- 3. For example, in a gold sol, if the particle size is very small, then it shows red colour, but if itssize increases, then the colour changes to purple, then blue and finally gold.
- 4. The colour factor also depends on how light is observed.

Colligative Properties – Osmotic Pressure

- Colloidal particles possess very high molecular mass; hence, the number of moles
 present in the solution is very small. Therefore, the value of the colligative property
 will be less as compared to the value obtained by true solutions.
- Some colloids have measurable osmotic pressure which has been determined with a reasonable degree of accuracy. Hence, the osmotic pressure is used to calculate the average molecular massof colloidal particles.

Mechanical Properties - Brownian Movement

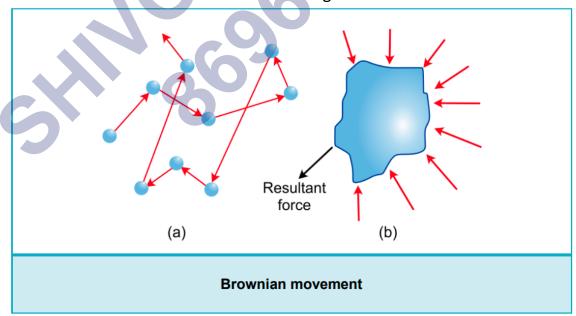
• In 1827, Robert Brown observed the movement of pollen grains suspended in water.

Like pollen grains, colloidal particles also continuously move in a zigzag manner when seen under an ultramicroscope. Hence, this movement is called Brownian movement.

- Brownian movement does not depend on the nature of the colloid. But it depends on the size of colloidal particles and the viscosity of the sol.
- Smaller the size and less viscosity of sol will give faster movement of particles.

Brownian movement: Continuous zigzag movement of colloidal particles in a colloidal sol.

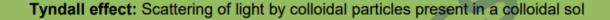
- > Cause of Brownian movement:
 - 1. The main cause of Brownian movement is the collision of molecules of the dispersion medium with the colloidal particles due to their kinetic motion from all sides with different force.
 - 2. Brownian movement depends on the size of colloidal particles. If particles are heavier, thenthe movement will be slower.
- > Importance of Brownian movement:
 - 1. Brownian movement opposes the force of gravity and does not allow the colloidal particles settle. Thus, it is responsible for the stability of colloidal particles.
 - 2. It is useful in the determination of Avogadro's number.

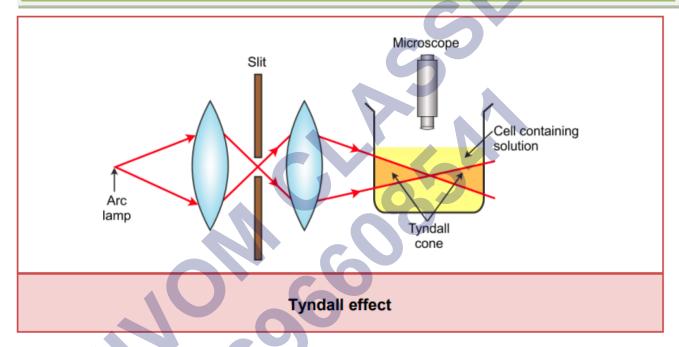


Optical Properties – Tyndall Effect

• In 1969, the scientist Tyndall observed an optical property of colloidal particles called

- the Tyndalleffect. This phenomenon is based on the scattering of light.
- He observed that when a converging beam of light is passed through the colloidal solution placed in a dark room, the path of the beam gets illuminated with bluish light when viewed at right angles to the direction of the passage of light.
- The path of light is visible because of the scattering of light by colloidal particles. This path isknown as Tyndall cone.

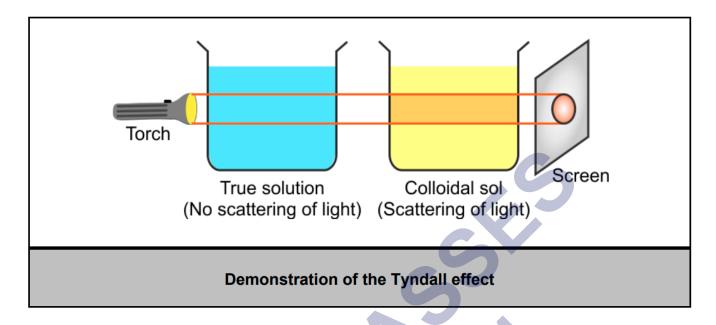




- We can simply explain the Tyndall effect in the laboratory by performing an experiment.
- Take two beakers arranged in linear manner. One containing a colloidal sol and the othercontaining a true solution. The path of light is incident on both beakers.
- The path of light is visible in a beaker containing a colloidal sol, and no path is observed in anotherbeaker containing a true solution.
- Hence, we can conclude the following conditions for the Tyndall effect to be observed:

Diameter of the dispersed particles is not much smaller as compared to the wavelength of light used.

There should be a large difference between the refractive indices of the dispersed phase and the dispersion medium.



> Importance of the Tyndall effect:

- 1. The ultramicroscope was devised in 1903. The working of the ultramicroscope is based onthe Tyndall effect.
- 2. A beam of light is focused on the colloidal solution taken in a glass vessel and is observedunder the microscope at right angles to the beam.
- 3. The light scattered by each colloidal particle looks bright against the dark background. Thus, the number of colloidal particles can be counted.
- 4. By knowing the volume of the solution, the number of particles per unit volume can be determined.
- 5. It also helps find the average mass of particles.
- 6. The ultramicroscope does not give information about the size and shape of particles as we cannot see the actual particles by it; only the light scattered by the particle is observed.

Electrical Properties

- (a) Stability of colloidal sols Electrical charge on colloidal particles:
 - 1. Colloidal particles in the sol are electrically charged; hence, they are stable. Therefore, these particles never come close to each other. They repel the neighbouring particles to form large non-colloidal particles.
 - 2. All the dispersed particles in the colloidal solution carry the same charge, while the dispersion medium has an equal and opposite charge. For example, ferric hydroxide particles are positively charged, while the dispersion medium water

is negatively charged.

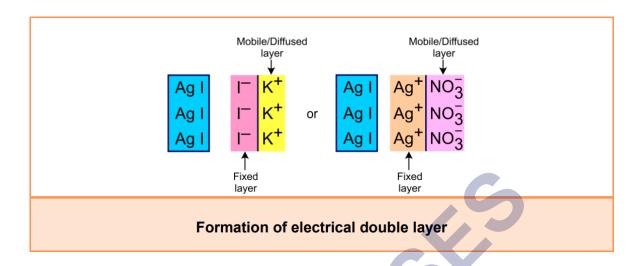
- > Origin of electrical charge on colloidal particles:
 - 1. An ionic colloid adsorbs ions common to its own lattice during the preparation of the colloidal sol. For example, if a colloidal sol of AgI is prepared by adding KI solution to AgNO₃ solution till KI is in slight excess, iodide ions will be adsorbed on the surface of AgIparticles giving them a negative charge.

$$AgI + \underset{\text{from KI}}{I^{-}} \rightarrow \underset{\text{Negative sol}}{AgI:I^{-}}$$

2. When a colloidal sol of AgI is prepared by adding AgNO₃ solution to KI solution till AgNO₃ is in slight excess; Ag⁺ ions will be adsorbed giving a positive charge to the colloidal particles.

$$AgI + Ag^+ \rightarrow AgI:Ag^+$$
from $AgNO_3$ Positive sol

- 3. In both cases, the remaining ions, i.e. K⁺ and NO ⁻, remain in the dispersion medium and give equal and opposite charge to the dispersion medium.
- > Electrokinetic or Zeta potential:
 - 1. When one type of ions of the electrolyte is adsorbed on the surface of the colloidal particles, it forms a fixed layer.
 - 2. Then it attacks the counter ions from the medium forming a second layer, which is movingand is known as the diffused layer.
 - 3. The double layer of opposite charges thus formed is called the Helmholtz electrical doublelayer.
 - 4. Because of this, a potential difference is created between the fixed layer and the diffusedlayer, which is known as the electrokinetic potential or Zeta potential.

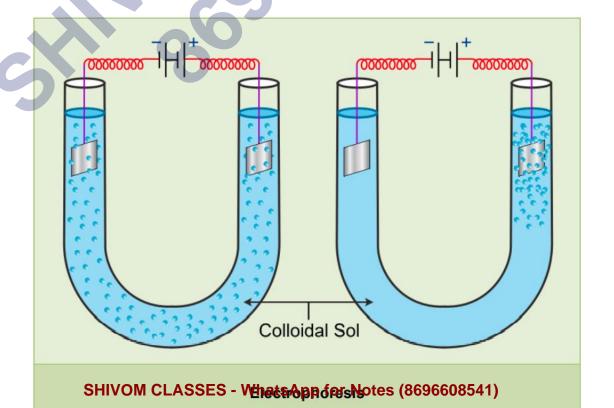


(b) Electrophoresis or cataphoresis:

- 1. By electrophoresis, we can show the presence of electrical charge.
- 2. It involves the movement of colloidal particles towards one or the other electrode when placed under the influence of an electric field.

Electrophoresis or **cataphoresis**: Movement of colloidal particles under the influence of an electric field

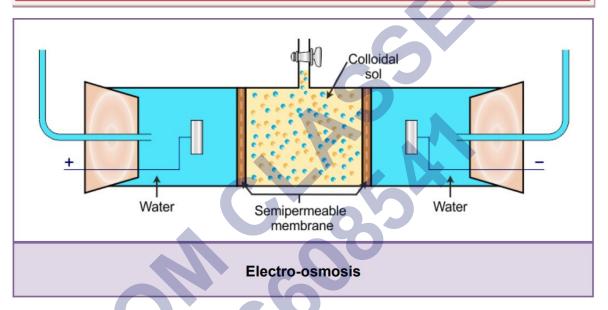
- 3. When these colloidal particles reach the oppositely charged electrode, they get neutralized and coagulated.
- 4. Electrophoresis can be used to find the nature of charge on colloidal particles.



(c) Electro-osmosis:

5. When a colloidal solution is placed under the influence of an electric field, the particles of the dispersion medium move towards the oppositely charged electrode. But colloidal particles do not move. This phenomenon is called electro-osmosis.

Electro-osmosis: A phenomenon in which the molecules of the dispersion medium are allowed to move under the influence of an electric field, whereas colloidal particles are not allowed to move.



(c) Coagulation or flocculation or precipitation:

Coagulation or **precipitation**: Process of aggregating colloidal particles so as to change them into large-sized particles which ultimately settle as a precipitate

- 1. When an electrolyte is added to a colloidal solution, the particles of the sol take up the ionswhich are oppositely charged and get neutralised.
- 2. These ions which are responsible for the neutralisation of charge on the colloidal particles are called coagulating ions or flocculating ions.
- 3. Neutral particles then come together to form larger particles which then settle.
- 4. When the concentration of the electrolyte is very low, the process is called flocculation. The process can be reversed on simple shaking.

Coagulation or flocculation or precipitation value of the electrolyte: The minimum amount of an electrolyte which must be added to one litre of colloidal solution so as to bring about complete coagulation. Thus, smaller the coagulation value of an electrolyte, greater is its coagulating or precipitating power.

Hardy Schulze Law

Hardy Schulze Law: Quantity of the electrolyte required to coagulate a definite amount of a colloidal solution depends on the valency of the coagulating ion

Main points of this law:

Effective ions of the electrolyte in bringing about coagulation are those which carry a charge opposite to that of the colloidal particles. These ions are called coagulating ions or flocculating ions.

Greater the valency of the coagulating or flocculating ion, greater is its power to bring about coagulation.

- For example, for the coagulation of negatively charged arsenious sulphide sol, trivalent cations (Al⁺) are far more effective than divalent cations (Ba²⁺). This in turn is more effective than monovalent cations (Na⁺).
- For the coagulation of positively charged ferric hydroxide sol, tetravalent anions $[Fe(CN)_6]^{4-}$ are more effective than trivalent anions (PO_4^{3-}) which are more effective than divalent anions (SO_4^{2-})
 - which are also more effective than monovalent anions (Cl⁻).
- The coagulating power is inversely proportional to the coagulation or flocculation value, so comparing the relative coagulating power of two electrolytes for the same colloidal solution, we get

Coagulating power of electrolyte 1 Coagulation value of electrolyte 2 Coagulation value of electrolyte 1

Causes of Coagulation

- (a) By electrophoresis:
 - 1. Particles of the dispersed phase move towards the oppositely charged electrode and get neutralised.
 - 2. When the process is continued for sufficient time, these neutral particles combine and settle.
- (b) By mutual precipitation:
 - 1. Oppositely charged sols are mixed in proper proportions to neutralise the charge of eachother which causes coagulation of both sols.
 - 2. If positively charged ferric hydroxide and negatively charged arsenious sulphide sols aremixed, then both sols get coagulated.
- (c) By prolonged dialysis:
 - 1. Stability of a colloidal solution is due to the electrolyte present in it.
 - 2. On prolonged dialysis, the electrolyte is completely removed. Thus, the colloidal solution becomes unstable and coagulates.
- (d) By heating or cooling:
 - 1. Heating the sol causes coagulation. Example: Coagulation of butter
 - 2. When a sol is heated, the adsorbed layer is disturbed because the number of collisions onthem by the molecules of the dispersion medium increases, i.e.

the charge on the particles decreases; thus, stability decreases and coagulation occurs.

3. Sometimes cooling the sol causes coagulation. Example: Coagulation of milk.



Class: 12th Chemistry Chapter-5: Surface Chemistry (Part_1)

Adsorbate

Molecular species which concentrates at the surface.

Sorption

Both absorption and absorption takes place simultaneously

Applications

roduction of high vacuum, gasmasks, control of humidity, separation of gases, chromatography, indicators Sorption.

Chemisorption

- Adsorption when gas molecules or atoms are held to surface by chemical bonds.
- Higher specific
- Irreversible
- Increases with increase of surface area
- 🦆 High enthalpy of adsorption.

Adsorbent

Material on the surface of which the adsorption takes place.

$$\frac{x}{m} = kp^{1/n}(n > 1)$$
$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$$

(i) Accumulation of molecular species at the surface rather than in the bulk of a solid or liquid.

- (ii) Surface phenomenon
- (iil) Concentration on the surface of adsorbent different from that in bulk.

Type

Physisorption

- Adsorption when accumulation of gas on the surface of solid occurs due to weak van der Waals'forces.
- Non-specific
- · Depends on nature of adsorbate
- Reversible
- · Increases with increases in surface area.
- Low enthalpy of adsorption.

Adsorption Isotherm means to express variation in the amount absorbent with pressure at constant temperature

Freundlich Adsorption Isotherm:

Empirical relationship between the

quantity of gas adsorbed by unit mass

of solid adsorbent and pressure at a

particular temperature.

Adsorption

Feature

- When $\Delta H = T\Delta S$, G = O, equilibrium is attained.
- ΔG, ΔH and ΔS are negative.
- Extent of adsorption increase with surface area.

Surface Chemistry

Heterogeneous system where one substance is dispersed (dispersed dispersion medium

Colloids

phase) in another substance called

colligative Properties: Values of colligative properties are of small order in comparison to values shown by true solutions.

Tyndall Effect: When a beam of light is passed and viewed perpendicular to the path of incident light, the path of beam is Illuminated by a bluish light. This process is Tyndall effect.

Electrophoresis: Movement of colloidal particles toward electrode in an electric field.

Colour: Depends on wavelength of light scattered by colloidal

Brownian Movement : Zig -zag movement of particles

Purification

Dialysis Electro-dialysis Ultrafiltration

Preparation

Bredig's Arc method Peptization Chemical methods

Based on Type of Particles of dispersed phase

Multimolecular: Large number of atoms/molecules aggregate (size 1-1000 nm)

Macromolecular: Formed by molecules of large size. Associated: Low concentration behave as normal range

electrolytes at high concentration as colloids.

Based on nature of interaction Lyophilic: Liquid loving

Lyophobic: Liquid-hating

Based on physical state

Liquid in liquids

Aerosol: Liquid in gas

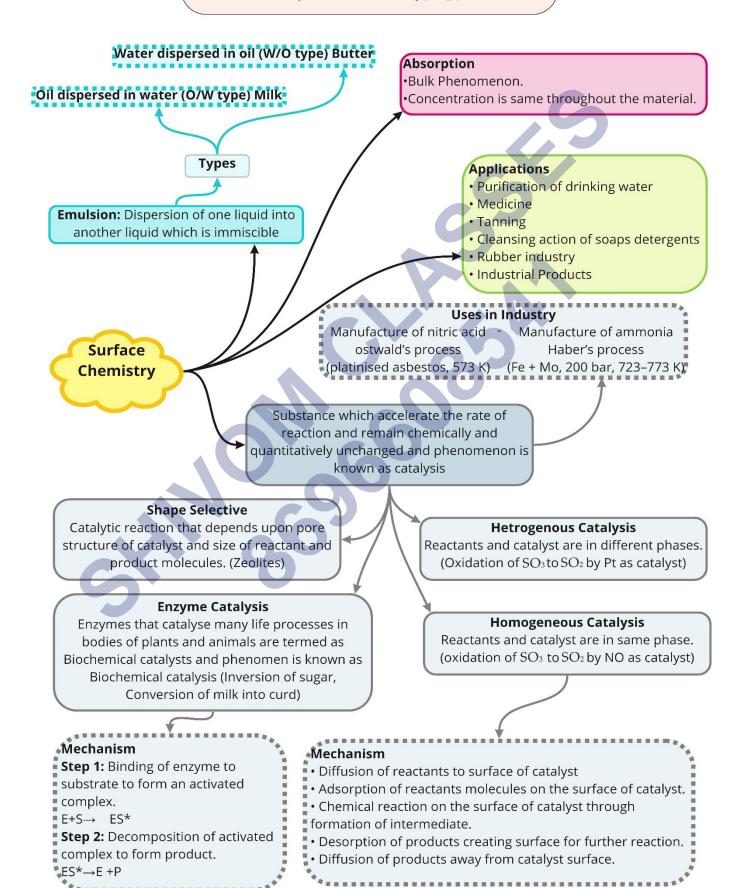
Sol: solids in liquids (Paints) Gel:

Liquids in solids (cheese) **Emulsion**:

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Classification

Class: 12th Chemistry
Chapter-5: Surface Chemistry (Part_2)



Important Questions

Multiple Choice questions-

Question 1. Movement of dispersion medium under the influence of electric field is known as

- (a) electrodialysis
- (b) electrophoresis
- (c) electroosmosis
- (d) cataphoresis.

Question 2. At CMC (Critical Micellisation Cone.) the surface molecules

- (a) associate
- (b) dissociate
- (c) decompose
- (d) become completely soluble.

Question 3. Milk is an example of

- (a) emulsion
- (b) suspension
- (c) foam
- (d) sol.

Question 4. Tyndall effect is due to

- (a) electric charge
- (b) scattering of light
- (c) absorption of light
- (d) none of these.

Question 5. Fog is a colloidal system of

- (a) liquid dispersed in a gas
- (b) gas dispersed in a gas
- (c) solid dispersed in gas
- (d) solid dispersed in liquid

Question 6. Blood may be purified by

- (a) coagulation
- (b) dialysis
- (c) electro-osmosis
- (d) filtration

Question 7. Blue colour of water in sea is due to

- (a) refraction of blue light by impurities in sea water
- (b) scattering of light by water
- (c) refraction of blue sky by water
- (d) None of these

Question 8. The cause of Brownian movement is

- (a) heat change in liquid state
- (b) attractive force between colloidal particles and dispersion medium
- (c) bombardment of the colloidal particles by the molecules of the dispersion medium
- (d) interaction of charged particles

Question 9.Emulsifying agent present in milk that makes it stable is

(a) maltose

- (b) casein
- (c) lactose
- (d) none of these

Question 10. Cloud is an example of

- (a) liquid dispersed in gas
- (b) solid dispersed in gas
- (c) solid dispersed in liquid
- (d) none of these

Very Short Question:

Question 1. What do you mean by the term -Adsorption?

Question 2. Explain the terms – Adsorbate and Adsorbent with examples

Question 3. Why do finely divided solids act as good adsorbents?

Question 4. What is the sign of $^{\Delta H}$, $^{\Delta S}$ and $^{\Delta G}$ when a gas is adsorbed by an adsorbent and when $^{\Delta G}$ becomes zero?

Question 5. Name the factors which influence the extent of adsorption of a gas on solid.

Question 6. What is adsorption isotherm?

Question 7. ΔH for chemisorption is high. why?

Question 8. Give an equation showing variation of extent of adsorption with concentration of a solution?

Question 9. What are positive and negative catalysts? Explain.

Question 10. What do you mean by the term promoter? Give an example.

Short Questions:

Question 1. Explain modern theory of heterogeneous catalysis:

Question 2. Differentiate between lyophobic and lyophilic sol?

Question 3. Distinguish between the meaning of the term's adsorption and absorption. Give one example of each.

Question 4. Why is adsorption always exothermic?

Question 5. How are colloids classified on the basis of

- Physical states of components
- Nature of dispersion medium and
- Interaction between dispersed phase and dispersion medium?

Question 6. Explain what is observed:

- When a beam of light is passed through a colloidal sol.
- An electrolyte, NaCl is added to hydrated ferric oxide sol.
- Electric current is passed through a colloidal sol?

Question 7. Action of soap is due to emulsification and micelle formation. Comment.

Question 8. What do you mean by activity and selectivity of catalysts?

Question 9. Explain the terms with suitable examples: (i) Alcosol (ii) Aerosol (iii) Hydrosol

Long Questions:

Question 1. Explain Freundlich adsorption isotherm.

Question 2. What are homogeneous and heterogeneous catalysis? Give example.

Question 3. Explain the mechanism of enzyme catalysis.

Question 4. What is the difference between physisorption and chemisorption?

Question 5. What are the factors which influence the adsorption of a gas on a solid?

Assertion and Reason Questions:

1. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
- b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
- c) Assertion is correct statement but reason is wrong statement.
- d) Assertion is wrong statement but reason is correct statement.

Assertion: Porous or finely divided fonns of adsorbents adsorb larger quantities of adsorbate.

Reason: The greater the specific area of the solid, the greater would be its adsorbing capacity.

- **2.** In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.
 - a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
 - b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
 - c) Assertion is correct statement but reason is wrong statement.
 - d) Assertion is wrong statement but reason is correct statement.

Assertion: Aqueous gold colloidal solution is red in colour.

Reason: The colour arises due to scattering of tight by colloidal gold particles.

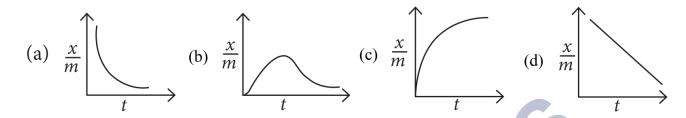
Case Study Questions:

1. Adsorption is a spontaneous process and involves unequal distribution of the molecules of the gaseous substance on the surface of solid or liquid. Adsorption is an exothermic process. The attractive forces between adsorbate and adsorbent are either van der Waals' forces or chemical bonds. Adsorption of gases on solids is generally controlled by the factors like temperature, pressure and nature of adsorbate and adsorbent.

The following questions are multiple choice questions. Choose the most appropriate answer:

- (i) In physisorption process, the attractive forces between adsorbate and adsorbent are:
 - a) Covalent bonds.
 - b) Ionic bonds.
 - c) Van der Waals' forces.
 - d) H-bonds.

(ii) Which of the following graph represents the variation of physical adsorption with temperature?



(iii) Which one of the following processes does not use adsorption?

- a) Froth floatation process.
- b) Chromatography.
- c) Decolourisation of sugar liquors.
- d) Dissolution of sugar in water.

(iv) Which of the following statements is true?

- a) Chemisorption forms unimolecular layer.
- b) Chemisorption is a reversible process.
- c) Chemisorption is independent of pressure.
- d) Chemisorption has low enthalpy change.
- (v) Methylene blue, from its aqueous solution, is adsorbed on activated charcoal at 25°C. For this process, the correct statement is:
 - a) The adsorption requires activation at 25°C.
 - b) The adsorption is accompanied by a decrease in enthalpy.
 - c) The adsorption increases with increase of temperature
 - d) The adsorption is irreversible.
- **2.** Adsorption depends on the nature of the adsorbent. The rough solid surface has more number of pores and adsorb more number of gases than the smooth surface. Most common adsorbents are silica gel, activated charcoal. The extent of adsorption also depends on the surface area of the solid. Specific surface area of an adsorbent is the surface area available for adsorption per gram of the adsorbent. The greater the surface area of the solid, the greater would be the adsorption. Charcoal is a more effective adsorbent than solid wood. Desorption is a process of removing an adsorbed substance from a surface on which it is absorbed.

Physisorpti on is non-specific and any gas can be adsorbed. But the gases which are easily liquefiable (e.g., NH_3 , HCl, CO_2) are adsorbed at a faster rate and to a large extent than the gases which are difficult to liquefy (e.g., H_2 , O_2 , N_2). It depends on the critical temperature.

(24)

Higher the critical temperature of a gas, more easily liquefiable the gas is and more is the rate of adsorption. Chemisorption is specific in nature. Therefore, only those gases can be adsorbed which are capable of forming chemical bonds with the adsorbent.

The following questions are multiple choice questions. Choose the most appropriate answer:

- (i) Select the correct statement regarding desorption.
 - a) It is done by cooling or by increasing the pressure applied.
 - b) It is done by cooling or by reducing the pressure applied.
 - c) It is done by heating or by reducing the pressure applied.
 - d) It is done by heating or by increasing the pressure applied.
- (ii) Which of the following statements regarding the physical adsorption of a gas on surface of solid is not correct?
 - a) On increasing temperature, adsorption increases continuously.
 - b) Enthalpy changes are negative.
 - c) It is non-specific in nature.
 - d) It is reversible in nature.
- (iii) At the same temperature and pressure, select the correct order of adsorption of the following gases on the same mass of charcoal.
 - a) $SO_2 > CH_4 > H_2$
 - b) $CH_4 < SO_2 < H_2$
 - c) $H_2 > CH_4 > SO_2$
 - d) $CH_4 < H_2 < SO_2$
- (iv) Select the correct option among the following when adsorption of a gas on solid metal surface is spontaneous and exothermic.
 - a) △S increases
 - b) △S decreases
 - c) $\triangle G$ increases
 - d) △H increases
- (v) Select the incorrect statement among the following.
 - a) Physical adsorption occurs at a low temperature and chemisorption occurs at all temperature.

(25)

b) In physisorption heat of adsorption is low while in chemisorption it is high.

- c) Chemisorption is irreversible and physisorption is reversible.
- d) Magnitude of chemisorption decreases with rise in temperature while physisorption increases with rise in temperature.

Answers key

MCQ answers:

- 1. Answer: (c) electroosmosis
- 2. Answer: (a) associate
- 3. Answer (a) emulsion
- 4. Answer: (b) scattering of light
- 5. Answer: (a) liquid dispersed in a gas
- 6. Answer: (b) dialysis
- 7. Answer: (a) refraction of blue light by impurities in sea water
- 8. Answer: (c) bombardment of the colloidal particles by the molecules of the dispersion medium
- 9. Answer: (b) casein
- 10. Answer: (a) liquid dispersed in gas

Very Short Answers:

- 1. The accumulation of molecular species at the surface rather than in bulk of a solid liquid is termed as Adsorption
- 2. The molecular species which get concentrated or accumulated at the surface are adsorbate eg. O_2 , H_2 , CO, Cl_2 , NH_3 , etc. and the material on the surface of which the adsorption takes place is adsorbent. eg. Charcoal, silica gel, alumina gel, clay etc
- 3. Answer: Powdering of solids increase its surface and therefore it can adsorb a greater amount of the adsorbate. Thus, finely divided solids act as good adsorbents.
- 4. Answer: ΔH is negative, ΔS is negative and ΔG is negative. When $\Delta H = \Delta S$ the ΔG is zero. This state equilibrium is attained.

- 5. Answer: Factors affecting extent of adsorption are -
 - (i) Nature of adsorbent and adsorbate.
 - (ii) Surface area of solid
 - (iii) Pressure of gas
 - (iv) Temperature.
- 6. Answer: The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a curve known as adsorption isotherm.
- 7. Answer: In chemisorption, chemical bonds are formed that evolves a large amount of energy. Therefore for chemisorption is high.
- $x/m = K C^{1/n} (n > 1)$

Where x/m is the extent of adsorption – k & n are constants and c is the concentration of solution.

- 9. . A catalyst which increases the rate of a reaction is positive catalyst and which decrease the rate is a negative catalyst.
- 10. Promoters are substances that enhance the activity of a catalyst e.g. molybdenum acts as a promoter in Haber's process.

Short Answers:

- **1. Answer** According to modern theory of catalysis, the mechanism of heterogeneous catalysis involves following steps
 - Diffusion of reactants on the surface of catalyst.
 - Adsorption of reactant molecules on the surface.
 - Occurrence of reaction on the catalysts surface through formation of an intermediate.
 - Desorption of products from surface.
 - Diffusion of products away from surface.

2. Answer:

<u>Lyophobic sol</u>	<u>Lyophilic sol.</u>
1. It is relatively unstable due to Repulsion	1. It is relatively more stable due to med-
between dispersion medium and	attraction between dispersion medium and

dispersed phase.	dispersed Phase.
2. It is irreversible.	2. It is reversible.
3. It cannot be easily peptised.	3. It can be easily peptised.
4. Small quantities of electrolyte cause	4. Small quantities of electrolyte has no effect
precipitation.	larger concentration causes precipitation.

- **3. Answer:** Adsorption is a surface phenomenon of accumulation of molecules of a substance at the surface rather than in the bulk of a solid or liquid. The substance that gets adsorbed is called the 'adsorbate' and the substance on whose surface the adsorption takes place is called the 'adsorbent'. Here, the concentration of the adsorbate on the surface of the adsorbent increases. In adsorption, the substance gets concentrated at the surface only. It does not penetrate through the surface to the bulk of the solid or liquid. For example, when we dip a chalk stick into an ink solution, only its surface becomes coloured. If we break the chalk stick, it will be found to be white from inside.On the other hand, the process of absorption is a bulk phenomenon. In absorption, the substance gets uniformly distributed throughout the bulk of the solid or liquid.
- **4. Answer:**Ans. Adsorption is always exothermic. This statement can be explained in two ways.
 - (i) Adsorption leads to a decrease in the residual forces on the surface of the adsorbent. This causes a decrease in the surface energy of the adsorbent. Therefore, adsorption is always exothermic.
 - (ii) ΔH of adsorption is always negative. When a gas is adsorbed on a solid surface, its movement is restricted leading to a decrease in the entropy of the gas i.e., ΔS is negative. Now for a process to be spontaneous, ΔG should be negative. Therefore, $\Delta G = \Delta H T\Delta S$

Since ΔS is negative, ΔH has to be negative to make ΔG negative. Hence, adsorption is always exothermic.

5. Answer:

Colloids can be classified on various bases:

- (i) On the basis of the physical state of the components (by components we mean the dispersed phase and dispersion medium). Depending on whether the components are solids, liquids, or gases, we can have eight types of colloids.
- (ii) On the basis of the dispersion medium, sols can be divided as:

Dispersion medium	Name of sol
-------------------	-------------

Water	Aquasol or hydrosol
Alcohol	Alcosol
Benzene	Benzosol
Gases	Aerosol

(iii) On the basis of the nature of the interaction between the dispersed phase and dispersion medium, the colloids can be classified as lyophilic (solvent attracting) and lyophobic (solvent repelling).

6. Answer:

- i) When a beam of light is passed through a colloidal solution, then scattering of light is observed. This is known as the Tyndall effect. This scattering of light illuminates the path of the beam in the colloidal solution.
- (ii) When NaCl is added to ferric oxide sol, it dissociates to give and ¬ ions. Particles of ferric oxide sol are positively charged. Thus, they get coagulated in the presence of negatively charged ions.
- (iii) The colloidal particles are charged and carry either a positive or negative charge. The dispersion medium carries an equal and opposite charge. This makes the whole system neutral. Under the influence of an electric current, the colloidal particles move towards the oppositely charged electrode. When they come in contact with the electrode, they lose their charge and coagulate.

7. Answer:

The cleansing action of soap is due to emulsification and micelle formation. Soaps are basically sodium and potassium salts of long chain fatty acids, . The end of the molecule to which the sodium is attached is polar in nature, while the alkyl-end is non-polar. Thus, a soap molecule contains a hydrophilic (polar) and a hydrophobic (non-polar) part.

When soap is added to water containing dirt, the soap molecules surround the dirt particles in such a manner that their hydrophobic parts get attached to the dirt molecule and the hydrophilic parts point away from the dirt molecule. This is known as micelle formation. Thus, we can say that the polar group dissolves in water while the non-polar group dissolves in the dirt particle. Now, as these micelles are negatively charged, they do not coalesce, and a stable emulsion is formed.

8. Answer:

The activity of a catalyst is its ability to increase the rate of a particular reaction. Chemisorption is the main factor in deciding the activity of a catalyst. The adsorption of reactants on the catalyst surface should be neither too strong nor too weak. It should just be strong enough to make the

catalyst active.

(b) Selectivity of the catalyst:

The ability of the catalyst to direct a reaction to yield a particular product is referred to as the selectivity of the catalyst. For example, by using different catalysts, we can get different products for the reaction between $^{\rm H_2}$ and CO.

(i)
$$CO_{(g)} + 3H_{2(g)} \xrightarrow{Ni} CH_{4(g)} + H_2O_{(g)}$$

(ii)
$$CO_{(g)} + 2H_{2(g)} \xrightarrow{Cu/ZnO-CrO_3} CH_3OH_{(g)}$$

(iii)
$$CO_{(g)} + H_{2(g)} \xrightarrow{Cu} HCHO_{(g)}$$

9. Answer:

A colloidal solution having alcohol as the dispersion medium and a solid substance as the dispersed phase is called an alcosol.

For example: colloidal sol of cellulose nitrate in ethyl alcohol is an alcosol.

(ii) Aerosol:

A colloidal solution having a gas as the dispersion medium and a solid as the dispersed phase is called an aerosol.

For example: fog

(iii) Hydrosol

A colloidal solution having water as the dispersion medium and a solid as the dispersed phase is called a hydrosol. For example: starch sol or gold sol.

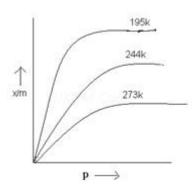
Long Answers:

1. Answer:

Freundlich adsorption isotherm gives an empirical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature

$$\frac{x}{=} = K \cdot P^{1/n \cdot (N \triangleright 1)}$$

The relationship is m Where x is a mass of gas adsorbed on mass m of adsorbent at pressure P, K &n are constant that depend on the nature of adsorbent and adsorbate – The Relationship can be represented by plotting curves between x/m and P. They show that at a fix pressure, the physical adsorption decreases with increase in temperature.



2. Answer:

When reactant and catalyst are in the same phase, the process is said to be homogeneous catalysis.

Examples -

(1) Oxidation of sulphur dioxide in the presence of oxygen gas and nitric oxide gas as catalyst. $2 SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2 SO_3(g)$

(2) Hydrolysis of methyl acetate catalysed by H+ ions.

$$CH_3COOCH_3(\ell) + H_2O(\ell) \xrightarrow{H_2SO_4(\ell O)} CH_3COOH(aq) + CH_3OH(aq)$$

(3) Hydrolysis of sugar catalysed by H_2S0_4 .

Heterogeneous Catalysis -

The catalytic process in which the reactant and catalyst are in different phases is known as heterogeneous catalysis.

Examples:

(1) Oxidation of sulphur dioxide in presence of platinum

$$O_2(g) + 2SO_2(g) \xrightarrow{pt(5)} 2SO_3(g)$$

(2) Preparation of ammonia by Haber's process

$$N_2(g) + 3H_2(g) \xrightarrow{\mathcal{B}(S)} 2NH_3(g)$$

(3) Oxidation of ammonia in Ostwald's process.

$$4NH_3(g) + 5O_2(g) \xrightarrow{Pt(s)} 4NO(g) + 6H_2O(g)$$

3. Answer

Mechanism of enzyme catalysed reactions-

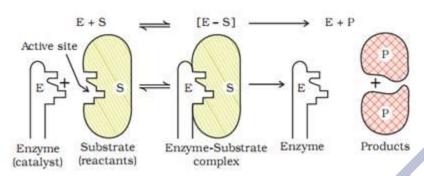
There are active centres or cavities on the surface of enzyme particles. The molecules of the reaction or substrate which have complementary shape fit into these just like a key fit into a lock. This forms an activated complex which decomposes to yield products. The reactions proceed in two steps —

Step 1: Binding of enzymes to substrate to form activated complex.

$$E+S \longrightarrow ES$$

Step 2: Decomposition of complex to form products.

$$ES \longrightarrow E + P$$
.



4. Answer:

	Physisorption	Chemisorption
	In this type of adsorption, the	In this type of adsorption, strong
1	adsorbate is attached to the surface of	chemical bonds are formed between
1	the adsorbent with weak van der	the adsorbate and the surface of the
	Waal's forces of attraction.	adsorbent.
2	No new compound is formed in the	New compounds are formed at the
	process.	surface of the adsorbent.
2	It is generally found to be reversible in	It is usually irroversible in pature
3	nature.	It is usually irreversible in nature.
	Enthalpy of adsorption is low as weak	Enthalpy of adsorption is high as
_		chemical bonds are formed. The
4		values lie in the range
	of ^{20-40kJ} mol ⁻¹ .	of 40-400 kJ mol ⁻¹ .
5	It is favoured by low temperature	It is favoured by high temperature
	conditions.	conditions.
6.	It is an example of multi-layer	It is an example of mono-layer
	adsorption	adsorption.

5. Answer:

There are various factors that affect the rate of adsorption of a gas on a solid surface.

- (1) Nature of the gas: Easily liquefiable gases such as $^{\mathrm{NH}_3}$, HCl etc. are adsorbed to a great extent in comparison to gases such as $^{\mathrm{H}_2$, O_2} etc. This is because Van der Waal's forces are stronger in easily liquefiable gases.
- **(2) Surface area of the solid :**The greater the surface area of the adsorbent, the greater is the adsorption of a gas on the solid surface.

- **(3) Effect of pressure :**Adsorption is a reversible process and is accompanied by a decrease in pressure. Therefore, adsorption increases with an increase in pressure.
- **(4) Effect of temperature :**Adsorption is an exothermic process. Thus, in accordance with Le-Chatelier's principle, the magnitude of adsorption decreases with an increase in temperature.

Assertion and Reason Answers:

1. (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

Explanation:

Porous or finely divided fonns of adsorbent possess greater specific area which is available for adsorption per gram of the adsorbent.

2. (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

Explanation:

The colour of colloidal solution depends on the wavelength of light scattered by the dispersed particles. The wavelength of light further depends on the size and nature of the particles. Finest gold sol is red in colour. As size of the particles increases, it becomes purple, then blue and finally golden yellow.

Case Study Answers:

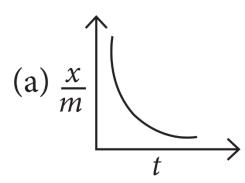
Answer:

(i) (c) Van der Waals' forces.

Explanation:

In physisorption process, the attractive forces between adsorbate and adsorbent are van der Waals' forces.

(ii)



- (iii) (d) Dissolution of sugar in water.
- (iv) (a) Chemisorption forms unimolecular layer.
- (v) (b) The adsorption is accompanied by a decrease in enthalpy.

Explanation:

The adsorption of methylene blue on activated charcoal is physical adsorption. It is accompanied by a decrease in enthalpy.

2. Answer:

(i) (c) It is done by heating or by reducing the pressure applied.

Explanation:

Desorption is done by heating or by reducing the pressure applied.

(ii) (a) On increasing temperature, adsorption increases continuously.

Explanation:

Physisorption is exothermic in nature. Therefore, according to Le Chatelier's principle, it occurs readily at low temperature and decreases with increase in temperature. Bonds between surface and adsorbate are weak so when temperature is increased the bonds break easily, so rate will decrease on increasing temperature.

(iii) (a)
$$SO_2 > CH_4 > H_2$$

Explanation:

Higher the critical temperature of a gas, greater is the amount of gas adsorbed. Critical temperature (in Kelvin) of the gases:

 $H_2 < CH_4 < SO_2$

33.2 190.6 430.3

(iv) (b) \triangle S decreases

Explanation:

Since for spontaneous and exothermic process,

 $\triangle G = -ve$, $\triangle H = -ve$ at all temperatures, therefore from $\triangle G = \triangle H - T\triangle S$, $\triangle S$ should be -ve. Also adsorption of gas on solid surface gives more orderly arrangement.

(v) (d) △H increases

Explanation:

Chemisorption first increases with increase of temperature. Physisorption decreases with rise in temperature.