23

Adsorption

When a solid surface is exposed to a gas or a liquid, molecules from the gas or the solution phase accumulate or concentrate at the surface.
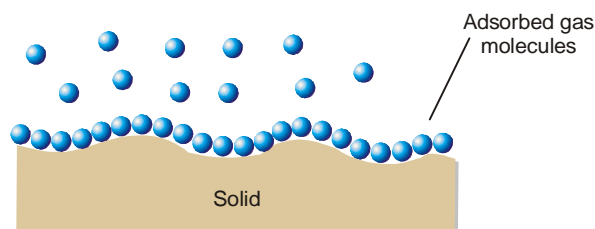
■ **Figure 23.1**
Adsorption of a gas at a solid surface.

The phenomenon of concentration of molecules of a gas or liquid at a solid surface is called adsorption.

The substance that deposits at the surface is called **Adsorbate** and the solid on whose surface the deposition occurs is called the **Adsorbent.**
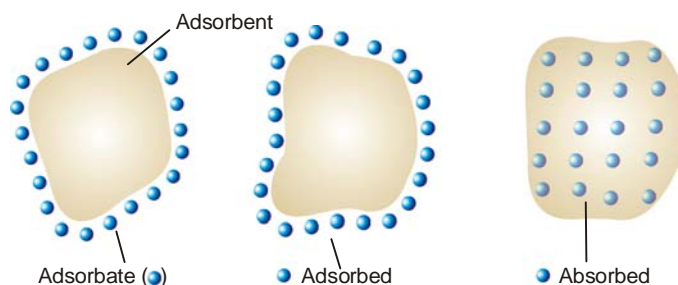
Adsorption *versus* absorption (illustration).

Examples of Adsorption

(1) **Adsorption of a dye by a charcoal.** If finely divided charcoal is stirred into a dilute solution of *methylene blue* (an organic dye), the depth of colour of the solution decreases appreciably. The dye molecules have been adsorbed by charcoal particles.

(2) **Adsorption of a gas by charcoal.** If a gas (SO_2, Cl_2, NH_3) is treated with powdered charcoal in a closed vessel, the gas pressure is found to decrease. The gas molecules concentrate on charcoal surface and are said to be adsorbed.

Adsorption versus Absorption

The term 'adsorption' must be carefully distinguished from another like-sounding term 'absorption'. **While adsorption implies deposition at the surface only, absorption implies penetration into the body of the solid** (Fig. 23.2). For illustration a chalk crayon when dipped in ink adsorbs the latter and on breaking it is found to be white from within. On the other hand, water is absorbed by a sponge and is distributed throughout the sponge uniformly.

Both adsorption and absorption often take place side by side. It is thus difficult to distinguish between the two processes experimentally. Mc Bain introduced the general term **Sorption** which includes both *the adsorption and absorption*.

Mechanism of Adsorption

Atoms or molecules of a solid surface behave like the surface molecules of a liquid. These are not surrounded by atoms or molecules of their kind. Therefore, they have unbalanced or residual attractive forces on the surface which can hold adsorbate particles.
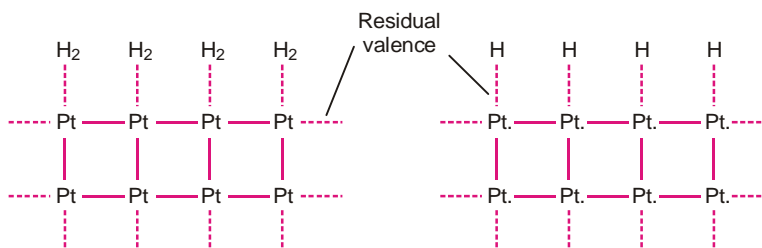
■ **Figure 23.3**
Hydrogen adsorbed molecularly on platinum.

■ **Figure 23.4**
Hydrogen adsorbed atomically on platinum.

The adsorbed atoms or molecules can be held on the surface of a metal such as platinum (Pt) by physical van der Waal's force or chemical forces due to residual valence bonds. Thus the adsorption of hydrogen on platinum may take place in two ways (molecularly or atomically as shown above).
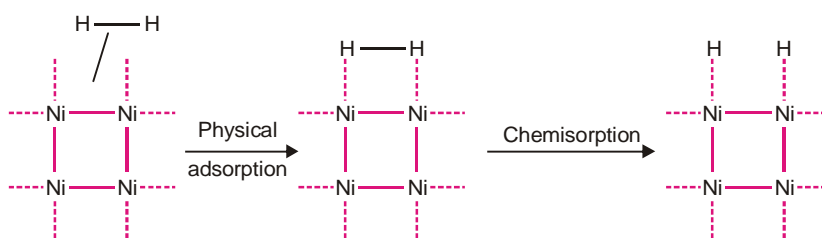
TYPES OF ADSORPTION

The adsorption of a gas into a solid surface is mainly of two types :

(*a*) Physical Adsorption

This is due to the gas molecules being held to the solid surface by van der Waal's attractive forces. It is also referred to as **van der Waal's Adsorption.** For example, adsorption of hydrogen or oxygen on charcoal is Physical Adsorption.

(*b*) Chemical Adsorption or Chemisorption

In this kind of adsorption, the gas molecules or atoms are held to the solid surface by chemical bonds. These bonds may be covalent or ionic in nature. For example, hydrogen is chemisorbed on nickel. Hydrogen molecules is first adsorbed by van der Waal's forces and then dissociates. The hydrogen atoms are thus chemisorbed on nickel.

■ **Figure 23.5**
Hydrogen dissociates before it is chemisorbed on nickel.

Often adsorption is a combination of the two types of adsorption stated above.

ADSORPTION OF GASES BY SOLIDS

The adsorption of gases by solid adsorbents has certain characteristic feature. Physical adsorption and chemisorption are found to differ in many respects.

(1) Adsorption and Surface area

Adsorption being a surface phenomenon, the extent of adsorption depends on the surface area. **Increase in the surface area of the adsorbent, increases the total amount of the gas adsorbed.** Thus finely divided metals (nickel, platinum) and porous substances (charcoal, silica gel) provide a large surface area and are best solid adsorbents.

(2) Nature of Gas

The amount of gas adsorbed by a solid depends on the nature of the gas. **In general, more easily liquefiable a gas is (*i.e.*, higher its critical temperature), the more readily will it be adsorbed.** Thus 1 g of activated charcoal adsorbs 380 ml of sulphur dioxide (critical temperature 157°C), 16 ml of methane (critical temperature – 83°C) and 4.5 ml of hydrogen (critical temperature –20°C).

Chemisorption on the other hand, is much more specific than physical adsorption. However, it will not occur when there is some possibility of chemical action between the gas adsorbed and the solid.

(3) Heats of Adsorption

Heat of adsorption is defined as the energy liberated when 1 gm mole of a gas is adsorbed on the solid surface. In physical adsorption, gas molecules concentrate on the solid surface. Thus it is similar to the condensation of a gas to liquid. Therefore**, adsorption like condensation is an exothermic process.** Since the attractions between gas molecules and solid surface are due to relatively weak van der Waal's forces, heats of adsorption are small (about 5 kcal mol^{-1}).

In chemisorption the attractive forces are due to the formation of true chemical bonds. Therefore,

the heats of adsorption are large (20 to 100 kcal mol^{-1}).

(4) Reversible character

Physical adsorption is a reversible process. The gas adsorbed onto a solid can be removed (desorbed) under reverse conditions of temperature and pressure. Thus,

$$Gas \rightleftharpoons Gas/Solid + Heat$$

Chemisorption, on the contrary, is not reversible because a surface compound is formed.

(5) Effect of temperature

Physical adsorption occurs rapidly at low temperature and decreases with increasing temperature (Le Chatelier's Principle).

Chemisorption, like most chemical changes, generally increase with temperature. Thus a rise of temperature can often cause physical adsorption to change to chemisorption. Nitrogen, for example, is physically adsorbed on iron at 190°C but chemisorbed to form a nitride at 500°C.

(6) Effect of pressure

Since a dynamic equilibrium exists between the adsorbed gas and the gas in contact with the solid as stated in (4), Le Chatelier's Principle is applied. Actually it has been found that **increase of pressure leads to increase of adsorption and decrease of pressure causes desorption.**

(7) Thickness of Adsorbed layer of gas

From a study of the isotherms relating to the amount of gas adsorbed to the equilibrium pressure, Langmuir showed that at low pressure, the physically adsorbed gas forms only one molecular thick layer. However, above a certain pressure, multimolecular thick layer is formed.

COMPARISON OF PHYSICAL ADSORPTION AND CHEMISORPTION

Physical adsorption	Chemisorption
1. Caused by intermolecular van der Waal's forces.	1. Caused by chemical bond formation.
2. Depends on nature of gas. Easily liquefiable gases are adsorbed readily.	2. Much more specific than physical adsorption.
3. Heat of adsorption is small (about 5 kcal mol^{-1}).	3. Heat of adsorption is large (20–100 kcal mol^{-1}).
4. Reversible.	4. Irreversible.
5. Occurs rapidly at low temperature; decreases with increasing temperature.	5. Increases with increase of temperature.
6. Increase of pressure increases adsorption; decrease of pressure causes desorption.	6. Change of pressure has no such effects.
7. Forms multimolecular layers on adsorbent surface.	7. Forms unimolecular layer.

In chemisorption, the adsorbed layer of gas is one-molecule thick since chemical combination can take place with the adsorbent surface only directly.

ADSORPTION ISOTHERMS

The adsorption of a gas on a solid adsorbent in a closed vessel is a reversible process.

$$Free\ Gas \rightleftharpoons Gas\ adsorbed\ on\ solid$$

The amount of the gas adsorbed depends on equilibrium pressure (P) and temperature.

The relationship between the equilibrium pressure of a gas and its amount adsorbed on the solid adsorbent at any constant temperature is called an Adsorption isotherm. It may be given in the form of an equation or graphical curve.

Freundlich Adsorption Isotherm

Freundlich proposed an empirical relation in the form of a mathematical equation.

$$\frac{w}{m} = k \ P^{1/n}$$

where w is the mass of the gas adsorbed on a mass m of adsorbent at a pressure P; k and n are constants depending on the nature of the gas and the adsorbent and on temperature. This relation is generally represented in the form of a curve obtained by plotting the mass of the gas adsorbed per unit mass of adsorbent (w/m) against equilibrium pressure.
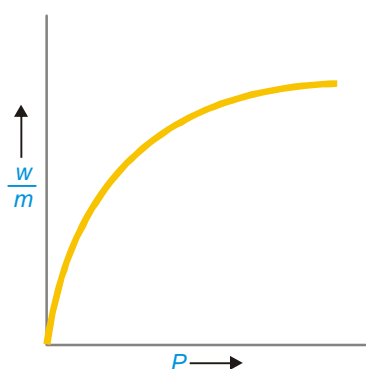
■ Figure 23.6
Freundlich isotherm; a plot of mass of adsorbed gas per unit mass of adsorbent.
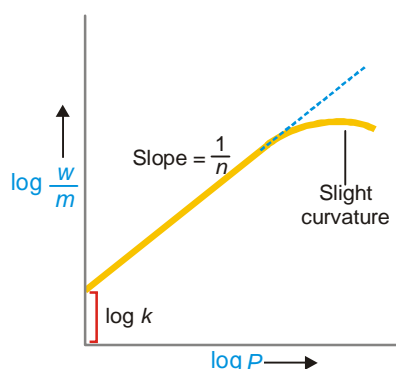
■ Figure 23.7
Plot of log *w/m* against log *P* shows slight curvature at higher pressures.

Freundlich isotherm is not applicable at high pressures. Taking logarithms on both sides of Freundlich equation, we have

$$\log \frac{w}{m} = \log k + \frac{1}{n} \log P$$

This is equation for a straight line. Thus a plot of log (w/m) against log P should be a straight line with slope $1/n$ and intercept log k. However, it is actually found that the plots were straight lines at low pressures, while at higher pressure they showed a slight curvature, especially at low temperature. This indicated that Freundlich equation is approximate and does not apply to adsorption of gases by solids at higher pressures.

LANGMUIR ADSORPTION ISOTHERM

Langmuir (1916) derived a simple adsorption isotherm based on theoretical considerations. It was named after him.

Assumptions

Langmuir made the following assumptions.

(1)   The layer of the gas adsorbed on the solid adsorbent is one-molecule thick.

(2)   The adsorbed layer is uniform all over the adsorbent.

(3)   There is no interaction between the adjacent adsorbed molecules.

Derivation of Langmuir Isotherm

Langmuir considered that the gas molecules strike a solid surface and are thus adsorbed. Some

of these molecules then evaporate or are 'desorbed' fairly rapidly. A dynamic equilibrium is eventually established between the two opposing processes, adsorption and desorption.

If θ is the fraction of the total surface covered by the adsorbed molecules, the fraction of the naked area is $(1-\theta)$. **The rate of desorption (R_d) is proportional to the covered surface θ. Therefore,**

$$R_d = k_d \theta$$

where k_d is the rate constant for the desorption process.

■ **Figure 23.8**
Dynamic equilibrium exists between free molecules and those adsorbed on the fraction of adsorbent surface.

The rate of adsorption (R_a) is proportional to the available naked surface $(1-\theta)$ and the pressure (P) of the gas.

$$R_a = k_a (1-\theta) P$$

where k_a is rate constant for the adsorption process.

At equilibrium the rate of desorption is equal to the rate of adsorption. That is,

$$k_d \theta = k_a (1-\theta) P$$

or

$$\theta = \frac{k_a P}{K_a + k_a P}$$

or

$$\theta = \frac{(k_a / k_d) P}{1 + (K_a / k_d) P}$$

or

$$\theta = \frac{K P}{1 + K P}$$

where K is the equilibrium constant and is referred to as the **adsorption coefficient.**

The amount of the gas adsorbed per gram of the adsorbent, x, is proportional to θ.

Hence,

$$x \propto \frac{K P}{1 + K P}$$

or

$$x = K' \frac{K P}{1 + K P} \qquad \qquad ...(1)$$

where K' is a new constant. Equation (1) gives the relation between the amount of gas adsorbed to the pressure of the gas at constant temperature and is known as **Langmuir Adsorption isotherm.**

In order to test the Langmuir isotherm, equation (1) is rearranged so that

$$\frac{P}{x} = \frac{1}{K'} + \frac{P}{K''} \qquad \qquad ...(2)$$

where K'' constant $= K'/K$.

The equation (2) is similar to an equation for a straight line. Thus if P/x is plotted against P, we should get a straight line with slope $1/K''$ and the intercept $1/K'$. It was found in most cases that the actual curves were straight lines. Thus Langmuir isotherm stood verified.

Figure 23.9
Verification of Langmuir isotherm for adsorption of N$_2$ on mica at 90°K.

Langmuir Isotherm holds at low pressures but fails at high pressures

As stated above, Langmuir Adsorption isotherm may be written as

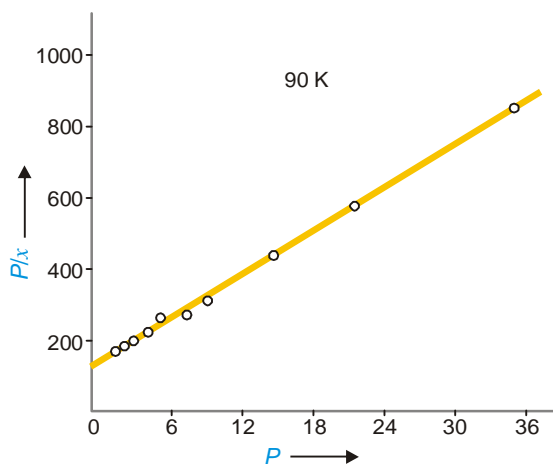$$\frac{P}{x} = \frac{1}{K'} + \frac{P}{K''}$$

If the pressure (P) is very low, the factor P/K'' may be ignored and the isotherm assumes the form

$$x = K'P \qquad\qquad\qquad\qquad (at\ low\ pressure)$$

If the pressure (P) is very high, the factor $1/K'$ may be ignored and the isotherm becomes

$$x = K'' \qquad\qquad\qquad\qquad (at\ high\ pressure)$$

Hence, at low pressures, the amount of gas adsorbed (x) is directly proportional to pressure (P). At high pressures the mass adsorbed reaches a constant value K'' when the adsorbent surface is completely covered with a unimolecular layer of the gas. At this stage adsorption is independent of pressure.

ADSORPTION OF SOLUTES FROM SOLUTIONS

Porous or finely divided solid substances can also adsorb dissolved substances from solution. Thus activated charcoal is used to remove coloured impurities from solutions. Charcoal will also adsorb many dyestuffs. When a solution of acetic acid is shaken with activated charcoal, part of the acid is removed by adsorption and concentration of solution is decreased. Again, precipitates obtained in qualitative analysis often act as absorbents. For example, magnesium hydroxide when precipitated in the presence of the dye-stuff *magneson* forms a blue 'lake'.

Adsorption from solution generally follows the same principles as laid down for adsorption of gases by solids and is subject to the same factors. Thus,

(1) Some adsorbents specifically adsorb certain solutes more effectively than others.

(2) An increase of temperature decreases the extent of adsorption.

(3) An increase in surface area increases the extent of adsorption.

(4) Adsorption of solutes also involves the establishment of an equilibrium between the amount adsorbed and the concentration of the solute in solution.

The precise mechanism of adsorption from solution is not clear. However there is a limit to the adsorption by a given mass of adsorbent and hence possibly adsorption takes place unless a

unimolecular layer is formed. **Freundlich Isotherm, using concentration instead of pressure is obeyed by adsorption from solution.**

That is,

$$\frac{w}{m} = k \times C^{\frac{1}{n}}$$

where w = mass of solute adsorbed on a mass m of adsorbent ; C = equilibrium concentration of the solution ; and k and n are constants. Taking logs of the above equation

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

This implies that a plot of log w/m against log C should be a straight line. The validity of Freundlich isotherm has been tested by plotting the experimental values of log w/m versus log C determined for adsorption of acetic acid on charcoal at $25°C$.
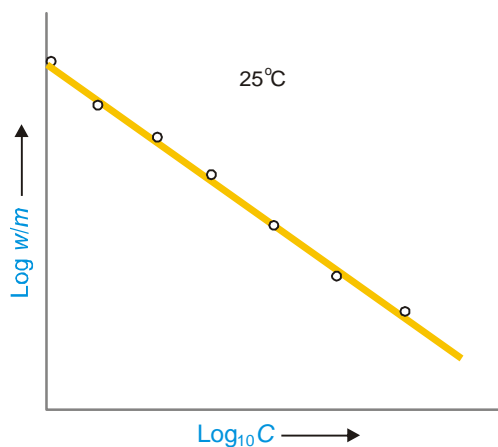
■ **Figure 23.10**
Verification of Freundlich equation by applying it to adsorption of acetic acid on charcoal at 25°C.

APPLICATIONS OF ADSORPTION

Adsorption finds numerous applications both in the laboratory and industry. Some of these are listed below.

(1) Production of high vacua

If a partially evacuated vessel is connected to a container of activated charcoal cooled with liquid air, the charcoal adsorbs all the gas molecules in the vessel. This results in a very high vacuum. This process is used in high vacuum equipments as Dewar flask for storage of liquid air or liquid hydrogen. Silica gel is also useful as an adsorbent in production of high vacua.

(2) Gas mask

All gas masks are devices containing an adsorbent (activated charcoal) or a series of adsorbents. These adsorbents remove poisonous gases by adsorption and thus purify the air for breathing.

(3) Heterogeneous catalysis

In heterogeneous catalysis, the molecules of reactants are adsorbed at the catalyst surface where they form an 'adsorption complex'. This decomposes to form the product molecules which then take off from the surface.

(4) Removal of colouring matter from solutions

Animal charcoal removes colours of solutions by adsorbing coloured impurities. Thus in the manufacture of cane-sugar, the coloured solution is clarified by treating with animal charcoal or activated charcoal.

(5) Froth Flotation process

The low grade sulphide ores (PbS, ZnS, Cu_2S) are freed from silica and other earthy matter by *Froth Flotation Process.* The finely divided ore is mixed with oil (pine oil) and agitated with water containing a detergent (foaming agent). When air is bubbled into this mixture, the air bubbles are stabilized by the detergent. These adsorb mineral particles wetted with oil and rise to the surface. The earthy matter wetted by water settles down at the bottom.
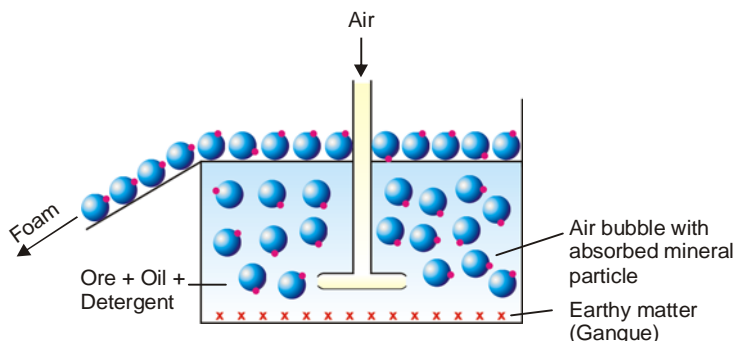
■ **Figure 23.11**
The oil-wetted mineral particles are adsorbed by stabilized air-bubbles which rise to the surface while gangue particles wetted by water settle down.

(6) Chromatographic analysis

Mixtures of small quantities of organic substances can be separated with the help of *Chromatography* which involves the principles of selective adsorption.

The mixture is dissolved in a suitable solvent (*hexane*) and poured through a tube containing the adsorbent (alumina). The component most readily adsorbed is removed in the upper part of the tube. The next most readily adsorbed component is removed next, and so on. Thus the material is separated into 'bands' in different parts of the tube. Now pure solvent is poured through the tube. Each component dissolved in the solvent comes down by turn and is collected in a separate receiver.

Mixtures of gases can be separated by selective adsorption of gases by liquids (*Gas chromatography*).

ION–EXCHANGE ADSORPTION

In recent years, many synthetic resins have been made which function as ion-exchangers. In effect, the resin has one ion adsorbed on it. The resin releases this ion and adsorb another like ion. The process is called **ion-exchange adsorption**. When cations are exchanged, the resin is known as **cation exchanger**. When anions are exchanged, it is referred to as **anion exchanger** .

Cation exchange resin   Anion exchange resin
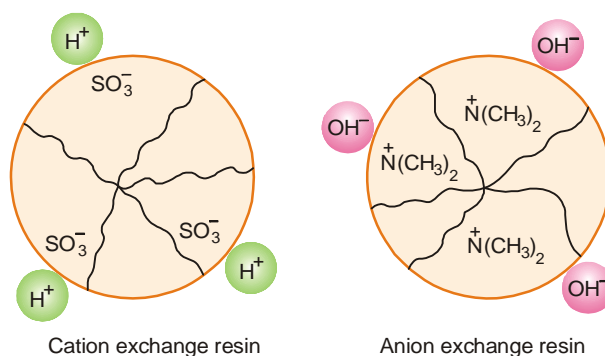
■ **Figure 23.12**
Macromolecules of ion-exchange resins.

Cationic exchange

The cationic exchangers are high polymers containing acidic groups such as sulphonic acid group, $-SO_3$, H. The resulting macro-anion has adsorbed H^+ ions. When solution of another cation (Na^+) is allowed to flow over it, H^+ ions are exchanged for Na^+ ions. This process in fact, consist of

desorption of H^+ ions and adsorption of Na^+ ions by the resin.

$$R^-H^+ \; + \; Na^+ \; \rightleftharpoons \; R^-Na^+ \; + \; H^+$$

cationic   sodium
resin   'salt'
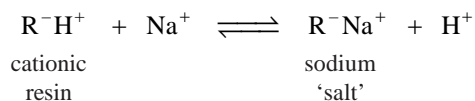
Since the above cationic exchange is reversible, the sodium 'salt' upon treatment with an acid regenerates the original resin.

Anionic exchange

A resin containing a basic group such as quaternary ammonium hydroxide, $-N^+ R_3 O^- H$, will act as anion exchanger. It will, for example, exchange OH^- ion for Cl^-.

$$R^+OH^- \; + \; Cl^- \; \rightleftharpoons \; R^+Cl^- \; + \; OH^-$$

anionic   resin
resin   'chloride'
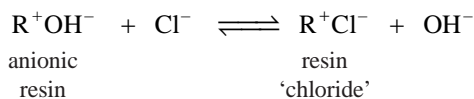
The original anion exchanger resin can be regenerated by treatment of the resin 'chloride' with a base (OH^- ions).

APPLICATIONS OF ION–EXCHANGE ADSORPTION

Ion-exchange adsorption has many useful applications in industry and medicine.
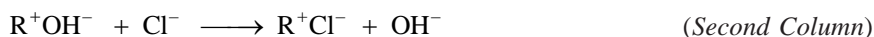
(1) Water softening

Hard water contains Ca^{2+} ions and Mg^{2+} ions. These form insoluble compound with soap and the latter does not function as detergent. Hard water is softened by passing through a column packed with sodium cation-exchanger resin, R^-Na^+. The Ca^{2+} and Mg^{2+} ions in hard water are replaced by Na^+ ions.

$$2R^-Na^+ \; + \; Ca^{2+} \; \longrightarrow \; R_2^-Ca^{2+} \; + \; 2Na^+$$
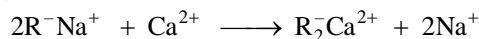
(2) Deionization of water

Water of very high purity can be obtained by removing all dissolved salts. This is accomplished by using both a cation and anion exchanger resin. The water freed from all ions (cations and anions) is referred to as **Deionized or Demineralized water**.

The water is first passed through a column containing a cation-exchanger resin, R^-H^+. Here any cations in water (say Na^+) are removed by exchange for H^+. The water is then passed through a second column packed with an anion-exchanger, $R^+ OH^-$. Any anions (Cl^-) are removed by exchange of OH^- for Cl^-.

$$R^-H^+ \; + \; Na^+ \; \longrightarrow \; R^-Na^+ \; + \; H^+ \qquad \qquad \textit{(First Column)}$$

$$R^+OH^- \; + \; Cl^- \; \longrightarrow \; R^+Cl^- \; + \; OH^- \qquad \qquad \textit{(Second Column)}$$

The H^+ and OH^- ions thus produced react to form water.

$$H^+ \; + \; OH^- \; \longrightarrow \; H_2O$$
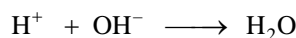
Thus the water coming out of the second column is entirely free from ions, whether cations or anions. The water is purer than distilled water and is called **Conductivity water**.

In another process, which is more common way, the tap water is passed into a column containing both types of resin (cation and anion exchanger). Here cations and anions are removed simultaneously.

Electrical demineralization of water

Ion-exchange resins supported on paper or fibre can be used as membranes through which only cations or anions will pass. Such membranes are used in electrical demineralization of water and they act as ionic sieves (Fig. 23.13). Upon application of the electric current, cations move through the

cation-exchanger membrane to the negative electrode. The anions move in the opposite direction through the anion exchanger membrane. Thus the water in the middle compartment is demineralized.
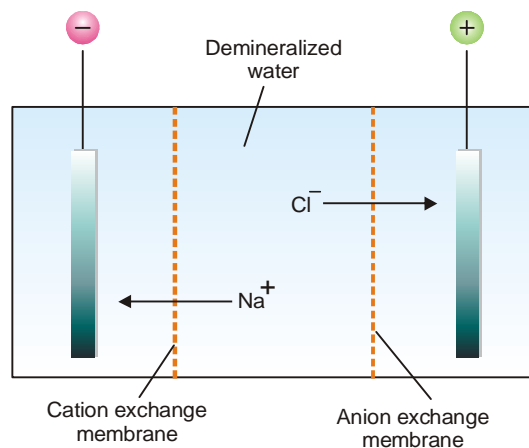
Figure 23.13
Electrical demineralization of saline water.

(3) Medical uses

Excess sodium salts can be removed from the body fluids by giving the patient a suitable ion-exchanger to eat. Weakly basic anion-exchangers are used to remove excess acid or ' acidity' in the stomach.

EXAMINATION QUESTIONS

1. Define or explain the following terms :
   (a) Adsorption
   (b) Physical Adsorption
   (c) Chemical Adsorption
   (d) Freundlich adsorption isotherm
   (e) Langmuir adsorption isotherm

2. What is adsorption? Define the terms 'adsorbent' and adsorbate' giving suitable examples. Describe the phenomenon of the adsorption of solids from a solution.

3. What is the effect of temperature on adsorption of gases on solids?

4. Write the assumptions of Langmuir adsorption isotherm and derive the equation pertaining to it.

5. Distinguish between Adsorption and Absorption. Discuss the factors which affect the adsorption of a gas on a solid adsorbent. Discuss in brief the type of adsorption isotherms commonly observed for the adsorption of gases on a variety of adsorbents at different temperatures.

6. (a) Write the main points of Langmuir's theory of adsorption.
   (b) Draw adsorption isobars for physical adsorption and chemical adsorption.

7. Discuss Langmuir theory of adsorption and derive expression for Langmuir monolayer adsorption isotherm.

8. Write what do you understand by the term adsorption. Give four points of differences between physical adsorption and chemical adsorption.

9. Derive Langmuir's adsorption isotherm stating the assumptions on which it is based. Show that for a moderate range of pressures it reduces to Freundlich adsorption isotherm.

10. Distinguish between physical adsorption and chemical adsorption. What are adsorption isobars?

(Madurai BSc, 2000)

11. What is an adsorption isotherm? Deduce Langmuir's adsorption isotherm. (*Nagpur BSc, 2000*)

12. Distinguish between physical adsorption and chemical adsorption. (*Delhi BSc, 2000*)

13. Discuss Freundlich adsorption isotherm of a gas on a solid surface. How are the constants in this isotherm equation determined? How will you prove that Langmuir adsorption isotherm is superior to Freundlich adsorption isotherm? (*Agra BSc, 2000*)

14. Write down the Langmuir's adsorption isotherm. Also write two objections in Langmuir's theory. (*Mysore BSc, 2000*)

15. (*a*) In a particular experiment it is required to have a large amount of gas absorbed on the surface of a solid. Suggest a few factors which may be helpful alongwith suitable explanations.

    (*b*) What signs of ΔH and ΔS in the case of physical adsorption are expected? Justify your answer.

    (*c*) Write a note on chemisorption. (*Panjab BSc, 2001*)

16. What are the postulates of Langmuir adsorption isotherm? On the basis of these postulates, derive Langmuir equation. How it can be used to determine the surface area of an adsorbent? (*Baroda BSc, 2001*)

17. (*a*) What do you understand by the term adsorption? What are the factors which affect adsorption?

    (*b*) Discuss the effect of temperature and pressure on the adsorption of a gas on a solid surface. (*Lucknow BSc, 2002*)

18. Show that Freundlich isotherm is a special case of Langmuir isotherm. (*Jamia Millia BSc, 2002*)

19. (*a*) Show diagrammatically the different types of adsorption isotherms obtained for adsorption of gases on solids.

    (*b*) Discuss the behaviour of Langmuir adsorption isotherm at very low and very high pressures. (*MD Rohtak BSc, 2002*)

20. What are the postulates of Langmuir theory of adsorption? Derive Langmuir adsorption equation in the form $y = \dfrac{ap}{1+bp}$. How is this equation verified? (*Jamia Millia BSc, 2002*)

21. (*a*) Distinguish between physisorption and chemisorption.

    (*b*) How is Langmuir adsorption isotherm related to Freundlich's isotherm? How are shapes of adsorption isotherms modified when multilayer adsorption takes place. (*Kalyani BSc, 2002*)

22. Deduce Gibbs adsorption equation thermodynamically. (*Allahabad BSc, 2002*)

23. (*a*) Give two applications of adsorption.

    (*b*) Explain the reason why a finally powdered substance is more effective adsorbent? (*Arunachal BSc, 2002*)

24. (*a*) How is chemisorption distinguished from physisorption on the basis of number of adsorbed layer?

    (*b*) How can Langmuir adsorption isotherm equation be used to explain the observation - the decomposition of PH_3 gas on tungsten metal surface is first order at low pressure and zeroth order at high pressure? (*Guru Nanak Dev BSc, 2003*)

25. Derive Freundlich adsorption isotherm from the Gibbs adsorption isotherm applied to a gas. (*Madras BSc, 2003*)

26. (*a*) Derive Langmuir isotherm equation. How does this isotherm interpret the kinetics of unimolecular reactions catalysed by the solid surfaces?

    (*b*) Explain the term adsorption and write why it is caused.

    (*c*) Give an account of the ways by which physisorption and chemisorption are distinguished from each other. (*Guru Nanak Dev BSc, 2004*)

27. Draw the typical adsorption isotherms obtained in the case of unimolecular and multimolecular adsorption. (*Dibrugarh BSc, 2004*)

28. What are the characteristics of adsorption? Derive expression for Langmuir's adsorption isotherm. (*Delhi BSc, 2004*)

29. Derive Langmuir adsorption isotherm equation. Show under what conditions it becomes identical with Freundlich adsorption isotherm equation. (*Gulbarga BSc, 2004*)

30. (*a*) Distinguish between the terms absorption and adsorption.

    (*b*) What is an adsorption isotherm? Give applications of adsorption. (*Avadh BSc, 2004*)

31. 10.0 g of oxygen is adsorbed on 2.5 g of metal powder at 273 K and 1 atm pressure. Calculate the volume of the gas adsorbed per gram of adsorbent.

    Answer. 2798.25 ml (*Madurai BSc, 2005*)

32. 100 ml of 0.3 M acetic acid is shaken with 0.8 g of wood charcoal. The final concentration of the solution after adsorption is 0.125 M. Calculate the weight of acetic acid adsorbed per gram of carbon.

    Answer. 1.31 g (*Nagpur BSc, 2005*)

33. Four grams of a gas is adsorbed on 1.5 g of metal powder at 300 K and 0.7 atm. Calculate the volume of the gas at STP adsorbed per gram of adsorbent.

    Answer. 2052.5 m (*Punjabi BSc, 2005*)

34. For an adsorbent – adsorbate system obeying the Langmuir adsorption isotherm, $a = 0.48$ bar^{-1} and $b = 0.16$ bar^{-1}. At what pressure will 50 % of the surface be covered ?

    Answer. 1.25 bar (*Agra BSc, 2006*)

35. Five grams of a catalyst absorb 400 cm^3 of N_2 at STP to form a monolayer. What is the surface area per gram if the area occupied by a molecule of N_2 is 16 Å.

    Answer. 344 m^2 g^{-1} (*Panjab BSc, 2006*)

MULTIPLE CHOICE QUESTIONS

1. The phenomenon of concentrations of molecules of a gas or liquid at a solid surface is called
   (*a*) absorption   (*b*) adsorption
   (*c*) catalysis   (*d*) none of these
   Answer. (*b*)

2. Adsorbate is that substance
   (*a*) which concentrates on the surface
   (*b*) where adsorption takes place
   (*c*) which evaporates from the surface of metals
   (*d*) none of these
   Answer. (*a*)

3. The adsorption of gases on metal surfaces is called
   (*a*) catalysis   (*b*) occlusion
   (*c*) adsorption   (*d*) absorption
   Answer. (*b*)

4. Increase in _____ of the adsorbent increases the total amount of the gas adsorbed
   (*a*) density   (*b*) volume
   (*c*) surface area   (*d*) surface tension
   Answer. (*c*)

5. _____ the critical temperature of the gas, the more readily will it be adsorbed
   (*a*) lower   (*b*) higher
   (*c*) intermediate   (*d*) none of these
   Answer. (*b*)

6. The process of adsorption is
   (a) exothermic
   (b) endothermic
   (c) sometimes exothermic, sometimes endothermic
   (d) none of the above
   Answer. (a)

7. Physical adsorption is a _____ process
   (a) reversible   (b) irreversible
   (c) exothermic   (d) none of these
   Answer. (a)

8. Physical adsorption occurs rapidly at _____ temperature
   (a) low   (b) high
   (c) absolute zero   (d) none of these
   Answer. (a)

9. Physical adsorption generally _____ with increasing temperature
   (a) decreases   (b) increases
   (c) sometimes decreases, sometime increases   (d) none of these
   Answer. (a)

10. Chemisorption generally _____ with temperature
    (a) increases   (b) decreases
    (c) remains the same   (d) none of these
    Answer. (a)

11. Multi-molecular layers are formed in
    (a) absorption   (b) physical adsorption
    (c) chemisorption   (d) reversible adsorption
    Answer. (c)

12. The relationship between equilibrium pressure of a gas and its amount adsorbed on the solid adsorbent at constant temperature is called
    (a) chemisorption   (b) adsorption isobars
    (c) adsorption isotherms   (d) none of these
    Answer. (c)

13. Freundlich isotherms is not applicable at
    (a) high pressure   (b) low pressure
    (c) 273 K   (d) room temperature
    Answer. (a)

14. At low pressures, the amount of the gas adsorbed is _____ proportional to the pressure
    (a) directly   (b) inversely
    (c) sometimes directly, sometimes inversely   (d) none of these
    Answer. (a)

15. Which of the following is not an equation for Freundlich isotherm?

    (a) $\dfrac{w}{m} = k \times C^{\frac{1}{n}}$ (b) $\dfrac{w}{m} = k \times P^{\frac{1}{n}}$

    (c) $\log \dfrac{w}{m} = \log k + \dfrac{1}{n} \log P$ (d) $\log \dfrac{w}{m} = \log k - \dfrac{1}{n} \log P$

    Answer. (d)

16. In gas masks the poisonous gases are removed by the adsorbent by the process of
    (a) absorption   (b) adsorption
    (c) catalysis   (d) none of these
    Answer. (b)

17. Froth flotation process for the concentration of sulphide ore makes use of the process of
    (a) adsorption   (b) heterogeneous catalysis
    (c) absorption   (d) equilibrium
    Answer. (a)

18. The water freed from all ions (cations and anions) is referred to as
    (a) heavy water   (b) concentrated water
    (c) mineral water   (d) demineralized water
    Answer. (d)

19. Heat of adsorption is defined as the energy liberated when _____ of a gas is adsorbed on the solid surface.
    (a) 1 molecule   (b) 1 gram
    (c) 1 gm mole   (d) 1 kg
    Answer. (c)

20. In physical adsorption the gas molecules are held to the solid surface by
    (a) hydrogen bond   (b) sigma bond
    (c) pi bond   (d) van der Waal's forces
    Answer. (d)

21. The adsorption of hydrogen on charcoal is
    (a) physical adsorption   (b) chemical adsorption
    (c) sorption   (d) none of these
    Answer. (a)

22. The process of desorption increases with _____ of pressure
    (a) decrease   (b) increase
    (c) sometime increases, sometimes decreases (d) none of these
    Answer. (a)

23. Adsorption takes place with
    (a) decrease in enthalpy of the system   (b) increase in enthalpy of the system
    (c) no change in enthalpy of the system   (d) none of these
    Answer. (a)

24. The heat of adsorption in physical adsorption lies in the range
    (a) $1-10$ kJ mol^{-1} (b) $10-400$ kJ mol^{-1}
    (c) $40-100$ kJ mol^{-1} (d) $40-400$ kJ mol^{-1}
    Answer. (a)

25. In chromatographic analysis, the principle used is
    (a) absorption   (b) adsorption
    (c) distribution   (d) evaporation
    Answer. (b)

26. Which of the following is not a characteristic of physical adsorption?
    (a) adsorption is reversible   (b) multi molecular layer is formed
    (c) ΔH is of the order 400 kJ   (d) occurs rapidly at low temperature
    Answer. (c)

27. In gas masks, the poisonous gases are adsorbed by activated charcoal. The activated charcoal acts as

(*a*) adsorbate (*b*) adsorbent

(*c*) catalysis (*d*) adsorption agent

Answer. (*b*)

28. Which is incorrect statement?

(*a*) physical adsorption is irreversible in water

(*b*) physical adsorption involves multi-molecular layers

(*c*) the energy evolved is small

(*d*) physical adsorption is caused by van der Waal's forces

Answer. (*a*)

29. Which out of the following is incorrect?

(*a*) chemisorption is reversible in nature (*b*) physical adsorption is reversible in nature

(*c*) ΔH is small in physical adsorption (*d*) ΔH is large in chemical adsorption

Answer. (*a*)

30. The efficiency of adsorbent increases with increase in

(*a*) viscosity (*b*) surface tension

(*c*) surface area (*d*) number of ions

Answer. (*c*)

31. The ion-exchange resins are the compounds with

(*a*) high molecular masses (*b*) high surface tension

(*c*) low viscosities (*d*) high surface area

Answer. (*a*)

32. Hard water is made soft by passing it through a column packed with high polymer resin. This process makes use of

(*a*) cation-exchange (*b*) chromatographic analysis

(*c*) adsorption of –vely charged ions (*d*) heterogeneous catalysis

Answer. (*a*)

33. Which of the following is not an application of adsorption?

(*a*) gas masks (*b*) heterogeneous catalysis

(*c*) froth flotation process (*d*) softening of water by boiling

Answer. (*d*)

34. Langmuir while deriving adsorption isotherms did not make the following assumptions

(*a*) the layer of the gas adsorbed on the solid surface is one-molecule thick

(*b*) the absorbed layer is uniform

(*c*) there is no attraction between the adjacent molecules

(*d*) the attraction between the adsorbent molecule is extremely large

Answer. (*d*)

35. Which of the following is incorrect?

(*a*) chemisorption is caused by bond formation

(*b*) chemisorption is specific in nature

(*c*) chemisorption is reversible

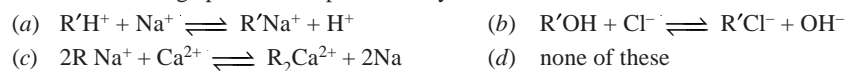(*d*) chemisorption increases with increase in temperature

Answer. (*c*)

36. The process represented by the equation

R′ H$^+$ + Na$^+$ → R′ Na$^+$ + H$^+$ is
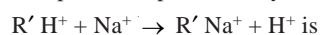
(a) cation exchange   (b) anion exchange

(c) resin exchange   (d) chromatographic analysis

Answer. (a)

37. An anion exchange process is represented by

(a) R′H$^+$ + Na$^+$ $\rightleftharpoons$ R′Na$^+$ + H$^+$ (b) R′OH + Cl$^-$ $\rightleftharpoons$ R′Cl$^-$ + OH$^-$

(c) 2R Na$^+$ + Ca^{2+} $\rightleftharpoons$ R$_2$Ca^{2+} + 2Na   (d) none of these

Answer. (b)

38. In an adsorption process unimolecular layer is formed. It is

(a) physical adsorption   (b) chemical adsorption

(c) ion-exchange   (d) chromatographic analysis

Answer. (b)

39. The rate of desorption R_d is given by (where θ is the fraction of total surface covered by the adsorbed molecules)

(a) $R_d = k_d \, \theta$ (b) $R_d = k_d \theta^2$

(c) $R_d = k_d/\theta$ (d) $R_d = k_d/\theta^2$

Answer. (a)

40. Langmuir Isotherms holds at low pressure but fails at

(a) low temperature   (b) high pressure

(c) intermediate pressure   (d) none of these

Answer. (b)

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