

COURSE CODE: SC202(CHEMISTRY)

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LECTURE- ADSORPTION & SURFACE CHEMISTRY

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Adsorption

Adsorption is the attachment of molecules to a surface; the substance that adsorbs is the adsorbate and the underlying material is the adsorbent or substrate. The reverse of adsorption is desorption.

The main **difference** between **absorption** and **adsorption** is that **absorption** is the process in which a fluid dissolves by a liquid or a solid

The solid on whose surface adsorption occurs is called the **adsorbent**. The adsorbed gas is the **adsorbate**.

An example of absorption is the reaction of water vapor with anhydrous CaCl_2 to form a hydrate compound.

The industrially important catalytic activity of finely divided Pt, Pd, and Ni results from adsorption of gases.

Commonly used gases in adsorption studies include He, H_2 , N_2 , O_2 , CO, CO_2 , CH_4 , C_2H_6 , C_2H_4 , NH_3 , and SO_2 .

Growth on Solid Surfaces

- When a gas molecule collides with the surface of a perfect crystal the molecule loses energy as it bounces, but it is likely to escape from the surface before it has lost enough kinetic energy to be trapped. The picture changes when the surface has defects, for then there are ridges of incomplete layers of atoms or ions.
- A common type of surface defect is a **step** between two otherwise flat layers of atoms called **terraces** (Fig. 1). A step defect might itself have defects, for it might have kinks.
- When an atom settles on a terrace it bounces across it under the influence of the intermolecular potential, and might come to a step or a corner formed by a kink.
- Instead of interacting with a single terrace atom, the molecule now interacts with several, and the interaction may be strong enough to trap it.

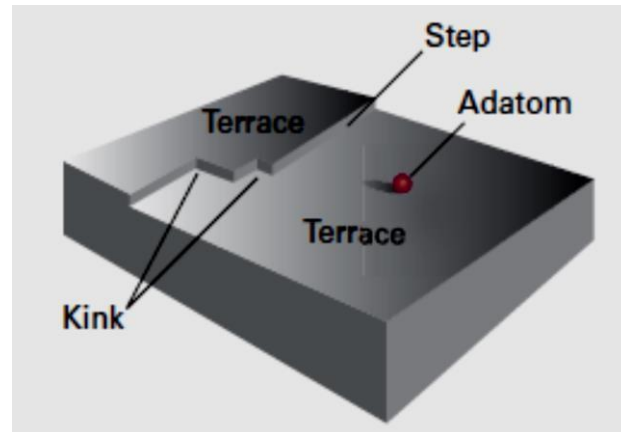


Fig 1: Some of the kinds of defects that may occur on otherwise perfect terraces. Defects play an important role in surface growth and catalysis.

The rapidity of growth depends on the crystal plane concerned, and the slowest growing faces dominate the appearance of the crystal. This feature is explained in Fig. 2, where although the horizontal face grows forward most rapidly, it grows itself out of existence, and the slower-growing faces survive.

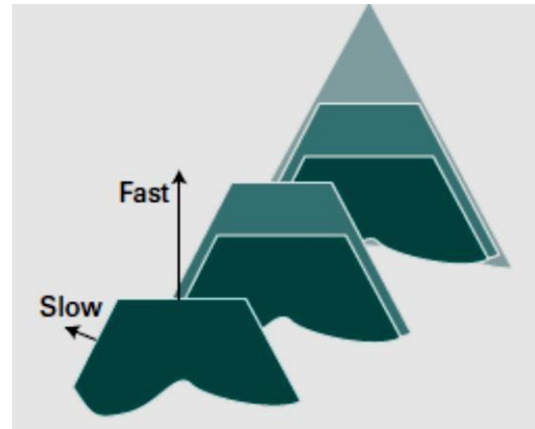


Fig 2: The more slowly growing faces of a crystal dominate its final external appearance. Three successive stages of the growth are shown

Chemisorption and Physical Adsorption

- Adsorption on solids is classified into **physical adsorption** (or *physisorption*) and *chemical adsorption* (or **chemisorption**). In **physical adsorption**, the gas molecules are held to the solid's surface by relatively weak intermolecular van der Waals forces.
- Physical adsorption is nonspecific. For example, N_2 will be physically adsorbed on any solid provided the temperature is low enough.
- In **chemisorption**, a chemical reaction occurs at the solid's surface, and the gas is held to the surface by relatively strong chemical bonds.
- Chemisorption is similar to ordinary chemical reactions in that it is highly specific. For example, N_2 is chemisorbed at room temperature on Fe, W, Ca, and Ti but not on Ni, Ag, Cu, or Pb.
- The enthalpy of chemisorption is much greater than that for physisorption.

Physisorption is adsorption by a van der Waals interaction; chemisorption is adsorption by formation of a chemical bond.

Definition of the fractional coverage

The extent of surface coverage is normally expressed as the **fractional coverage**, θ .

It is the ratio of the number of occupied sites to the number of available sites.

$$\theta = \frac{\text{number of adsorption sites occupied}}{\text{number of adsorption sites available}}$$

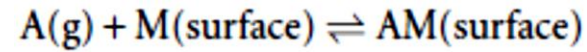
Adsorption Isotherms

In chemisorption the free gas and the adsorbed gas are in dynamic equilibrium, and the fractional coverage of the surface depends on the pressure of the overlying gas. The variation of θ with pressure at a chosen temperature is called the **adsorption isotherm**.

The simplest physically plausible isotherm is based on three assumptions:

- Adsorption cannot proceed beyond monolayer coverage.
- All sites are equivalent and the surface is uniform (that is, the surface is perfectly flat on a microscopic scale).
- The ability of a molecule to adsorb at a given site is independent of the occupation of neighboring sites (that is, there are no interactions between adsorbed molecules).

The dynamic equilibrium is



with rate constants k_a for adsorption and k_d for desorption.

The rate of change of surface coverage due to adsorption is proportional to the partial pressure p of A and the number of vacant sites $N(1 - \theta)$, where N is the total number of sites:

$$\frac{d\theta}{dt} = k_a p N (1 - \theta) \quad \boxed{\text{Rate of adsorption}} \longrightarrow (1)$$

The rate of change of θ due to desorption is proportional to the number of adsorbed species, $N\theta$:

$$\frac{d\theta}{dt} = -k_d N \theta \quad \boxed{\text{Rate of desorption}} \longrightarrow (2)$$

At equilibrium there is no net change (that is, the sum of these two rates is zero), and solving for θ gives the

Langmuir isotherm:

$$\theta = \frac{Kp}{1 + Kp} \quad K = \frac{k_a}{k_d} \quad \boxed{\text{Langmuir isotherm}} \longrightarrow (3)$$

For adsorption with dissociation, the rate of adsorption is proportional to the pressure and to the probability that both atoms will find sites, which is proportional to the square of the number of vacant sites,

$$\frac{d\theta}{dt} = k_a p \{N(1 - \theta)\}^2 \longrightarrow (4)$$

The rate of desorption is proportional to the frequency of encounters of atoms on the surface, and is therefore second-order in the number of atoms present:

$$\frac{d\theta}{dt} = -k_d (N\theta)^2 \longrightarrow (5)$$

The condition for no net change leads to the isotherm

$$\theta = \frac{(Kp)^{1/2}}{1 + (Kp)^{1/2}}$$

Langmuir isotherm
for adsorption with
dissociation

$\longrightarrow (6)$

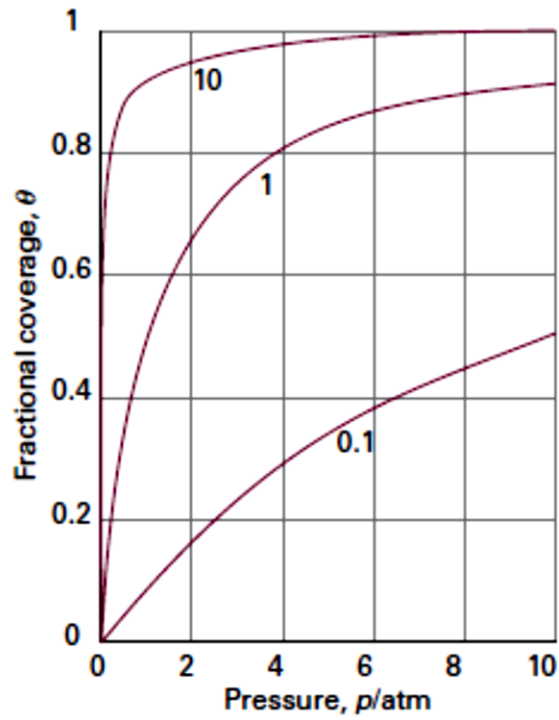


Fig. 3: The Langmuir isotherm for dissociative adsorption, $X_2(g) \rightarrow 2 X(\text{surface})$, for different values of K .

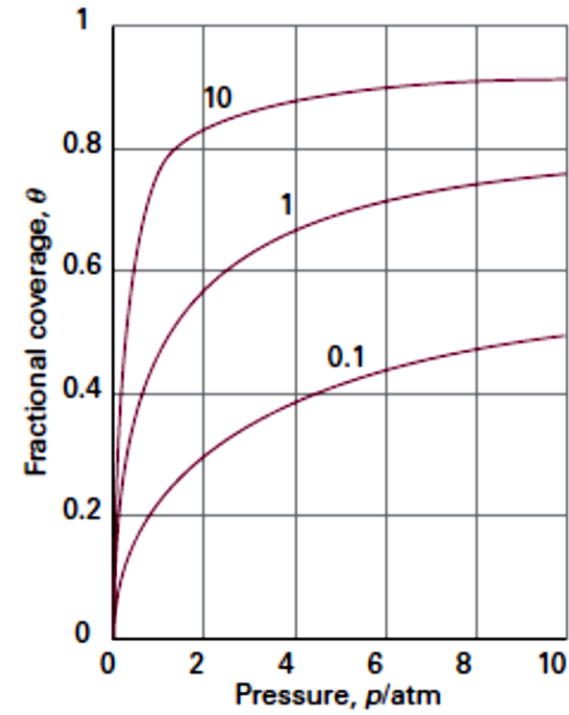


Fig. 4: The Langmuir isotherm for non-dissociative adsorption for different values of K .

The shapes of the Langmuir isotherms with and without dissociation are shown in Figs. 3 and 4. The fractional coverage increases with increasing pressure, and approaches 1 only at very high pressure, when the gas is forced on to every available site of the surface. Different curves (and therefore different values of K) are obtained at different temperatures, and the temperature dependence of K can be used to determine the **isosteric enthalpy of adsorption**, $\Delta_{\text{ad}}H^\ominus$, the standard enthalpy of adsorption at a fixed surface coverage. To determine this quantity we recognize that K is essentially an equilibrium constant, and then use the van't Hoff equation (eqn 7) to write:

$$\left(\frac{\partial \ln K}{\partial T} \right)_\theta = \frac{\Delta_{\text{ad}}H^\ominus}{RT^2} \longrightarrow (7)$$

Isosteric enthalpy of
adsorption from the
equilibrium constant

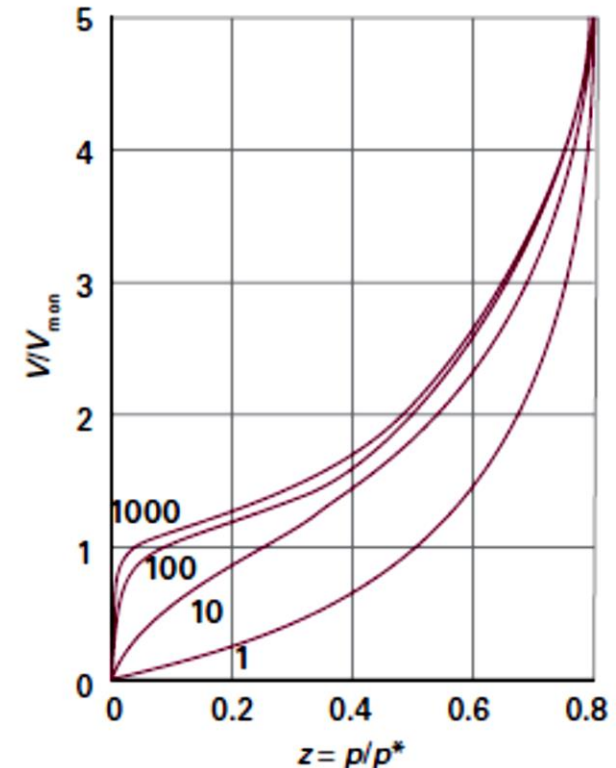
BET isotherm, the most widely used isotherm dealing with multilayer adsorption is given by:

$$\frac{V}{V_{\text{mon}}} = \frac{cz}{(1-z)\{1-(1-c)z\}} \quad \text{with} \quad z = \frac{p}{p^*} \quad \longrightarrow (8)$$

In this expression, p^* is the vapour pressure above a layer of adsorbate that is more than one molecule thick and which resembles a pure bulk liquid, v_{mon} is the volume corresponding to monolayer coverage, and c is a constant that is large when the enthalpy of desorption from a monolayer is large compared with the enthalpy of vaporization of the liquid adsorbate

$$c = e^{(\Delta_{\text{des}}H^{\circ} - \Delta_{\text{vap}}H^{\circ})/RT} \quad \longrightarrow (9)$$

Fig 5: illustrates the shapes of BET isotherms. They rise indefinitely as the pressure is increased because there is no limit to the amount of material that may condense when multilayer coverage may occur



When $c \gg 1$, the BET isotherm takes the simpler form

$$\frac{v}{v_{mon}} = \frac{1}{1 - z} \longrightarrow (10)$$

The BET isotherm fits experimental observations moderately well over restricted pressure ranges, but it errs by underestimating the extent of adsorption at low pressures and by overestimating it at high pressures. An assumption of the Langmuir isotherm is the independence and equivalence of the adsorption sites. Deviations from the isotherm can often be traced to the failure of these assumptions. For example, the enthalpy of adsorption often becomes less negative as θ increases, which suggests that the energetically most favourable sites are occupied first. Various attempts have been made to take these variations into account.

The **Temkin isotherm**,

$$\theta = c_1 \ln(c_2 p) \longrightarrow (11)$$

where c_1 and c_2 are constants, corresponds to supposing that the adsorption enthalpy changes linearly with pressure. The

Freundlich isotherm

$$\theta = c_1 p^{1/c_2} \longrightarrow (12)$$

corresponds to a logarithmic change. This isotherm attempts to incorporate the role of substrate–substrate interactions on the surface.

Homogenous and Heterogenous Catalyst

A **homogeneous catalyst** is a catalyst in the same phase as the reaction mixture. For example, the decomposition of hydrogen peroxide in aqueous solution is catalyzed by iodide ion.

A **heterogeneous catalyst** is a catalyst in a different phase from the reaction mixture. For example, the hydrogenation of ethene to ethane, a gas-phase reaction, is accelerated in the presence of a solid catalyst such as palladium, platinum, or nickel.

- Most heterogeneous catalysts are metals, metal oxides, or acids. Many metallic catalysts like Fe, Co, Ni, Pd, Pt, are transition metals with partly vacant *d* orbitals that can be used in bonding to the chemisorbed species.
- The activity of a catalyst may be increased and its lifetime extended by addition of substances called **promoters**. The iron catalyst used in NH_3 synthesis contains small amounts of the oxides of K, Ca, Al, Si, Mg, Ti, Zr, and V.
- Small amounts of certain substances that bond strongly to the catalyst can inactivate (or **poison**) it. Catalytic poisons include compounds of S, N, and P having lone pairs of electrons (eg, H_2S , CS_2 , HCN , PH_3 , CO) and certain metals (eg, Hg, Pb, As).

The rate of adsorption

The rate at which a surface is covered by adsorbate depends on the ability of the substrate to dissipate the energy of the incoming particle as thermal motion as it crashes on to the surface. If the energy is not dissipated quickly, the particle migrates over the surface until a vibration expels it into the overlying gas or it reaches an edge. The proportion of collisions with the surface that successfully lead to adsorption is called the sticking probability, s :

$$s = \text{rate of adsorption per unit area} / \text{rate of gas-solid collisions per unit area} \\ = r_{\text{ads}} / P(2\pi MRT)^{-1/2} \longrightarrow (13)$$

Values of s vary widely. Beam studies on specific crystal planes show a pronounced specificity: for N_2 on tungsten, s ranges from 0.74 on the (320) faces down to less than 0.01 on the (110) faces at room temperature. The sticking probability decreases as the surface coverage increases (Fig.6). A simple assumption is that s is proportional to $1 - \theta$, the fraction uncovered, and it is common to write

$$s = (1 - \theta)s_0 \longrightarrow (14)$$

where s_0 is the sticking probability on a perfectly clean surface.

The sticking probability is the proportion of collisions with the surface that lead to adsorption.

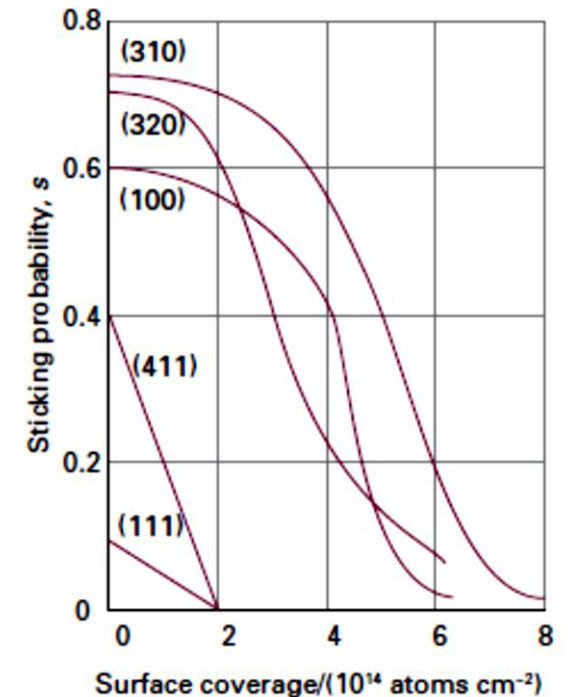


Fig 6: The sticking probability of N_2 on various faces of a tungsten crystal and its dependence on surface coverage. the very low sticking probability for the (110) and (111) faces.

The rate of desorption

Desorption is always activated because the particles have to be lifted from the foot of a potential well. A physisorbed particle vibrates in its shallow potential well, and might shake itself off the surface after a short time. The temperature dependence of the first-order rate of departure can be expected to be Arrhenius-like, with an activation energy for desorption, E_d , comparable to the enthalpy of physisorption:

$$k_d = A e^{-E_d/RT} \longrightarrow (15)$$

Therefore, the half-life for remaining on the surface has a temperature dependence

$$t_{1/2} = \frac{\ln 2}{k_d} = \tau_0 e^{E_d/RT} \quad \tau_0 = \frac{\ln 2}{A} \longrightarrow (16)$$

The kinetics of desorption can be studied by *thermal-desorption* experiments. Here, a solid with adsorbed gas is heated at a known rate in a vacuum system with a known pumping rate, and the system pressure is monitored versus time. A mass spectrometer is used to identify the desorbed gas(es). If the temperature increase is rapid (dT/dt in the range 10 to 1000 K/s), we have *flash desorption*, if slow (10 K/min to 10 K/s), *temperature-programmed desorption*.

Desorption is an activated process; the desorption activation energy is measured by temperature-programmed desorption) or thermal desorption spectroscopy.

Catalytic Activity at Surfaces

- The catalytic activity of a surface depends on its structure as well as its composition.
- For the reaction $\text{H}_2 + \text{D}_2 \rightarrow 2\text{HD}$, terrace sites are inactive but one molecule in ten reacts when it strikes a step.
- Likewise, the dehydrogenation of hexane to hexene depends strongly on the kink density, and it appears that kinks are needed to cleave C–C bonds. Hence, even small amounts of impurities may poison a catalyst: they are likely to attach to step and kink sites, and so impair the activity of the catalyst entirely.

The activity of a catalyst depends on the strength of chemisorption as indicated by the ‘volcano’ curve in Fig.7.

- The most active catalysts should be those lying near the summit of the volcano.
- Most active metals are those that lie close to the middle of the d block.

The activity of a catalyst depends on the strength of chemisorption.

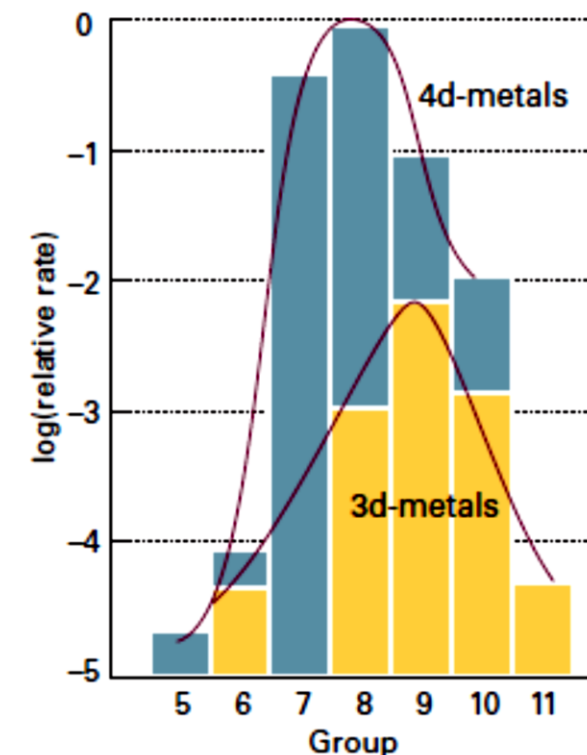


Fig 7: A volcano curve of catalytic activity arises because, although the reactants must adsorb reasonably strongly, they must not adsorb so strongly that they are immobilized. The lower curve refers to the first series of d-block metals, the upper curve to the second and third series d-block metals.

Surface Chemistry

The liquid vapour interface

Surface tension

Liquids tend to adopt shapes that minimize their surface area, for then the maximum number of molecules are in the bulk and hence surrounded by and interacting with neighbours. Droplets of liquids therefore tend to be spherical, because a sphere is the shape with the smallest surface-to-volume ratio.

The work needed to change the surface area, σ , of a sample by an infinitesimal amount $d\sigma$ is proportional to $d\sigma$, and we write

$$dw = \gamma d\sigma \longrightarrow (1)$$

The constant of proportionality, γ , is called the **surface tension**; its units are typically joules per metre squared (J m^{-2}).

The work of surface formation at constant volume and temperature can be identified with the change in the Helmholtz energy, dA and we can write

$$dA = \gamma d\sigma \longrightarrow (2)$$

Because the Helmholtz energy decreases ($dA < 0$) if the surface area decreases ($d\sigma < 0$), surfaces have a natural tendency to contract.

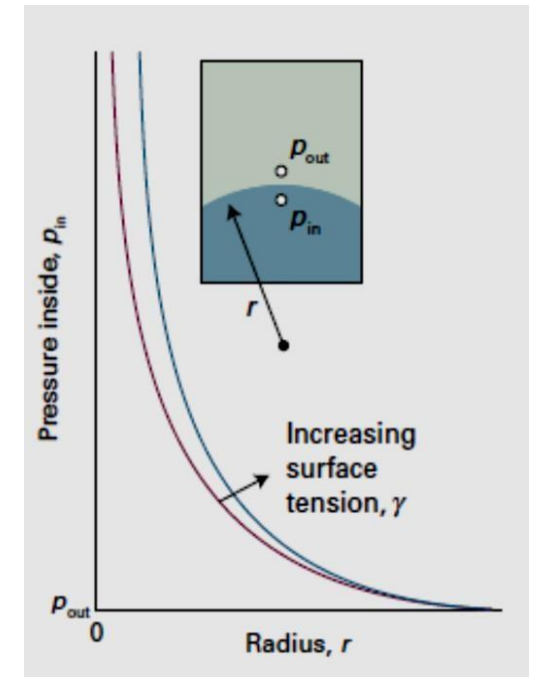
Curved surfaces

The minimization of the surface area of a liquid may result in the formation of a curved surface. A **bubble** is a region in which vapour (and possibly air too) is trapped by a thin film; a **cavity** is a vapour-filled hole in a liquid. True bubbles have two surfaces (one on each side of the film); cavities have only one. The treatments of both are similar, but a factor of 2 is required for bubbles to take into account the doubled surface area.

A **droplet** is a small volume of liquid at equilibrium surrounded by its vapour (and possibly also air). The pressure on the concave side of an interface, p_{in} , is always greater than the pressure on the convex side, p_{out} . This relation is expressed by the **Laplace equation**

$$p_{\text{in}} = p_{\text{out}} + \frac{2\gamma}{r} \longrightarrow (3)$$

The Laplace equation shows that the difference in pressure decreases to zero as the radius of curvature becomes infinite (when the surface is flat, Fig.1). Small cavities have small radii of curvature, so the pressure difference across their surface is quite large. For instance, a ‘bubble’ (actually, a cavity) of radius 0.10 mm implies a pressure difference of 1.5 kPa, which is enough to sustain a column of water of height 15 cm.



Capillary action

The tendency of liquids to rise up capillary tubes (tubes of narrow bore; the name comes from the Latin word for ‘hair’), which is called **capillary action**, is a consequence of surface tension.

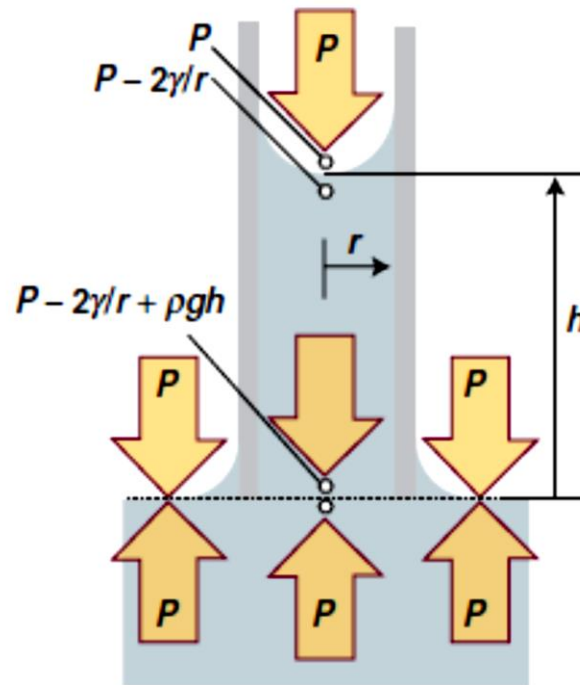


Fig 2: When a capillary tube is first stood in a liquid, the latter climbs up the walls, so curving the surface. The pressure just under the meniscus is less than that arising from the atmosphere by $2\gamma / r$. The pressure is equal at equal heights throughout the liquid provided the hydrostatic pressure (which is equal to ρgh) cancels the pressure difference arising from the curvature.

To calculate the height to which the liquid rises, we note that the pressure exerted by a column of liquid of mass density ρ and height h is

$$p = \rho gh \longrightarrow (4)$$

This hydrostatic pressure matches the pressure difference $2\gamma / r$ at equilibrium.

Therefore, the height of the column at equilibrium is obtained by equating $2\gamma / r$ and ρgh , which gives

$$h = \frac{2\gamma}{\rho gr} \longrightarrow (5)$$

This simple expression provides a reasonably accurate way of measuring the surface tension of liquids.

Surface tension decreases with increasing temperature

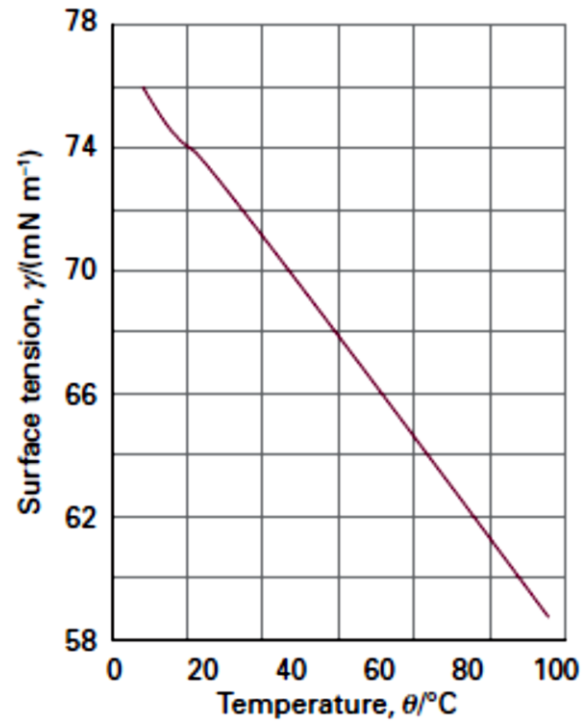


Fig: The variation of the surface tension of water with temperature.

If water at 25°C (and density 997.1 kg m^{-3}) rises through 7.36 cm in a capillary of radius 0.20 mm, its surface tension at that temperature is

$$\begin{aligned}
 \gamma &= \frac{1}{2} \rho g h r \\
 &= \frac{1}{2} \times (997.1 \text{ kg m}^{-3}) \times (9.81 \text{ m s}^{-2}) \times (7.36 \times 10^{-2} \text{ m}) \times (2.0 \times 10^{-4} \text{ m}) \\
 &= 72 \text{ mN m}^{-1}
 \end{aligned}$$

where we have used $1 \text{ kg m s}^{-2} = 1 \text{ N}$.

Q 1. For a water–air interface at 25°C and 1 atm, calculate the capillary rise in a glass capillary tube with inside diameter 0.200 mm. The surface tension of water at 25°C is 0.072 N/m. The densities of air and water at 25°C and 1 atm are 0.001 g/cm³ and 0.997 g/cm³.

Q 2. Find the inside diameter of a glass capillary in which water shows a capillary rise of 88 mm at 25°C.

Surface films

Surface pressure

The principal apparatus used for the study of surface monolayers is a **surface film balance** (Fig. 3). This device consists of a shallow trough and a barrier that can be moved along the surface of the liquid in the trough, and hence compress any monolayer on the surface. The **surface pressure**, π , the difference between the surface tension of the pure solvent and the solution ($\pi = \gamma^* - \gamma$) is measured by using a torsion wire attached to a strip of mica that rests on the surface and pressing against one edge of the monolayer. The parts of the apparatus that are in touch with liquids are coated in polytetrafluoroethene to eliminate effects arising from the liquid–solid interface. In an actual experiment, a small amount (about 0.01 mg) of the surfactant under investigation is dissolved in a volatile solvent and then poured on to the surface of the water; the compression barrier is then moved across the surface and the surface pressure exerted on the mica bar is monitored.

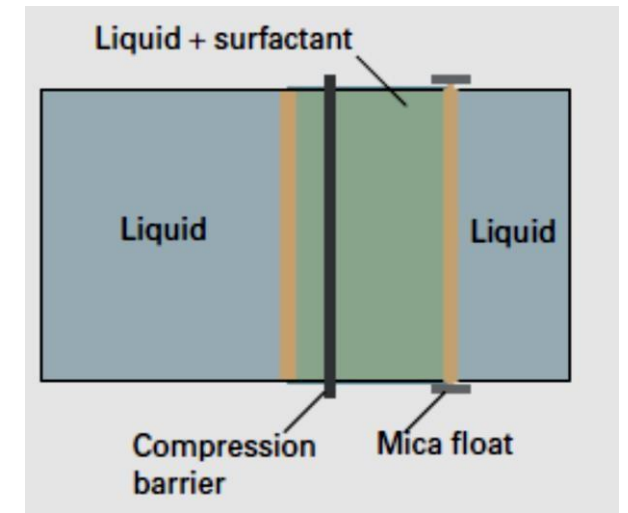


Fig 3 : A schematic diagram of the apparatus used to measure the surface pressure and other characteristics of a surface film. The surfactant is spread on the surface of the liquid in the trough, and then compressed horizontally by moving the compression barrier towards the mica float. The latter is connected to a torsion wire, so the difference in force on either side of the float can be monitored.

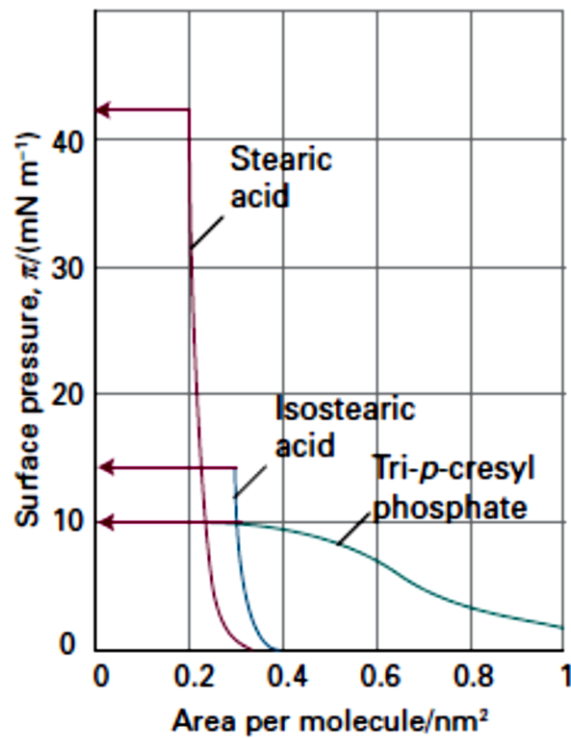


Fig 4 The variation of surface pressure with the area occupied by each surfactant molecule. The collapse pressures are indicated by the horizontal arrow.

- One parameter obtained from the isotherms is the area occupied by the molecules when the monolayer is closely packed. This quantity is obtained from the extrapolation of the steepest part of the isotherm to the horizontal axis.
- The second feature is that the tri-*p*-cresyl phosphate isotherm is much less steep than the stearic acid isotherms. This difference indicates that the tri-*p*-cresyl phosphate film is more compressible than the stearic acid films, which is consistent with their different molecular structures.
- A third feature of the isotherms is the **collapse pressure**, the highest surface pressure. When the monolayer is compressed beyond the collapse pressure, the monolayer buckles and collapses into a film several molecules thick. Stearic acid has a high collapse pressure, but that of tri-*p*-cresyl phosphate is significantly smaller, indicating a much weaker film.

The thermodynamics of surface layers

A **surfactant** is a species that is active at the interface between two phases, such as at the interface between hydrophilic and hydrophobic phases. A surfactant accumulates at the interface, and modifies its surface tension and hence the surface pressure.

To establish the relation between the concentration of surfactant at a surface and the change in surface tension it brings about, we consider two phases α and β in contact and suppose that the system consists of several components J , each one present in an overall amount n_J . If the components were distributed uniformly through the two phases right up to the interface, which is taken to be a plane of surface area σ , the total Gibbs energy, G , would be the sum of the Gibbs energies of both phases, $G = G(\alpha) + G(\beta)$.

However, the components are not uniformly distributed because one may accumulate at the interface. As a result, the sum of the two Gibbs energies differs from G by an amount called the **surface Gibbs energy**, $G(\sigma)$:

$$G(\sigma) = G - \{G(\alpha) + G(\beta)\} \longrightarrow (6)$$

Definition of surface
Gibbs energy

Similarly, if it is supposed that the concentration of a species J is uniform right up to the interface, then from its volume we would conclude that it contains an amount $n_J(\alpha)$ of J in phase α and an amount $n_J(\beta)$ in phase β . However, because a species may accumulate at the interface, the total amount of J differs from the sum of these two amounts by $n_J(\sigma) = n_J - \{n_J(\alpha) + n_J(\beta)\}$. This difference is expressed in terms of the **surface excess**, Γ_J :

$$\Gamma_J = n_J(\sigma)/\sigma \longrightarrow (7)$$

Definition of
surface excess

The surface excess may be either positive (an accumulation of J at the interface) or negative (a deficiency there).

The relation between the change in surface tension and the composition of a surface (as expressed by the surface excess) was derived by Gibbs. The **Gibbs isotherm** gives the relation between the changes in the chemical potentials of the substances present in the interface and the change in surface tension:

$$d\gamma = - \sum_J \Gamma_J d\mu_J \longrightarrow (8)$$

Gibbs isotherm

Colloids

Colloidal System: A colloidal system consists of particles that have in at least one direction a dimension lying in the approximate range 30 to 10^4 \AA and a medium in which the particles are dispersed. The particles are called colloidal particles or the dispersed phase; the medium is called the dispersion medium or the continuous phase.

A **sol** is a colloidal system whose dispersion medium is a liquid or gas. When the dispersion medium is a gas, the sol is called aerosol. Fog is an aerosol with liquid particles. Smoke is an aerosol with liquid or solid particles.

A sol that consists of liquid dispersed in a liquid is called an **emulsion**.

A sol that consists of solid particles suspended in a liquid is called a **colloidal suspension**.

A **foam** is a colloidal system in which gas bubbles are dispersed in a liquid or solid. A pumic stone is a foam with air bubbles dispersed in rock of volcanic origin.

Colloidal systems can be classified into those in which the dispersed particles are single molecules (monomolecular particles) and those in which the particles are aggregates of many molecules (polymolecular particles). Colloidal dispersions of AgCl , As_2S_3 , and Au in water contain polymolecular particles, and the system has two phases: water and the dispersed particles. The tiny size of the particles results in a very large interfacial area, and surface effects (for example, adsorption on the colloidal particles) are of major importance in determining the system's properties.

On the other hand, in a polymer solution (for example, a solution of a protein in water) the colloidal particle is a single molecule, and the system has one phase. Here, there are no interfaces, but solvation of the polymer molecules is significant. The large size of the solute molecules causes a polymer solution to resemble a colloidal dispersion of polymolecular particles in such properties as scattering of light and sedimentation in a centrifuge, so polymer solutions are classified as colloidal systems.

Lyophilic Colloids

When a protein crystal is dropped into water, the polymer molecules spontaneously dissolve to produce a colloidal dispersion. Colloidal dispersions that can be formed by spontaneous dispersion of the dry bulk material of the colloidal particles in the dispersion medium are called **lyophilic** (“solvent-loving”). A lyophilic sol is thermodynamically more stable than the two-phase system of dispersion medium and bulk colloid material.

Certain compounds in solution yield lyophilic colloidal systems as a result of spontaneous association of their molecules to form colloidal particles.

If one plots the osmotic pressure of an aqueous solution of a soap (a compound with the formula RCOOM , where R is a straight chain with 10 to 20 carbons, and M is Na or K) versus the solute's stoichiometric concentration, one finds that at a certain concentration (called the critical micelle concentration, cmc) the solution shows a sharp drop in the slope of this curve.

Above the cmc, a substantial portion of the solute ions are aggregated to form units of colloidal size for their hydrophobic tails tend to congregate (through hydrophobic interactions), and their hydrophilic head groups provide protection. Such aggregates are called micelles. Dilution of the solution below the cmc eliminates the micelles, so micelle formation is reversible.

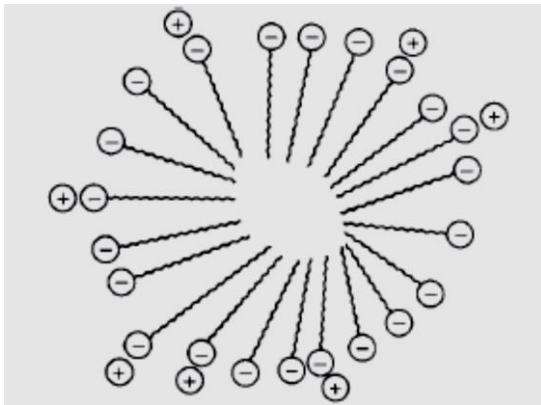


Fig. 5 shows the structure of a soap micelle in aqueous solution

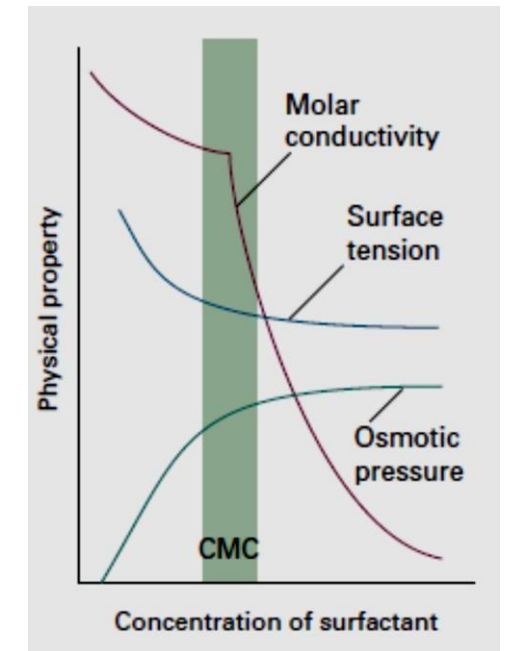


Fig 6: The typical variation of some physical properties of an aqueous solution of sodium dodecylsulfate close to the critical micelle concentration (CMC).

Lyophobic Colloids

Sols that cannot be formed by spontaneous dispersion are called **lyophobic** (“solvent-hating”). Lyophobic sols are thermodynamically unstable with respect to separation into two unmixed bulk phases. The long life of lyophobic sols is commonly due to adsorbed ions on the colloidal particles; repulsion between like charges keeps the particles from aggregating. The presence of adsorbed ions can be shown by the migration of the colloidal particles in an applied electric field (a phenomenon called *electrophoresis*). A lyophobic sol can also be stabilized by the presence of a polymer (for example, the protein gelatin) in the solution. The polymer molecules become adsorbed on and surround each colloidal particle, thereby preventing coagulation of the particles.

Many lyophobic colloids can be prepared by precipitation reactions. Precipitation in either very dilute or very concentrated solutions tends to produce colloids.

Sedimentation

The particles in a noncolloidal suspension of a solid in a liquid will eventually settle out under the influence of gravity, a process called **sedimentation**. For colloidal particles whose size is well below 10^3 \AA , accidental thermal convection currents and the random collisions between the colloidal particles and molecules of the dispersion medium prevent sedimentation. A sol with larger colloidal particles will show sedimentation with time.

Emulsions

Emulsions are lyophobic colloids. They are stabilized by the presence of an *emulsifying agent*, which is commonly a species that forms a surface film at the interface between each colloidal droplet and the dispersion medium, thereby lowering the interfacial tension and preventing coagulation. The cleansing action of soaps and other detergents results in part from their acting as emulsifying agents to keep tiny droplets of grease suspended in water.

The liquids in most emulsions are water and an oil, where “oil” denotes an organic liquid essentially immiscible with water. Such emulsions are classified as either oil-in water (O/W) emulsions, in which water is the continuous phase and the oil is present as tiny droplets, or water-in-oil (W/O) emulsions, in which the oil is the continuous phase. Milk is an O/W emulsion of butterfat droplets in water; the emulsifying agent is the protein casein. Many pharmaceutical preparations and cosmetics (salves, ointments, cold cream) are emulsions.

Gels

A **gel** is a semirigid colloidal system of at least two components in which both components extend continuously throughout the system. An inorganic gel typically consists of water trapped within a three-dimensional network of tiny crystals of an inorganic solid. The polysaccharide agar forms a polymer gel with water, which is used as a culture medium for bacteria.

If the liquid phase of a gel is removed by heating and pressurizing the gel above the critical temperature and pressure of the liquid and allowing the fluid to vent, one obtains an **aerogel**. An aerogel is a strong, low density solid whose volume is only a bit less than that of the original gel. The space formerly filled by the liquid in a gel contains air in the aerogel, so the aerogel is permeated by tiny pores. The most-studied aerogel is silica aerogel, where the solid is SiO_2 (silica), which is a covalent-network solid with a three-dimensional array of bonded Si and O atoms. (Silica occurs in nature as sand and is the main ingredient in glass.) The original gel can be made by the reaction $\text{Si}(\text{OC}_2\text{H}_5)_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2(s) + 4\text{C}_2\text{H}_5\text{OH}$ carried out in the solvent ethanol and yielding a gel with ethanol as the liquid. Aerogels may find uses in catalysis and in thermal insulation.

References

1. P. W. Atkins, J. De Paula Physical Chemistry, 9th Ed., OXFORD UNIVERSITY PRESS, 2011.
2. I. A. Levine, Physical Chemistry, 6th Ed., Tata-McGraw-Hill, 2011.