SURFACE PHENOMENA

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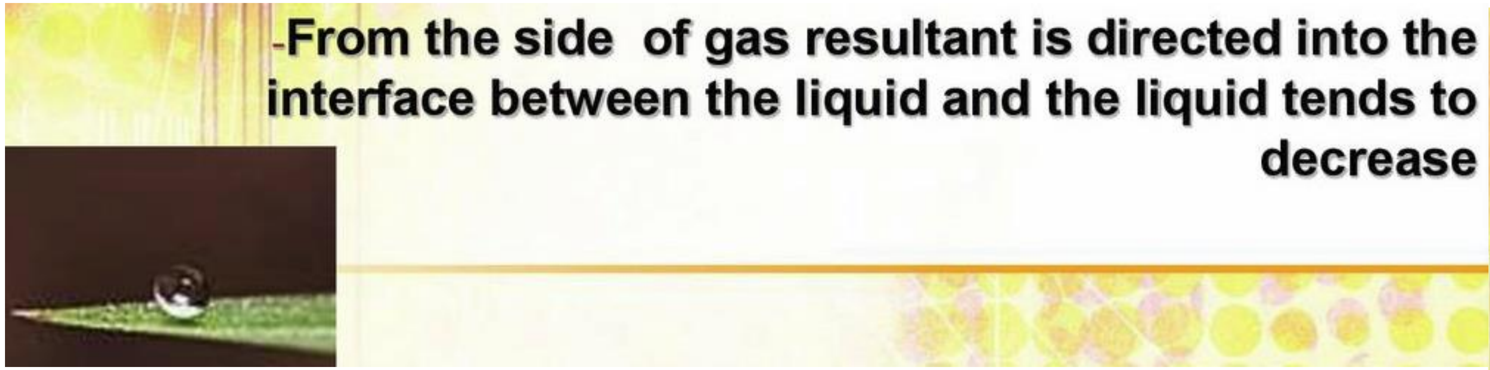
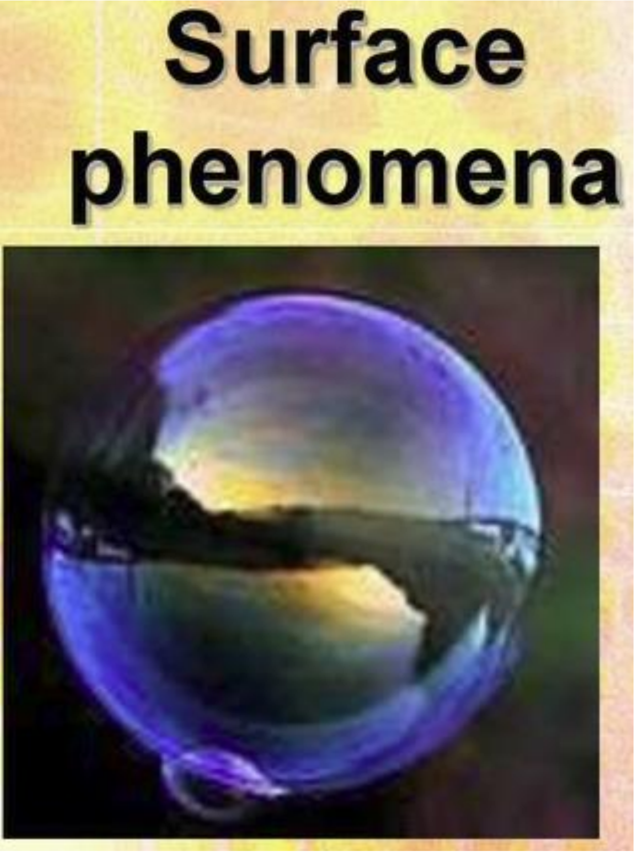
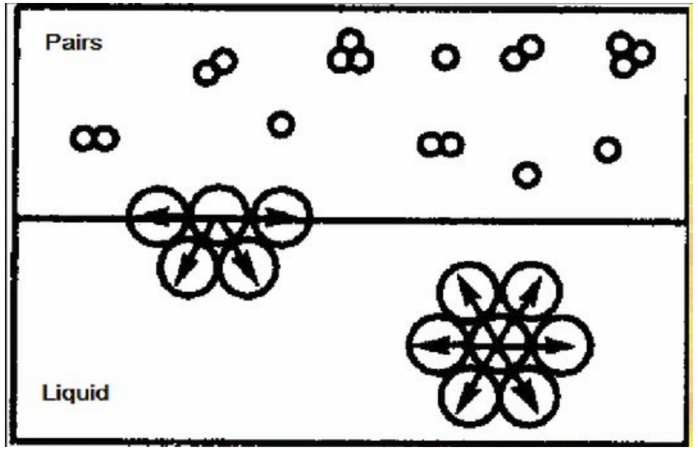


-From the side of gas resultant is directed into the interface between the liquid and the liquid tends to decrease



Surface phenomena



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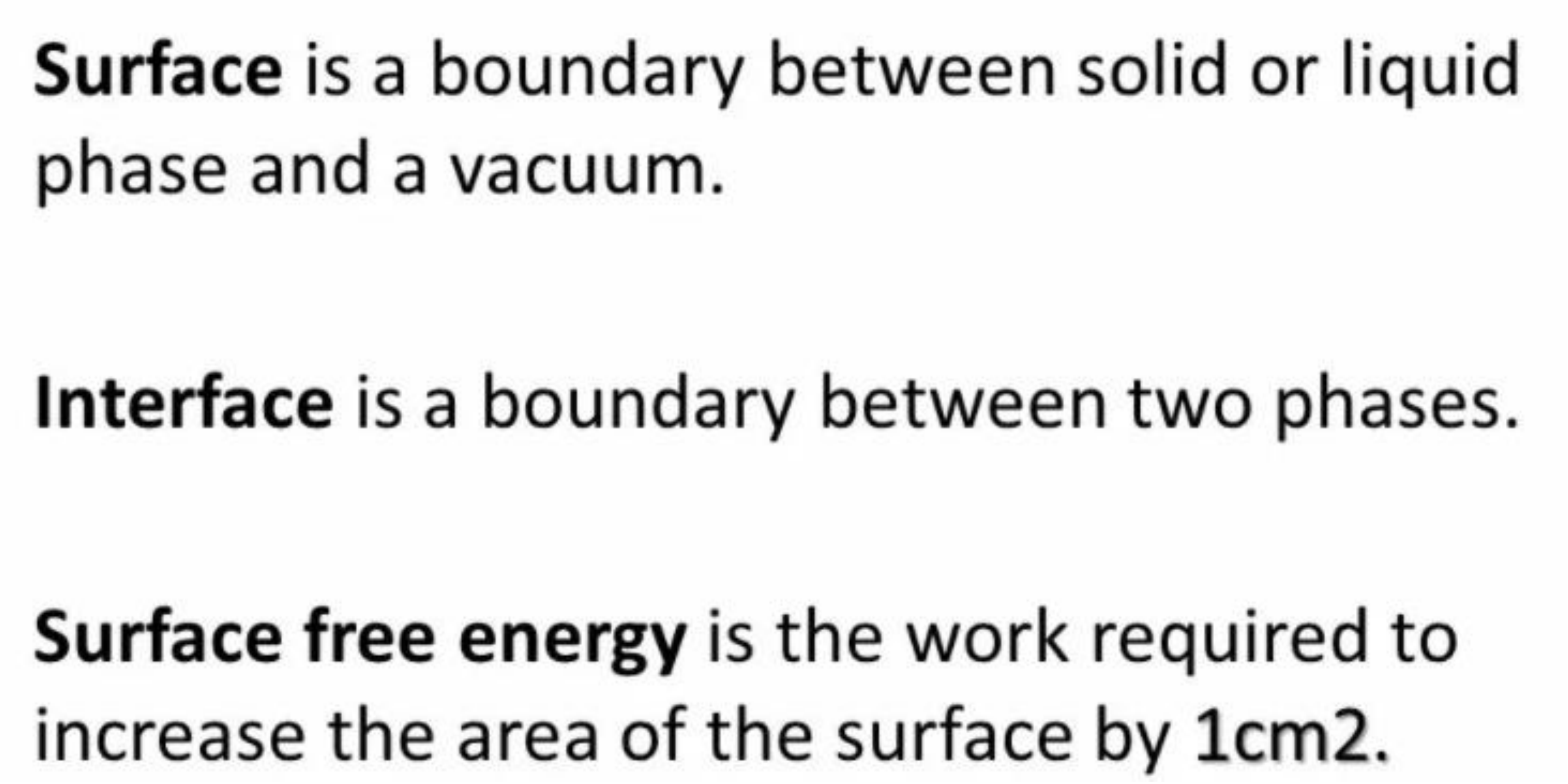


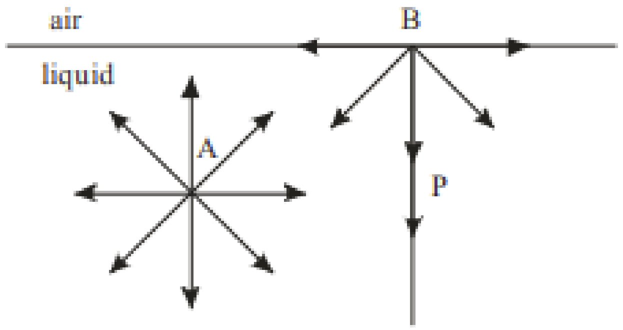
Surface is a boundary between solid or liquid phase and a vacuum.

Interface is a boundary between two phases.

Surface free energy is the work required to increase the area of the surface by **1cm2.**

SURFACE PHENOMENA

In a system composed of two or more phases, molecules at or very near to the region of phase contact have different molecular environment than molecules in the bulk of either of phases. Molecules in the inner layers of a substance experience the same average force of attraction in all the directions by surrounding molecules, while molecules in the surface layer experience different forces of attraction from inside the substance and from the side bordering with the surface layer of the medium For this reason the properties of the surface layer differ somewhat from those of the substance in the bulk. In turn, the properties of the surface layer may affect other properties of the substance. Thus, at a liquid-air interface the molecules of liquid in the surface layer are attracted more strongly by the underlying molecules than by the molecules of the gas, hence total force acting on the surface molecule is directed down and called inner pressure (P). For this reason, systems tend to assume a configuration of minimum surface area. Thus an isolated drop of liquid is spherical, since a sphere is the shape with a minimum ratio of surface area to volume.



Surface tension

Due to the unique environment of the molecules in the surface layer and presence of the inner pressure positive work, it is required to increase the area of an interface between two phases. Therefore, the more interphase area the more work needed for its formation, and as it should be the more surface ***Gibbs free energy***:

$$dG = \sigma\, dS$$

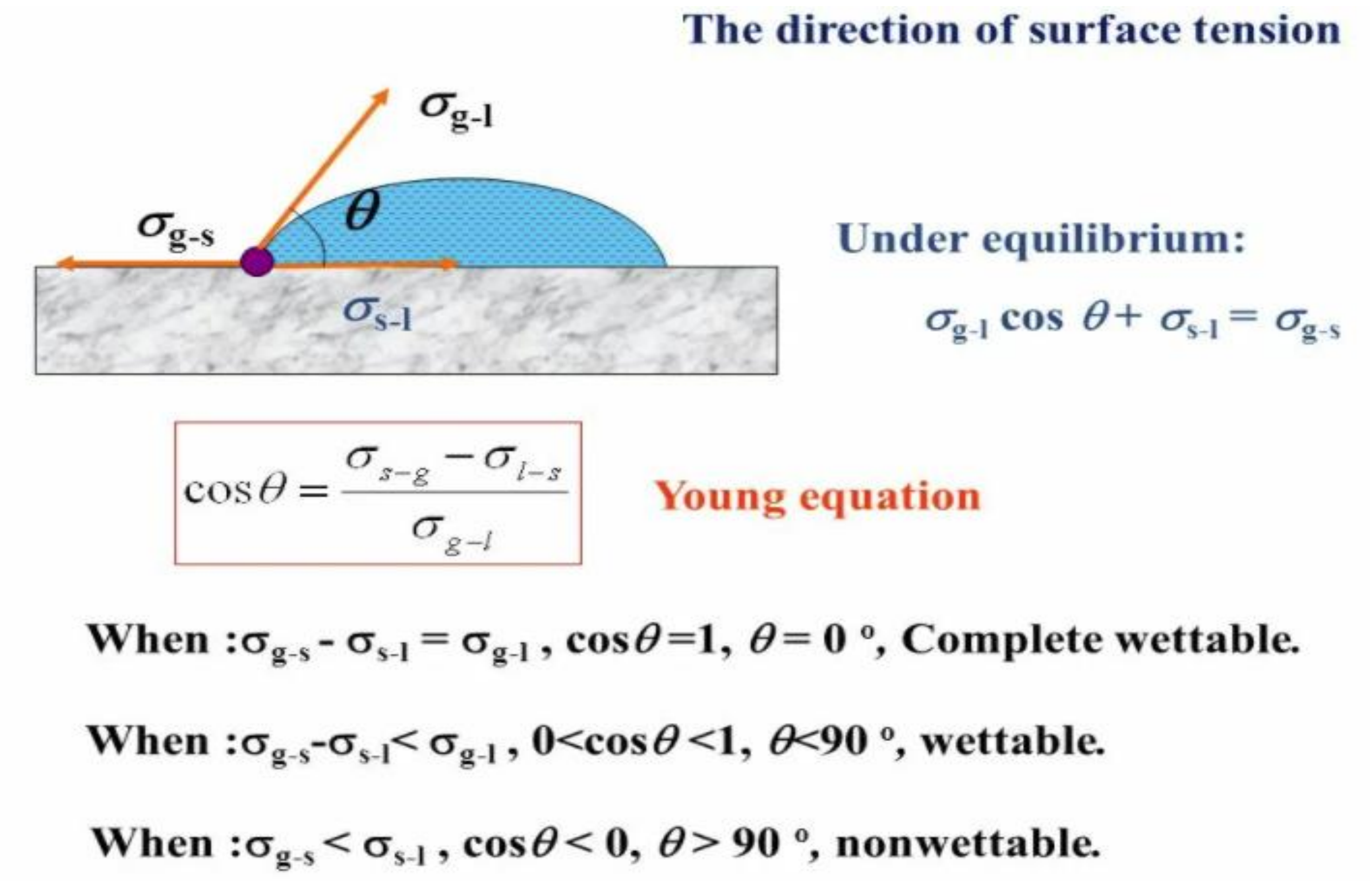
where σ is the constant of proportionality and called the ***surface tension***. From equation it's equal to:

$$\sigma = \frac{dG}{dS}$$

Surface tension

- ***Surface tension*** is the Gibbs free energy of a unit of surface, or it is the maximum useful work done for the formation of a unit of surface area. It could be defined also as force acting parallel to the surface and perpendicular to a line of unit length anywhere in the surface. The units of surface tension are mN m^{-1} .
- ***The surface tension*** depends on the molar volume, the polarity of the molecules and the nature of the substances. The surface tension of water is much higher than of most common liquids.
- As for polarity, there is the ***rule of Rebinder*** according to which: the more polarity difference of two phases the more surface tension of their boundary surface.
- ***Surface tension*** diminishes with a rise in temperature up to the critical or absolute boiling point, the temperature at which the surface tension becomes zero.

Surface tension



The direction of surface tension

Under equilibrium:

$$\sigma_{g\text{-}l}\cos\theta + \sigma_{s\text{-}l} = \sigma_{g\text{-}s}$$

$$\boxed{\cos\theta = \frac{\sigma_{s-g} - \sigma_{l-s}}{\sigma_{g-l}}}$$

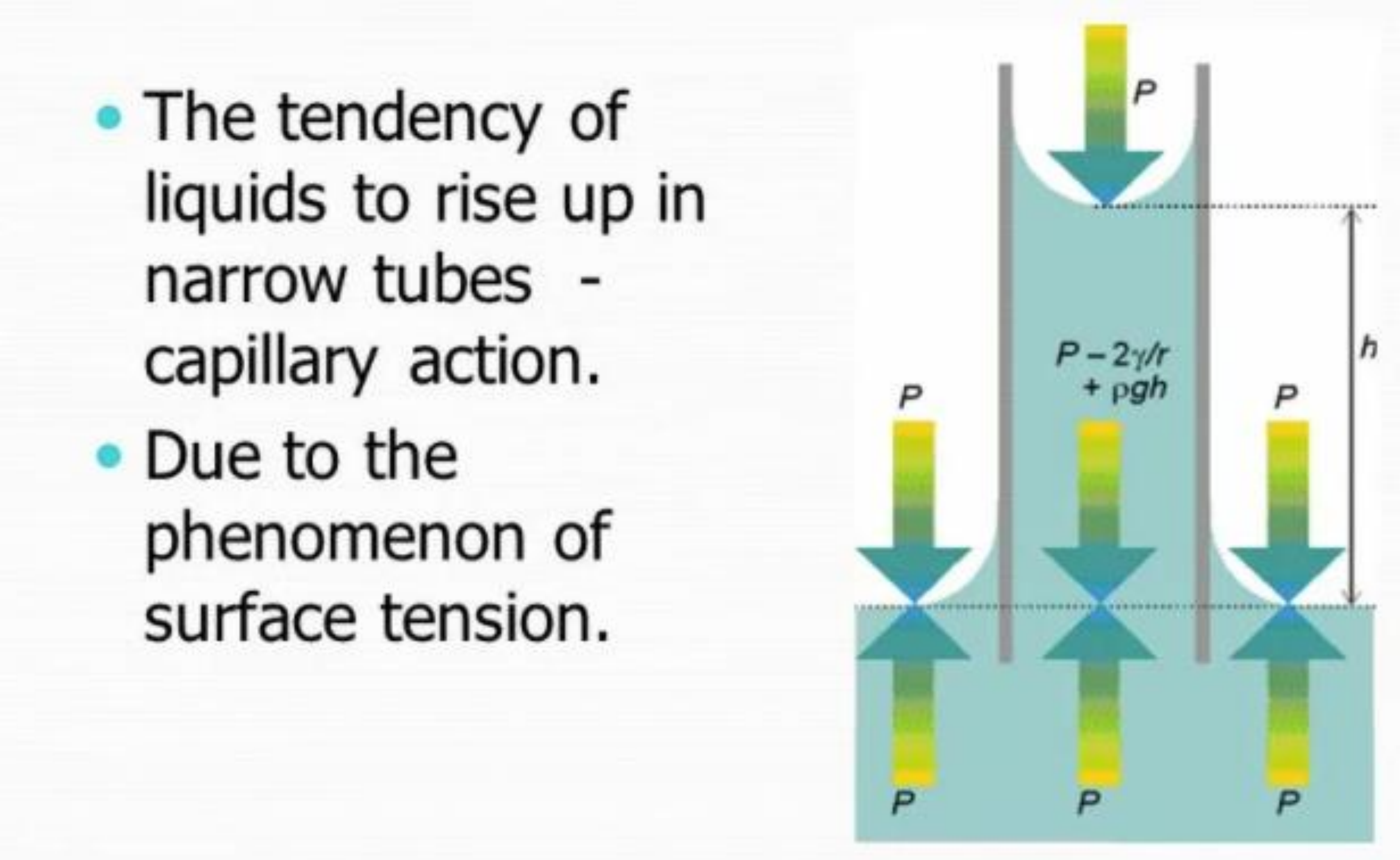
Young equation

When : $\sigma_{g\text{-}s} - \sigma_{s\text{-}l} = \sigma_{g\text{-}l}$, $\cos\theta = 1$, $\theta = 0$ °, **Complete wettable.**

When : $\sigma_{g\text{-}s} - \sigma_{s\text{-}l} < \sigma_{g\text{-}l}$, $0 < \cos\theta < 1$, $\theta < 90$ °, **wettable.**

When : $\sigma_{g\text{-}s} < \sigma_{s\text{-}l}$, $\cos\theta < 0$, $\theta > 90$ °, **nonwettable.**

Capillary action

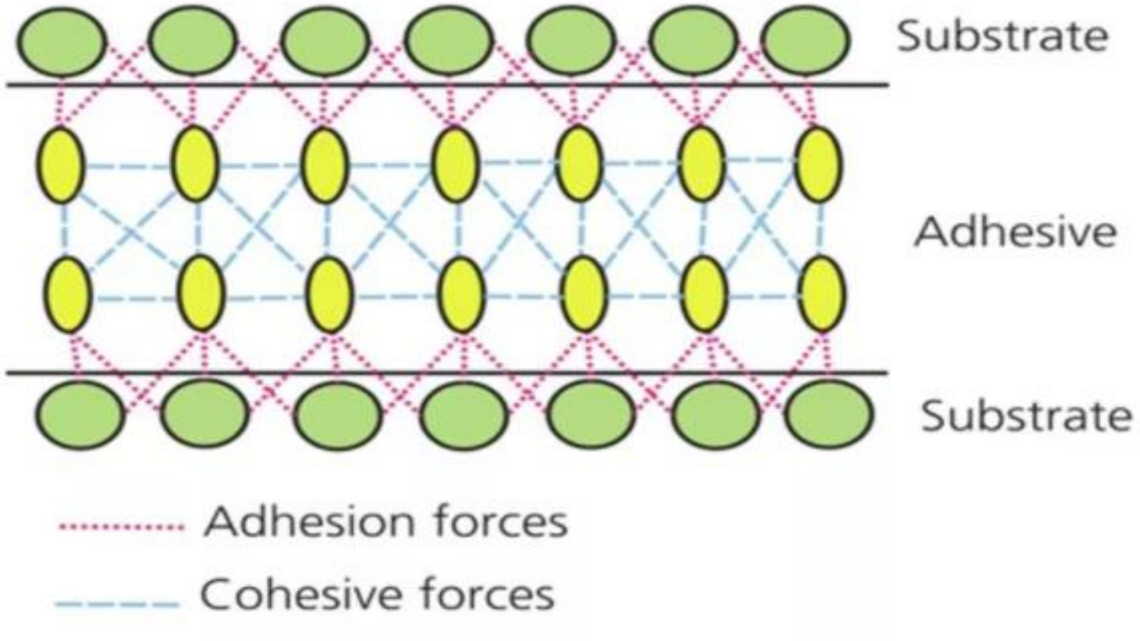


- The tendency of liquids to rise up in narrow tubes - capillary action.
- Due to the phenomenon of surface tension.

Cohesion and Adhesion

- **Cohesive force** is the force existing between like molecules in the surface of a liquid
- **Adhesive force** is the force existing between unlike molecules, such as that between a liquid and the wall of a glass capillary tube

✓ *When the force of Adhesion is greater than the cohesion, the liquid is said to wet the capillary wall, spreading over it, and rising in the tube.*



Sorption

- The difference in concentration of a component in the surface layer and in the bulk of the substance is called adsorption. In other words adsorption is the enrichment of a component with a lower surface tension in the interphase region compared with a bulk region, or it is attachment of such particles to a surface.
- The substance that adsorbs is called the **adsorbate** and the underlaying material on whose surface adsorption occurs is called the **adsorbent**. “Adsorption” should be clearly differentiated from “absorption”, in which physical penetration of one phase (adsorbate) is involved (for instance, gas absorption by liquid). With adsorption process simultaneously the reverse of it – desorption occurs and in the end the equilibrium is stated.
- The quantitative characteristic of adsorption is ***specific adsorption***, Γ (capital gamma), which shows moles of adsorbate (x) adsorbed per gram (or unit surface), of adsorbent: $\Gamma = x/m$ or $\Gamma = x/S$

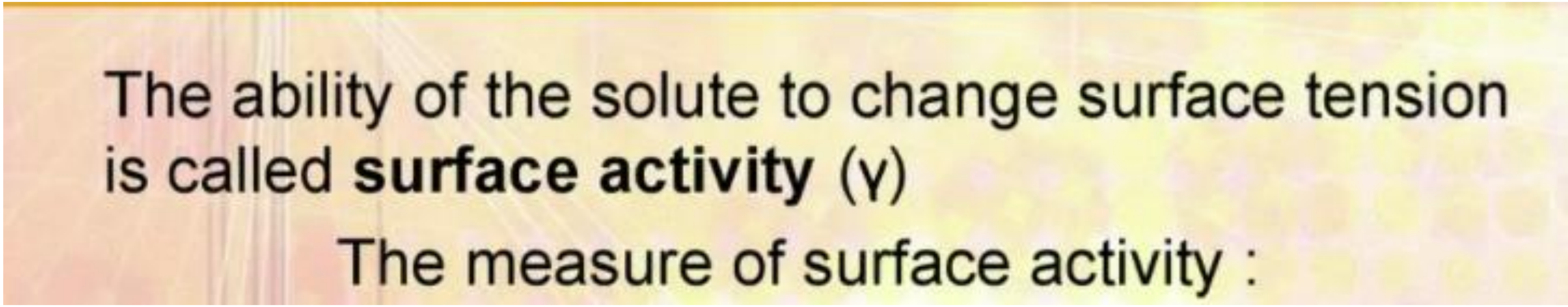
Adsorption

- ***Adsorption*** is classified into physical adsorption and chemical adsorption; the dividing line between these two tipe is not always sharp.
- ***In physical adsorption*** the molecules of the adsorbate are held to the surface by relatively weak intermolecular van der Waals forces.
- ***In chemosorption***, a chemical reaction occurs at the surface, and the adsorbate is held to the surface by relatively strong chemical bonds. Physical adsorption is nonspecific.
- The distance between the surface and the closest adsorbate atom is shorter for chemosorption than for physysorption.
- The enthalpy changes for chemosorption are usually substantially greater in magnitude than those for physical adsorption

Adsorption on the liquid surface

The surface properties of solutions differ from those of pure liquids first and foremost in that the composition of the surface layer of a solution differs to a certain extent from that of the inner layers. The surface tension of a solution can greatly depend on the composition of the surface layer, and in the surface layer spontaneously increases those of the component which lowers the surface tension and, hence, reduces the total Gibbs energy of the system.

Adsorption on the liquid surface



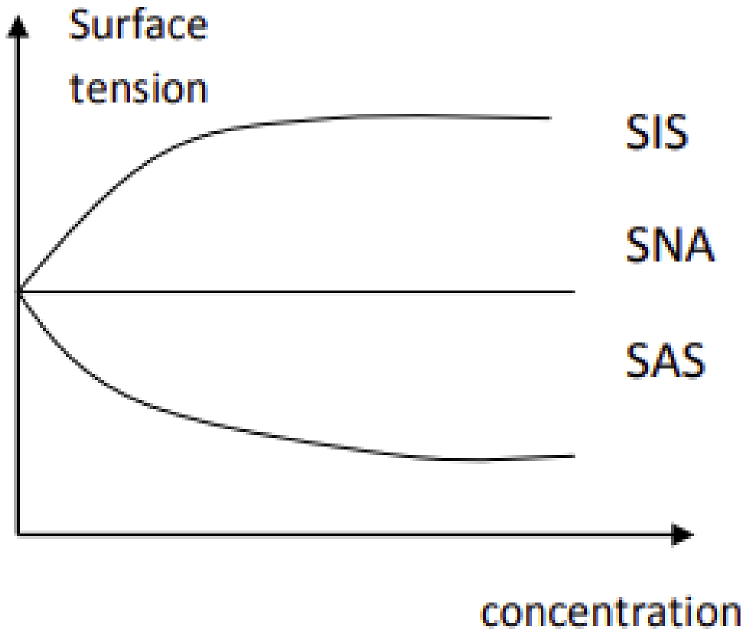
The ability of the solute to change surface tension is called **surface activity** (γ)

The measure of surface activity :

$$g = -\frac{\Delta\sigma}{\Delta c}$$

Adsorption on the liquid surface

Surface tension isotherm shape: The equilibrium curve relating the surface tension value and C is also mainly used to determine the nature of the sorption process.



Adsorption on the liquid surface

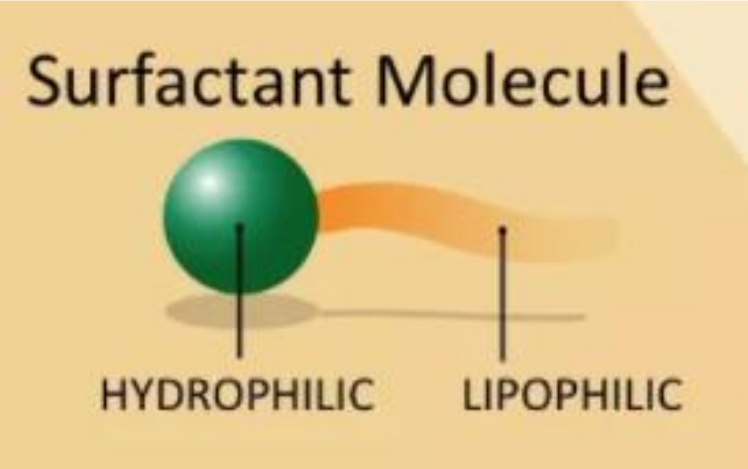
1. **Surface-active substances (SAS):**
   reduce σ solvent. σ solution < σ solvent; $g > O$.
   SAS: alcohols, organic acids, esters, proteins, cholesterol, fats, lipids, soaps.

2. **Surface-inactive substance (SIS):**
   increase σ of solvent. σ solution > σ solvent; $g < O$.
   SIS: inorganic acids, bases, salts, glycerol, α - amino acids.

3. **Surfactants-nonactive substance (SNS):**
   do not alter the surface tension of the solvent. σ solution = σ solvent; $g = O$.
   SNS: sucrose.

Adsorption on the liquid surface

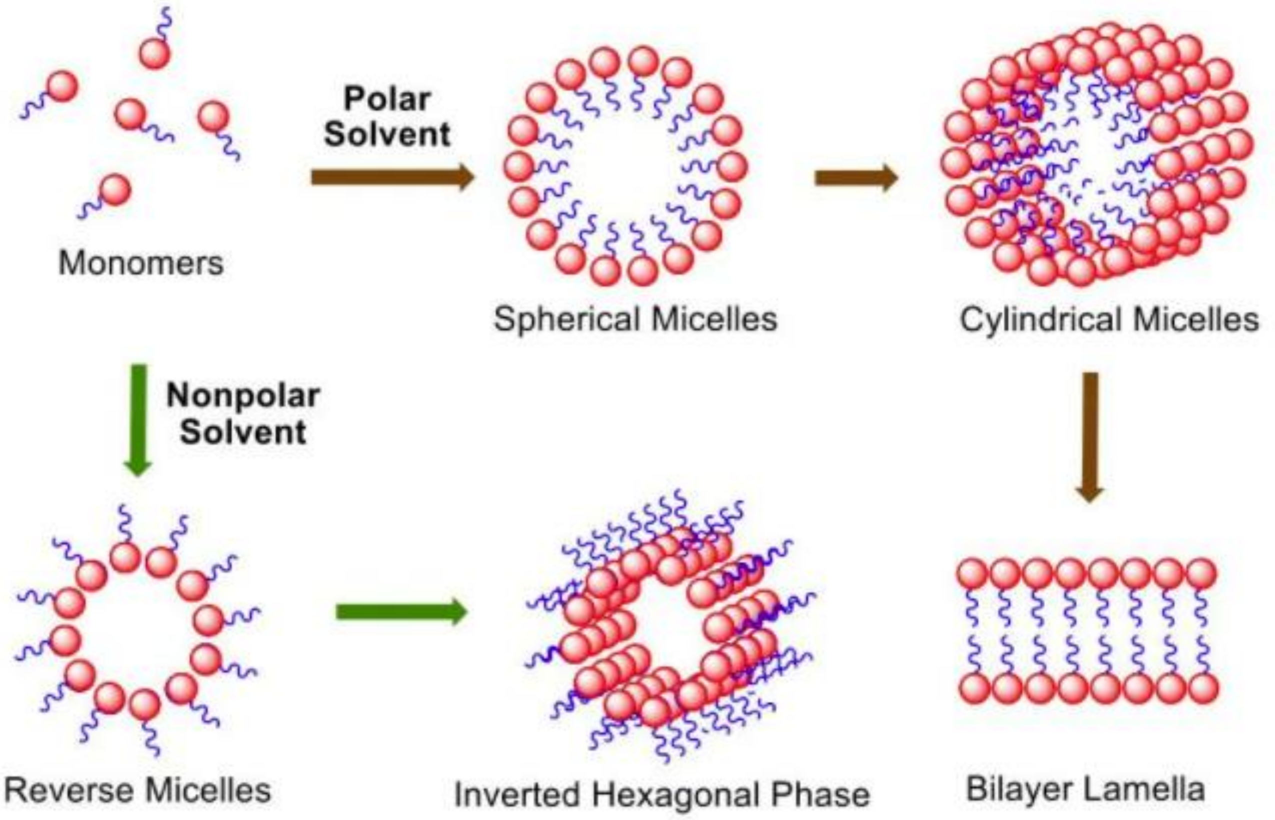
Both detergents and soaps are classed as **surfactants (SAS).** Surfactants are characterized by the essential features that we saw in sodium oleate. A surfactant molecule has a hydrophilic (water-loving) head and a long hydrophobic (water-hating or oil-loving) tail. For this reason, we often describe surfactants is being amphiphilic molecules – they love everything.



Adsorption on the liquid surface

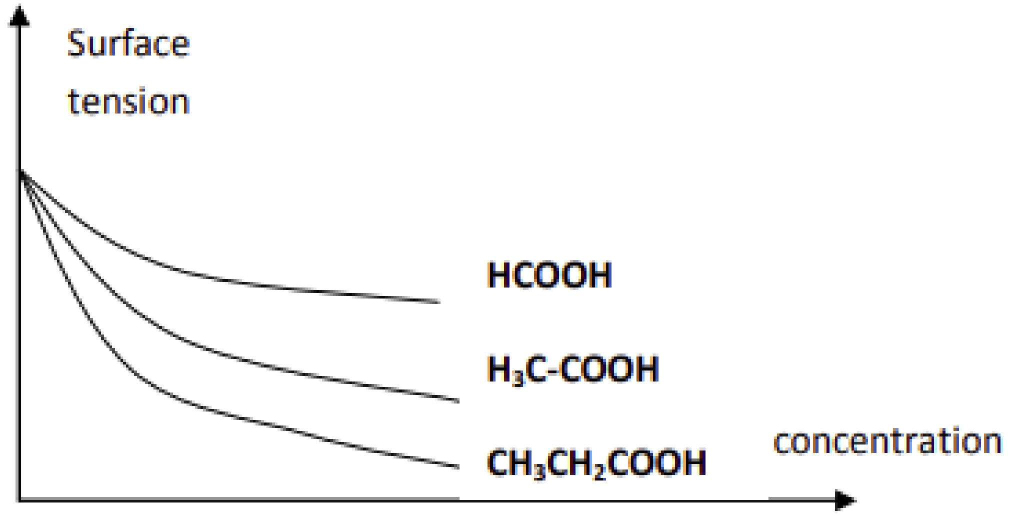
When a ***detergent*** is placed in water, the long non-polar hydrocarbon tails tend to aggregate because of favorable intermolecular interactions ("like dissolves like" in the interior and ion-dipole interactions at the exterior). The surfactant molecules thereby organize themselves into 3-dimensional spheres called micelles which have a hydrocarbon core and sulfate groups around the outer surface.

Adsorption on the liquid surface.
Surfactant aggregates.



Adsorption on the liquid surface

The surface activity of **SAS** depends on the length of hydrophobic tail. In accordance with the **Traube's Rule**, the surface activity is increasing in 3 times when the hydrophobic radical (tail) gets longer with one –CH2–group.



Adsorption on the liquid surface

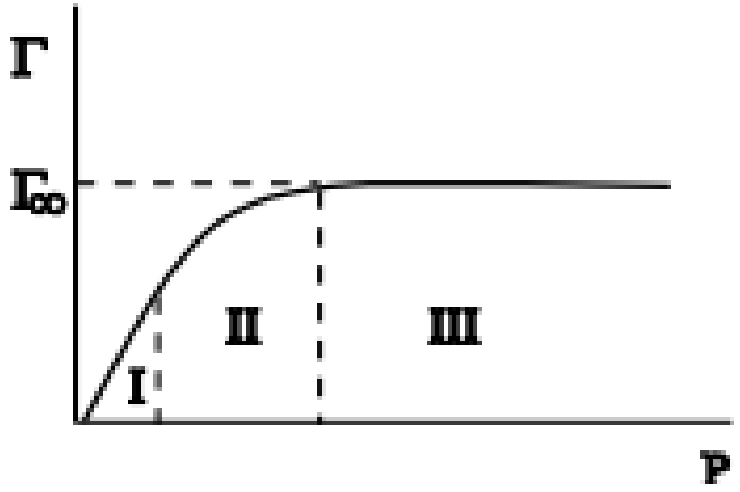
Adsorption in the surface layer of a solution is described quantitatively by **Gibb’s equation**, obtained by thermodynamic treatment. If we denote the concentration of the solute in the solution by C and the degree of adsorption in the surface layer by Γ then Gibbs’s equation can be written in the form:

$$\Gamma = -\frac{C}{RT}\left(\frac{d\sigma}{dC}\right)_T$$

Application of surfactants in medicine and pharmacy

- They are used to obtain emulsions because of decreasing water/oil interphase tension.
- Surfactants adsorption on hydrophobic surfaces of insoluble substances reverses their solubility and adjuvant to obtain suspensions.
- Surfactants are used for stabilization of different disperse systems.
- Because of surfactants abilities to form surface membranes they are used as drug covering.
- Some of drugs are surfactants by themselves.

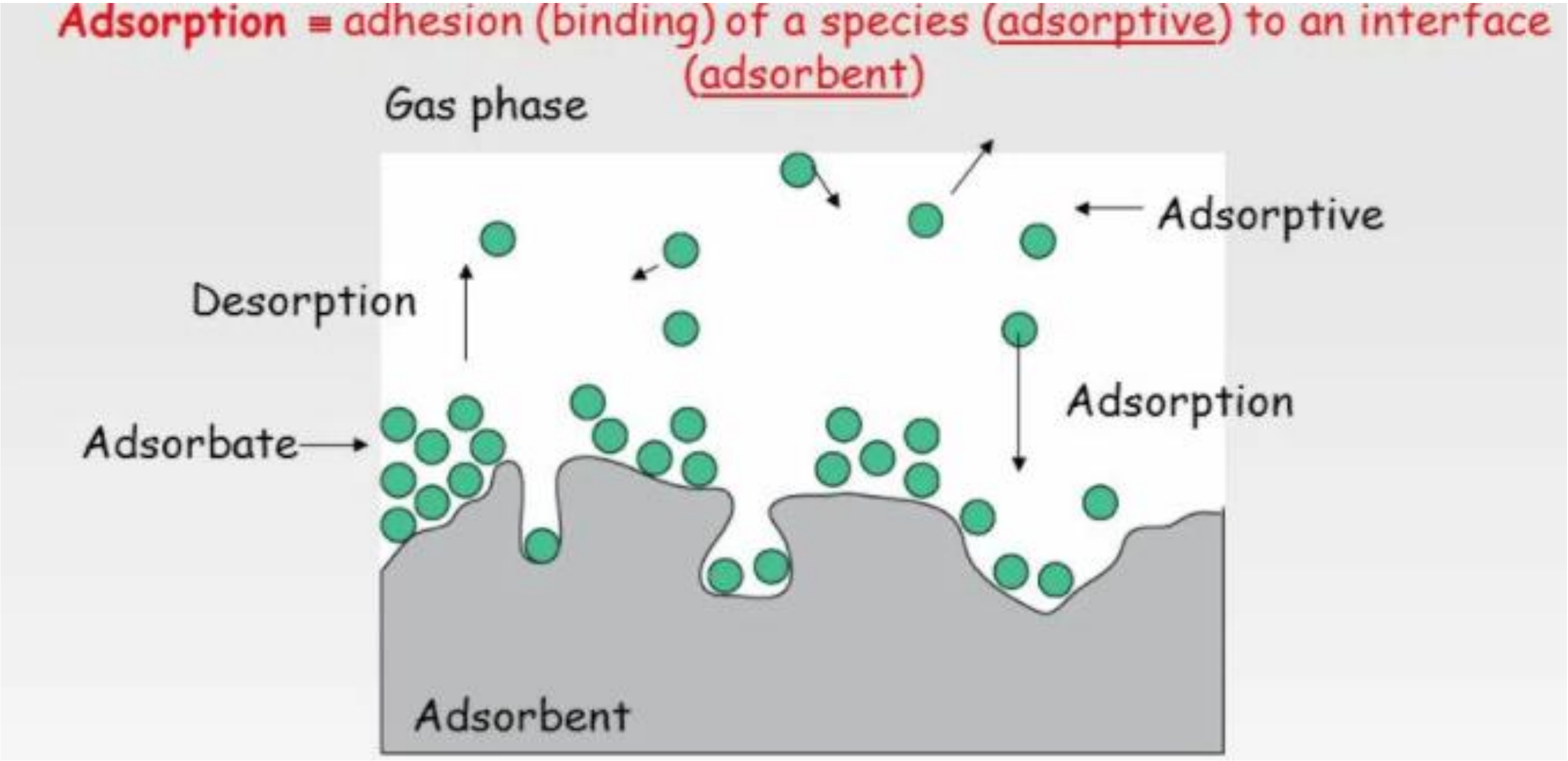
Adsorption of gases on solids



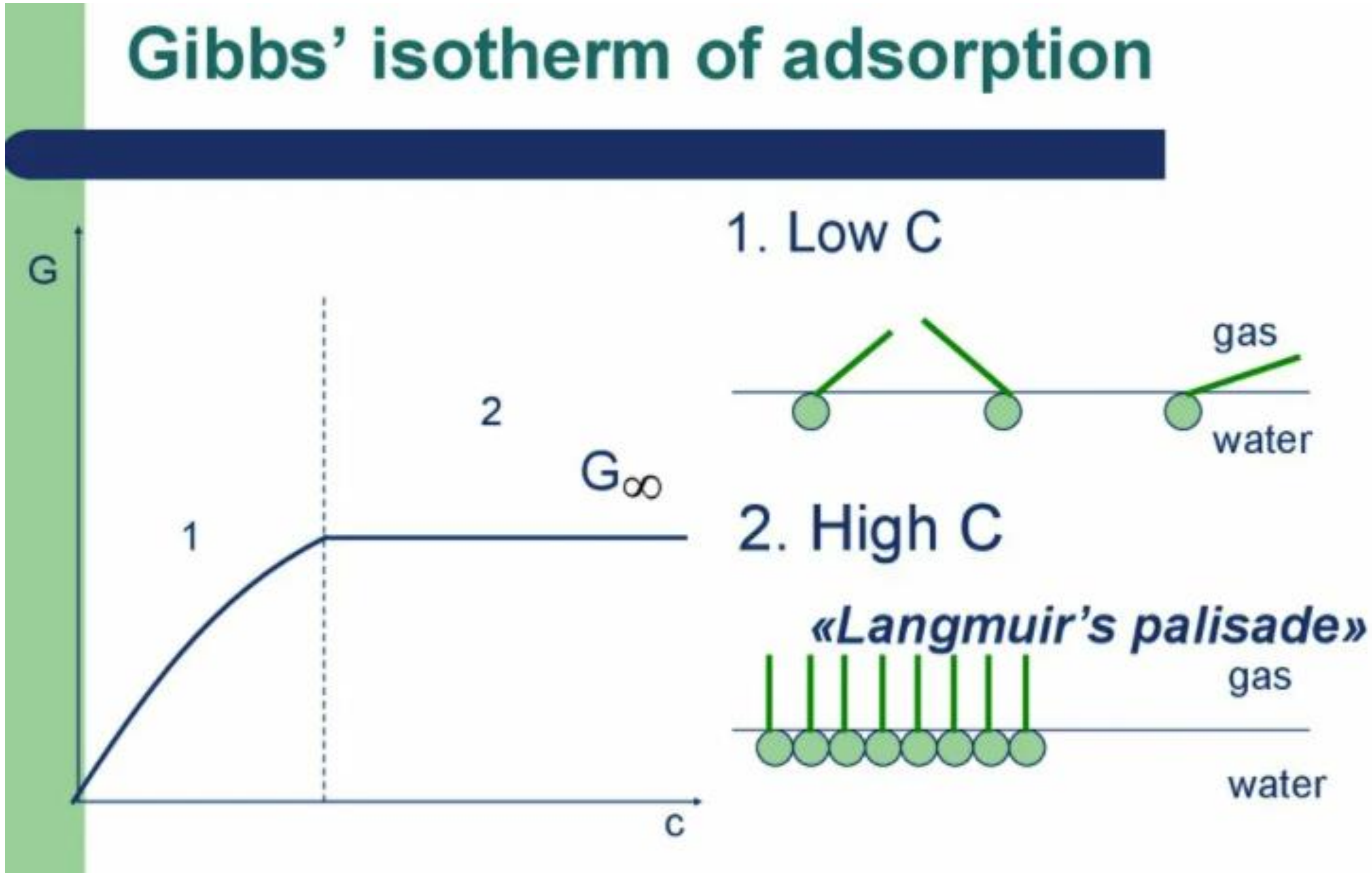
Adsorption isotherm

- Solids have an ability to adsorb molecules, atoms or ions from a surrounding medium on their surface to a certain degree. This adsorption is a spontaneous process when it leads to a decrease in Gibbs free energy of the surface. Substances are adsorbed on the surface that reduces the surface tension with respect to the surrounding medium.
- The amount of gas adsorbed by a given amount of adsorbent depends on the nature and on the pressure of the gas. All the other conditions being equal, the effect of pressure on the amount of gas adsorbed can be depicted by the curve, which is called adsorption isotherm.

Adsorption of gases on solids



Adsorption of gases on solids



Gibbs' isotherm of adsorption

1. Low C

2. High C

«Langmuir's palisade»

Monomolecular adsorption theory. Langmuir Isotherm.

- A solid has a uniform surface
- Adsorbed molecules don’t interact with one another and can’t move on a surface
- Adsorbed molecules are localized at active centers of adsorbent
- Adsorption is restricted to monolayer coverage
- A gas behaves as ideal one

Monomolecular adsorption theory. Langmuir Isotherm

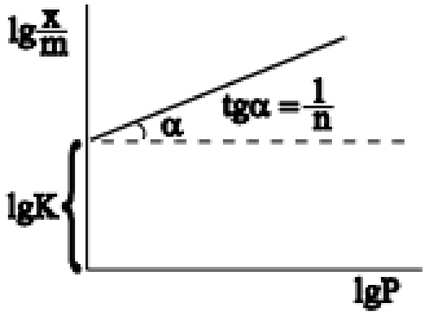
$$\Gamma = \Gamma_{\infty} \frac{KP}{KP + 1}$$

The equation then becomes to **form $\Gamma = \Gamma_{\infty} KP$**, which expresses a direct proportionality between the amount of adsorbed gas and its pressure (. In the high pressure region, on the contrary, the term **KP** becomes much greater than unity, and the latter can be neglected in the denominator. As a result, the equation takes the form **$\Gamma = \Gamma_{\infty}$**, which shows that the quantity of adsorbed gas does not change with pressure. This actually does correspond to the adsorption isotherm at sufficiently high pressure

Freundlich equation

$$\frac{x}{m} = KP^{\frac{1}{n}}$$

$$\lg\frac{x}{m} = \lg K + \frac{1}{n}\lg P$$



- One of the analytical expressions for the adsorption isotherm is the empirical ***Freundlich equation***.
- where P is equilibrium pressure of the gas, K and n are empirical parameters, constant for given adsorbent and gas at constant temperature.
- This equation does not give good results in the low and high pressure regions, but it is in good agreement with experimental data over a wide range of intermediate pressures. ***The Freundlich equation*** also has other shortcomings; it is not supported by any theory and its constants have not a theoretical meaning.

Multilayer adsorption is the most based on BET (Brunauer-Emmet-Teller) therory

- **In multilayer adsorption** the adsorption space accommodates more than one layer of molecules and not all adsorbed molecules are in contact with the surface layer of the adsorbent. Molecules of the first layer are the active sites for the second layer, and so on Micropore filling is the process in which molecules are adsorbed in the adsorption space within micropores.
- Molecules are kept at adsorption layers by physical forces.
- Molecules do not react in the layers.

Multilayer adsorption is the most based on BET (Brunauer-Emmet-Teller) therory

$$\frac{P/P_0}{V(1-P/P_0)}=\frac{1}{cV_m}+\frac{c-1}{cV_m}(P/P_0)$$

Where P - equilibrium pressure

P_0 - saturate vapour pressure of the adsorbed gas at the temperature

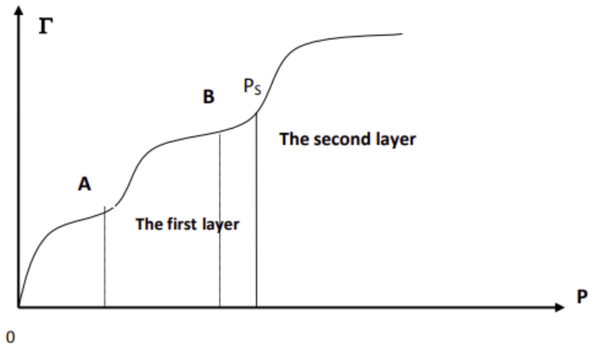
P/P_0 is called *relative pressure*

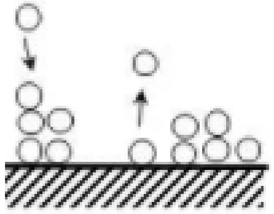
V - volume of adsorbed gas per kg adsorbent

V_m - volume of monolayer adsorbed gas per kg adsorbent

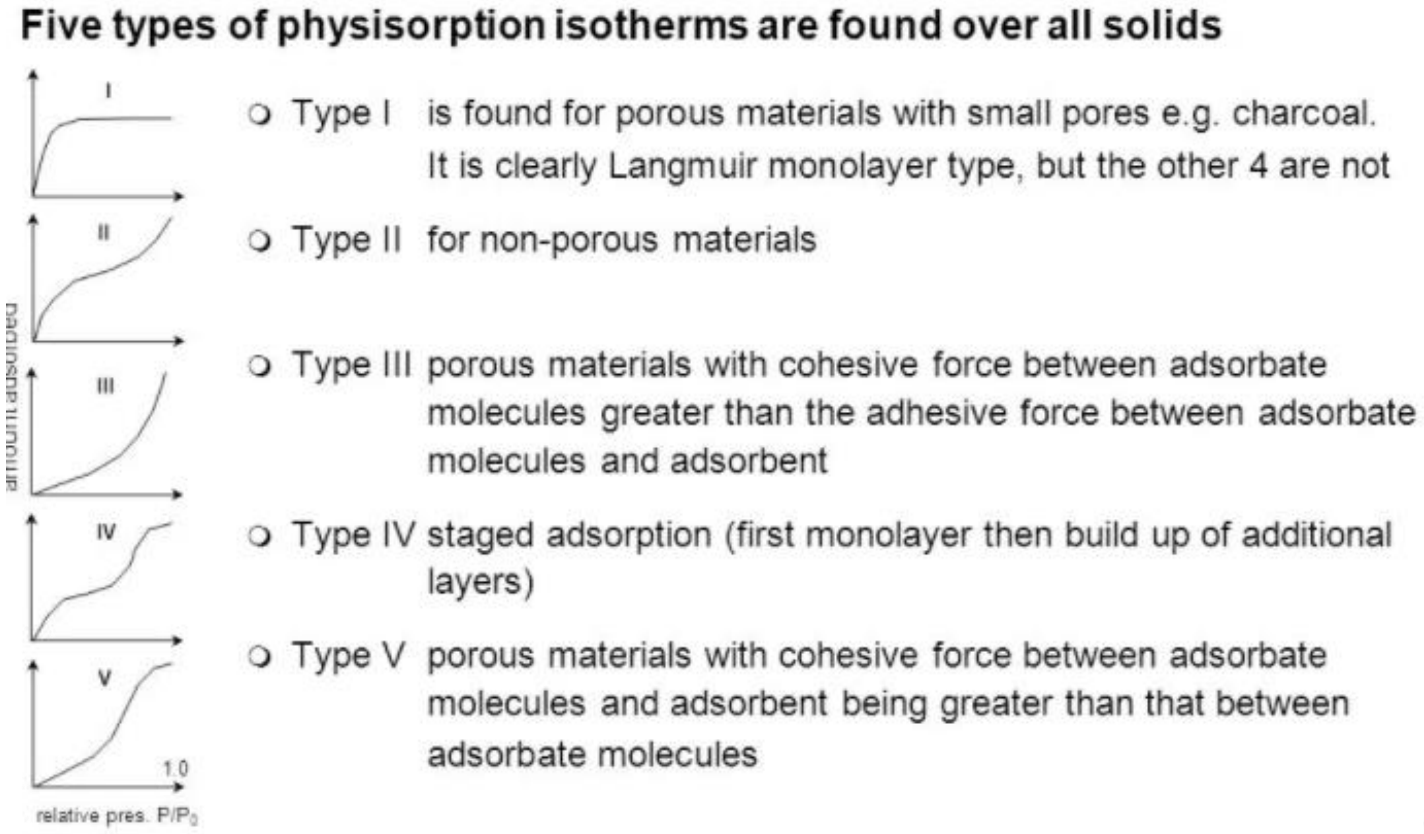
c - constant associated with adsorption heat and condensation heat

Note: for many adsorption systems $c=\exp[(H_1-H_L)/RT]$, where H_1 is adsorption heat of 1st layer & H_L is liquefaction heat, so that the adsorption heat can be determined from constant c.





Adsorption of gases on solids



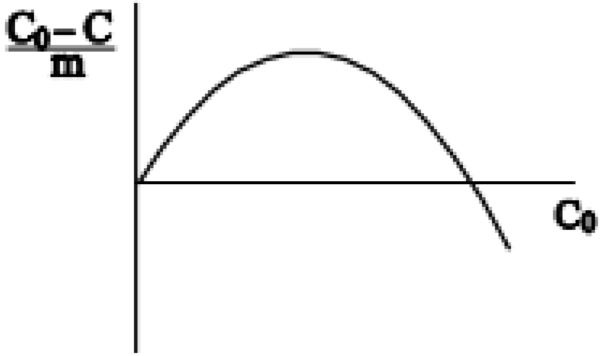
Five types of physisorption isotherms are found over all solids

- Type I is found for porous materials with small pores e.g. charcoal. It is clearly Langmuir monolayer type, but the other 4 are not
- Type II for non-porous materials
- Type III porous materials with cohesive force between adsorbate molecules greater than the adhesive force between adsorbate molecules and adsorbent
- Type IV staged adsorption (first monolayer then build up of additional layers)
- Type V porous materials with cohesive force between adsorbate molecules and adsorbent being greater than that between adsorbate molecules

Adsorption on solids from solution

- Adsorption of the solute is occurs well from dilute solution, and the adsorption of the solvent occurs well from concentric solution.
- The nature of the solid surface involved in the adsorption process is a major factor in determining the mode and extent of solute adsorption. It involves three mainly groups of solids: nonpolar, polar and strongly charged surfaces
- Adsorption of the solute is occurs well from such solution. Adsorption isotherm for case of solution-solid adsorption, where there is a great difference in polarity between the solute and the solvent.

Adsorption on solids from solution



Adsorption isotherm for case of solution-solid adsorption

The experimental evaluation of adsorption of this case involves the measurement of changes in the concentration of the solute in the solution after adsorption has occurred. Adsorption dependence on the concentration (adsorption isotherm). Co is the initial concentration of the solution, and C is the concentration after adsorption, hence their difference shows an amount of the adsorbed solute. As m is the weight of the adsorbent hence (Co–C)/m is equal to Γ. As shown in the diagram, at first adsorption of the solute increases with increasing of concentration, but after certain concentration it becomes decreased.

Electrolytes adsorption on solids from solution

- In adsorption from such solutions ions can be adsorbed as well as neutral molecules. This leads to some peculiar phenomena, when not only adsorption forces but electrostatic ones as well take place in the process.
- Adsorption of ions can occur only on the polar surfaces.
- There are two mechanisms of electrolytes adsorption – **equivalent** and **exchange**.

Electrolytes adsorption on solids from solution

- **In equivalent adsorption** both cations and anions are adsorbed in equivalent amounts.
- First are adsorbed one type of ions either cations or anions. It depends on the nature of the solid surface; first selective adsorbs the ions which is the same of the composition of the solid. For example, if the solid is AgCl and in the solution we have Ag^+ and NO_3^- ions, first Ag^+ ions will be adsorbed because the same ions are in the solid phase.
- Due to it the solid surface obtains the corresponding charge and the ions having the opposite charge also come near to the first layer of ions due to electrostatic forces of attraction. As a result double electrical layer is formed.

Electrolytes adsorption on solids from solution

- **In ion-exchange adsorption** an exchange of ions occurs between the adsorbent and the solution due to ion chemical potential difference between these two phases.
- The adsorbent is adsorbed by certain ions from the solution simultaneously sending other ions but of the same charge from its surface to the solution. In the result the charge of the surface is not changed.
- Adsorbents available for ion exchange are called ion-exchangers. Others, called anion exchangers, exchange various anions for hydroxyl ions. The exchangers themselves are easily recovered: the cation exchangers – by washing with an acid solution, the anion exchangers – with base solutions.
- One of the important properties of the exchangers is the exchange capacity. It is equal to the numbers of ionic groups (which could exchange ions) of the unit weight of the exchanger (mmol/g).