

Physico-Chemistry of Surface Phenomena

In any living organism there is a huge number of heterogeneous systems at the surface of which a lot of biochemical processes take place. All the processes occurring at the border of phase division are called surface phenomena. All surface phenomena can be characterized by low activation energy. This is the reason why biochemical reactions occur at the borders of the division at a high speed at the temperature of the environment.

Surface Energy and Surface Tension

All interfaces are divided according to their aggregate state into two classes:

1. Mobile interfaces:

liquid – gas (l-g) and liquid – liquid (l-l);

2. Immobile interfaces:

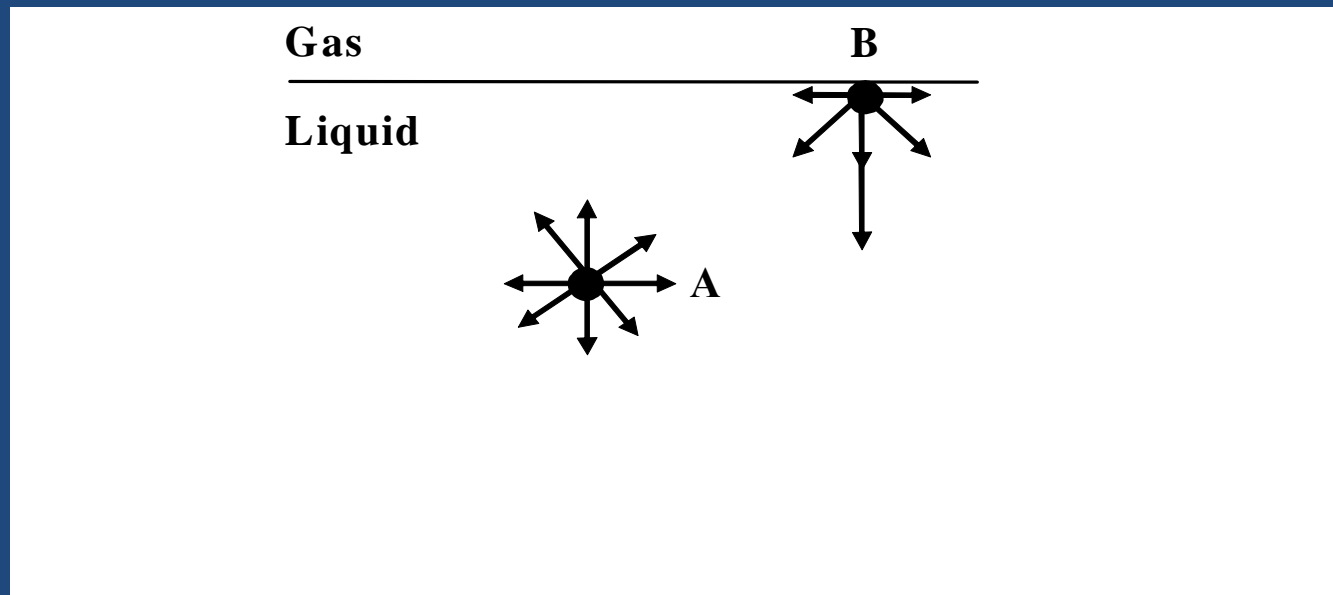
solid – gas (s-g), solid – liquid (s-l), solid – solid (s-s)

Gibbs' surface energy G_s

of the system is proportionate to interfacial area:

$$G_s = \sigma \cdot S,$$

where σ is the constant of proportionality called surface tension, Joul/m^2 ; S – interface area, m^2 .



Intermolecular forces affecting the molecules in the surface layer and in the volume of the liquid.

Let's consider the mechanism of initiation of Gibbs' surface energy by the example of bi-phase water system: water – water vapor (l-g).

1. Intermolecular forces affecting a water molecule A are evenly exhibited by neighboring molecules. The resultant of these forces is equal to 0.
2. The molecule B situated at the interface is influenced by the total attraction forces of a unit of volume of a liquid to a greater extent than by a unit of volume of a gas because of its tenuity.

That's why the resultant of molecular forces for the surface molecules is not equal to 0 but it is directed inside the liquid and as a result of it the surface molecules tend to be drawn into the liquid phase.

The molecules in the surface layer have uncompensated attraction forces and that's why possess excess surface energy.

From the thermodynamic point of view such a condition is not beneficial energetically. The molecules in the surface layer tend to be drawn into the liquid phase and that causes the decrease in interfacial area of phases. This can be explained by the spherical form of small drops and by ideally smooth surface of a liquid in a wide vessel.

The activity directed at the surface increase transfers into the potential energy of molecules in the surface layer which is the surface energy.

The surface energy accounted for a unit of surface area (specific surface energy) is called surface tension (σ): $\sigma = G_s / S$.

In SI system $[\sigma] = [\text{J}/\text{m}^2]$ or $[\text{Newton}/\text{m}]$,
as $\text{Joule} = \text{Newton} \cdot \text{m}$.

Surface tension of different liquids is different and depends on:

- the nature of a liquid,
- the nature of an adjoining phase,
- temperature,
- pressure (if boundary phase is a gas),
- the nature and concentration of solutes.

1. $\uparrow T, \sigma \downarrow$. With the increase in temperature surface tension decreases and at the temperature of boiling the boundary between the phases disappears and the system gas-liquid becomes homogeneous. That's why the value of surface tension is the measure of both heterogeneous systems either gas-liquid or liquid-liquid.
2. $\uparrow p, \sigma \downarrow$. With the increase in pressure surface tension at the border liquid-gas decreases as the molecular concentration in the gaseous phase increases and the energy excess of molecules on the surface decreases.

3. Dissolved substances depending on their nature can influence the surface tension of liquids in different ways. The ability of dissolved substances to change the surface tension of a solvent is called surface activity.

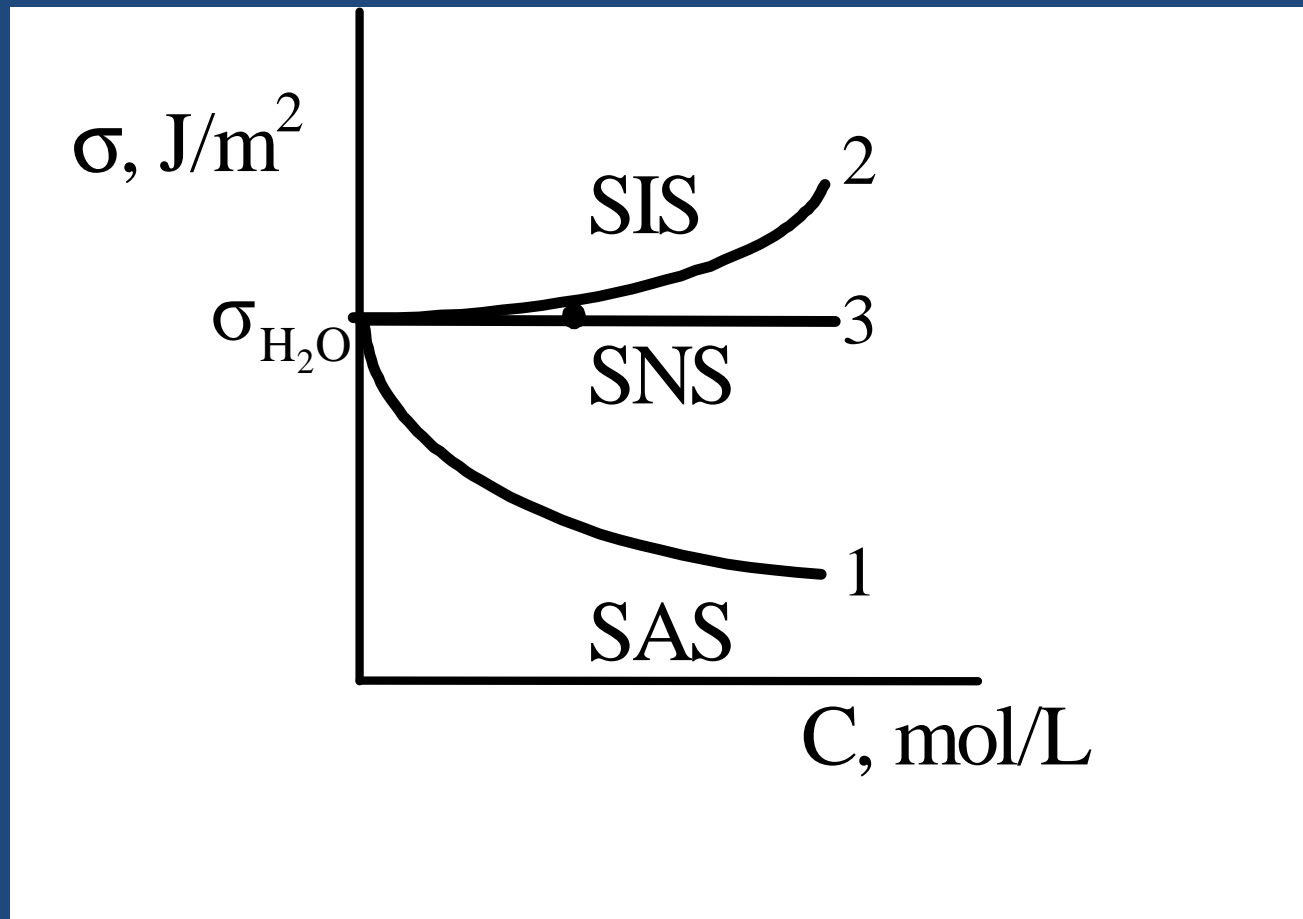
According to the ability to change the surface tension all the substances are divided into three groups:

I. Surface-active substances (SAS) which reduce the surface tension of a solvent. With respect to water SAS are a number of organic substances: alcohols, acids of aliphatic series and their salts (soaps), esters, amines, proteins and so on. $\uparrow C$ (SAS), $s \downarrow$.

II. Surface-inactive substances (SIS) which increase insignificantly the surface tension of a solvent. With respect to water SIS are a number of inorganic acids, bases, salts and some organic substances like glycine (aminoacetic acid). $\uparrow C \text{ (SIS)}, s \uparrow$.

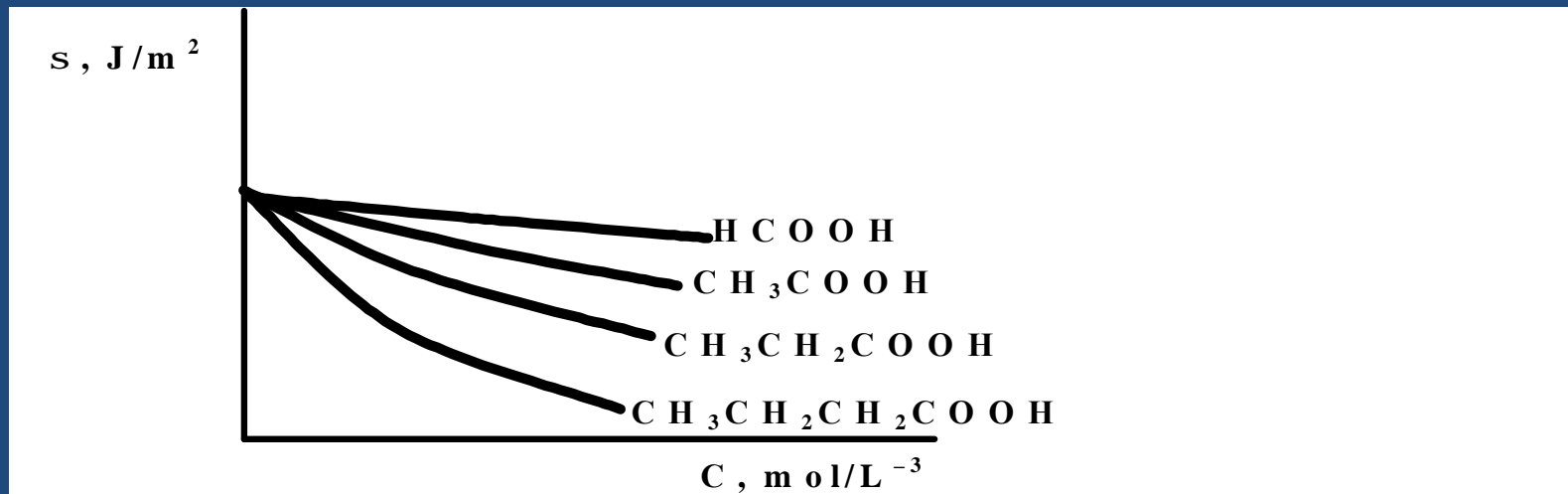
III. Surface-non-active substances (SNS) which don't change the surface tension at all. With respect to water SNS is saccharose and some other substances. $\uparrow C \text{ (SNS)}, \Delta s = 0$.

The dependence of surface tension change of substance aqueous solutions on their concentration is called isothermal curve of surface tension, ($T=\text{const}$).



Ducklo-Traube rule.

Surface activity of substances in the same homologous series increases » three times with the increase in hydrocarbon chain in $-\text{CH}_2-$ group (for diluted aqueous solutions). At the same time the surface tension of their solutions decreases.



Set of isotherms of surface tension for aqueous solutions of homologous series of fatty acids.

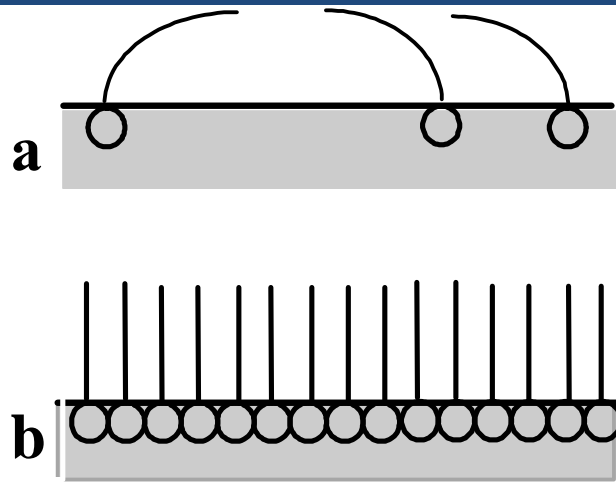
SAS molecules consist of non-polar hydrocarbon part and the polar one represented by the following functional groups $-\text{COOH}$; $-\text{OH}$, $-\text{NH}_2$ and others. Such substances are called diphilic.

Diphilic SAS molecules are denoted by symbol $\text{—}\bigcirc$, where a circle is a polar group and a dash is a non-polar radical.

Orientation of SAS Molecules in the Surface Layer.

Structure of Biological membranes

The polar group having a great similarity to polar phase (e.g. water) is drawn into it. The non-polar group is pushed out into the non-polar phase (gas).

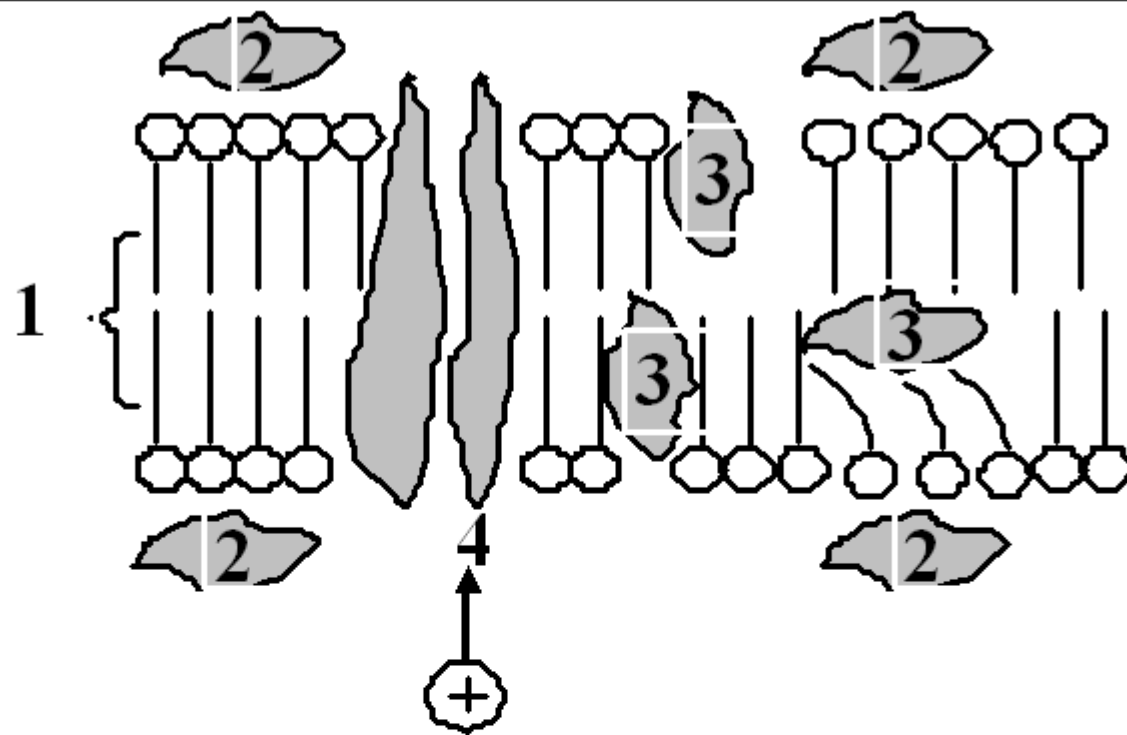


Monomolecular layer structure.

C_1

$C_2 > C_1$

C_2



Mosaic structure model of a biological membrane:

- 1 – lipid bilayer;
- 2 – surface proteins;
- 3 – integral proteins;
- 4 – ionic channel

Adsorption at the Mobile Interface of Phases

The spontaneous change of solute concentration at the interface of phases is called adsorption.

Its value is calculated with the help of Gibb's equation:

$$\Gamma = - \frac{\Delta\sigma}{\Delta C} \cdot \frac{C}{RT} ,$$

where Γ is the amount of substance, adsorbed by a unit of interface of phases, mol/m²; C is the equilibrium molar concentration of a solute, mol/L, R is the gas constant equal to 8,341 J/mol·K; $\Delta\sigma = \sigma_2 - \sigma_1$ changes in the surface tension in the solution; concentration change of a solute: $\Delta C = C_2 - C_1$.

Analysis of Gibb's equation

The minus shows the inverse interdependence between the value of Γ and the s .

1. If $s_2 < s_1$ then $Ds / DC < 0$ and $\Gamma > 0$, i.e. the adsorption is positive (substance is accumulated at the interface), it's characteristic of SAS.
2. If $s_2 > s_1$ then $Ds / DC > 0$ and $\Gamma < 0$, i.e. the adsorption is negative (substance is accumulated in the volume), it's characteristic of SIS.

The adsorption of a substance is a reversible process which finishes up with the establishment of adsorption equilibrium when the rate of adsorption is equal to the rate of the reverse process, i.e. desorption.

- *Adsorption at the Immobile Interface of Phases
(at the surface of a solid)*

A solid at the surface of which another substance is accumulated is called the adsorbent and the adsorbed substance is called the adsorptive.

Separate atoms or groups of atoms standing out on the adsorbent surface are called active centers.

They have a great amount of Gibbs' surface energy and the adsorption takes place on them first of all.

We should differentiate between chemical and physical adsorption.

At physical adsorption adsorbent and adsorptive interact due to Van der Waals forces. This adsorption occurs spontaneously, it's reversible and not very specific. With the increase in temperature the physical adsorption decreases.

The interaction energy at physical adsorption is 10 – 40 kJ/mol.

At chemical adsorption (chemisorption) there is a chemical bond between adsorbent and adsorptive and each of the two loses its individuality. This adsorption is similar to a chemical reaction and is usually accompanied by the formation of compounds at the interface of phases.

The interaction energy at chemical adsorption is 40 – 400 kJ/mol.

Chemisorption is often irreversible. At chemical adsorption instead of the adsorbed substance another substance can be desorbed.

Adsorption depends on:

1. the nature of adsorbent and adsorptive,
2. temperature,
3. specific surface area of adsorbent,
4. pressure of adsorptive (for gas adsorption),
5. the nature of solvent,
6. the concentration of adsorptive in the solution (for adsorption from the solutions).

The Rule

Non-polar adsorbents like graphitic carbon or activated coal adsorb non-polar organic substances better.

Polar adsorptive are better adsorbed at the surface of polar adsorbents like, for example, silica gel, aluminum oxide, cellulose and others.

At the same mass of the adsorbent adsorption increases with the increase of specific surface area (i.e. grinding) of adsorbent.

To describe adsorption on the surface of a solid or a liquid we can use a great number of equations but the most frequently used are the equations of Langmure and Freindlikh.

The monomolecular adsorption theory was suggested in 1915 by an American physicist and chemist

I. Langmure and it contains the following ideas:

1) Particles of a substance are situated only on the active centers of the adsorbent.

2) Each particle of the adsorptive occupies one active center of the adsorbent.

3) Adsorption finishes with the formation of a monomolecular layer.

4) In a certain period of time the adsorbed molecules leave the active centers and are replaced by other molecules, i.e.: adsorption \rightleftharpoons desorption.

5) It is assumed that there is no interaction between the adsorbed molecules.

Based on these postulates Langmure suggested the equation of adsorption isotherm:

$$\Gamma = \Gamma_{\infty} \frac{C}{K + C} \quad \text{Langmure's equation.}$$

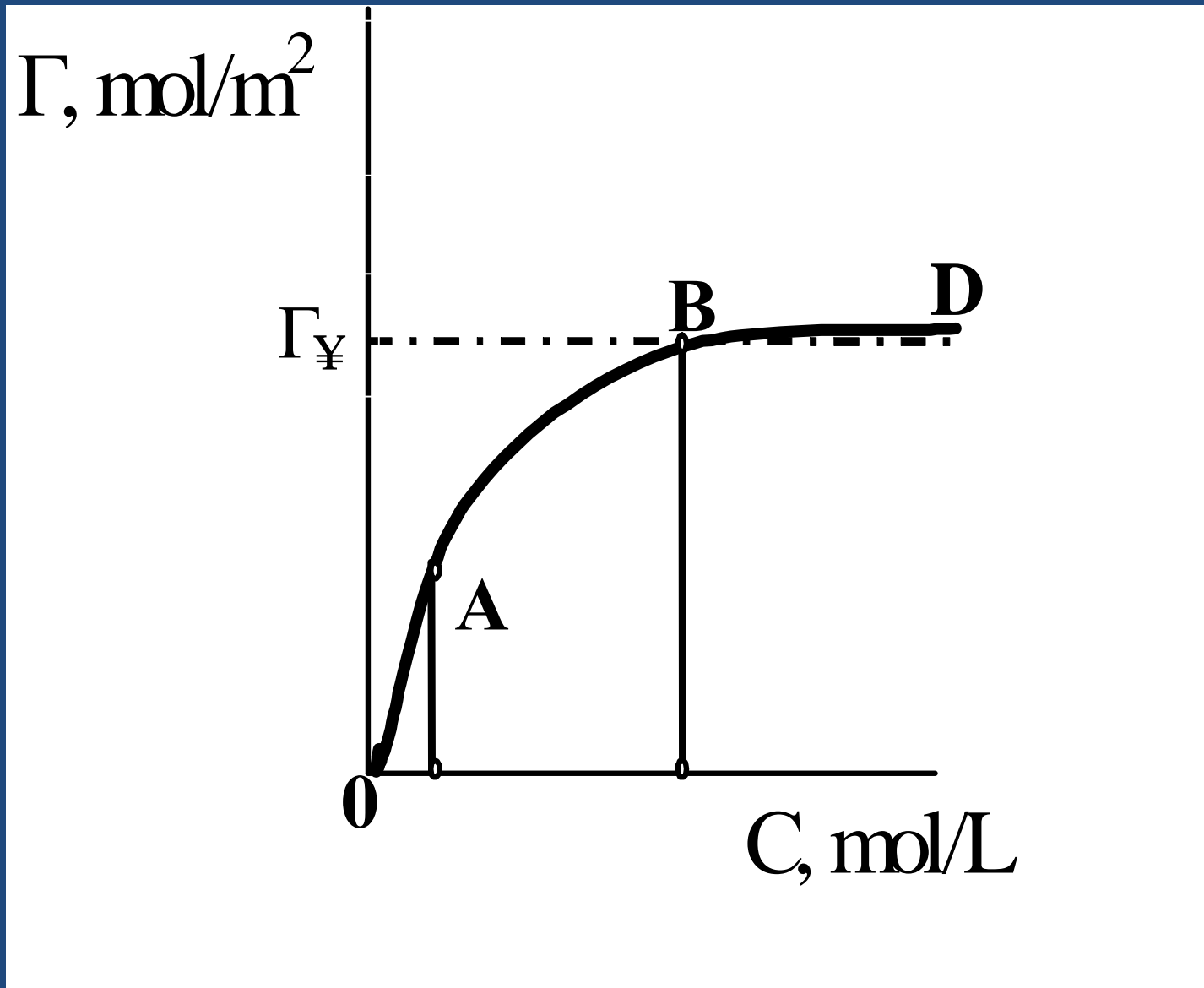
Where:

Γ_{∞} is a constant equal to the maximum adsorption, observed at relatively big equilibrium concentrations, mol/m²;

K is the constant equal to the ratio of the constant of desorption rate to the constant of adsorption rate;

C is the equilibrium solution concentration, mol/L.

Langmuire's adsorption isotherm.



Analysis of Langmuire's equation.

1. At very small concentrations ($C \ll K$) the value C in the denominator of the equation can be neglected and the equation has a linear form: $\Gamma = \Gamma_{\infty} \frac{C}{K}$
i.e. the dependence between the adsorption and the concentration is illustrated by a line which goes through the initial point of data lines (section 0A on Langmuire's adsorption isotherm).

2. If the concentration is high ($C \gg K$), the value K in the denominator of the equation can be neglected and then $\Gamma = \Gamma_{\infty}$ i.e. the amount of adsorbed substance reaches its maximum and doesn't depend on the concentration (section BD).

When $K=C$, then $\Gamma = \frac{1}{2} \Gamma_{\infty}$. As it appears from this, constant K in Langmure's equation is quantitatively equal to such equilibrium concentration when one half of active centers at the adsorbent surface is occupied by adsorptive molecules and the other half is free.

At medium concentrations Langmure's equation doesn't illustrate adsorption quantitatively (the parabolic section AB of adsorption isotherm).

Friendlikh's equation.

$$\Gamma = Kp^{1/n} \quad \text{or} \quad \Gamma = KC^{1/n}, \quad [\Gamma] = [\text{mol/gram}].$$

Where:

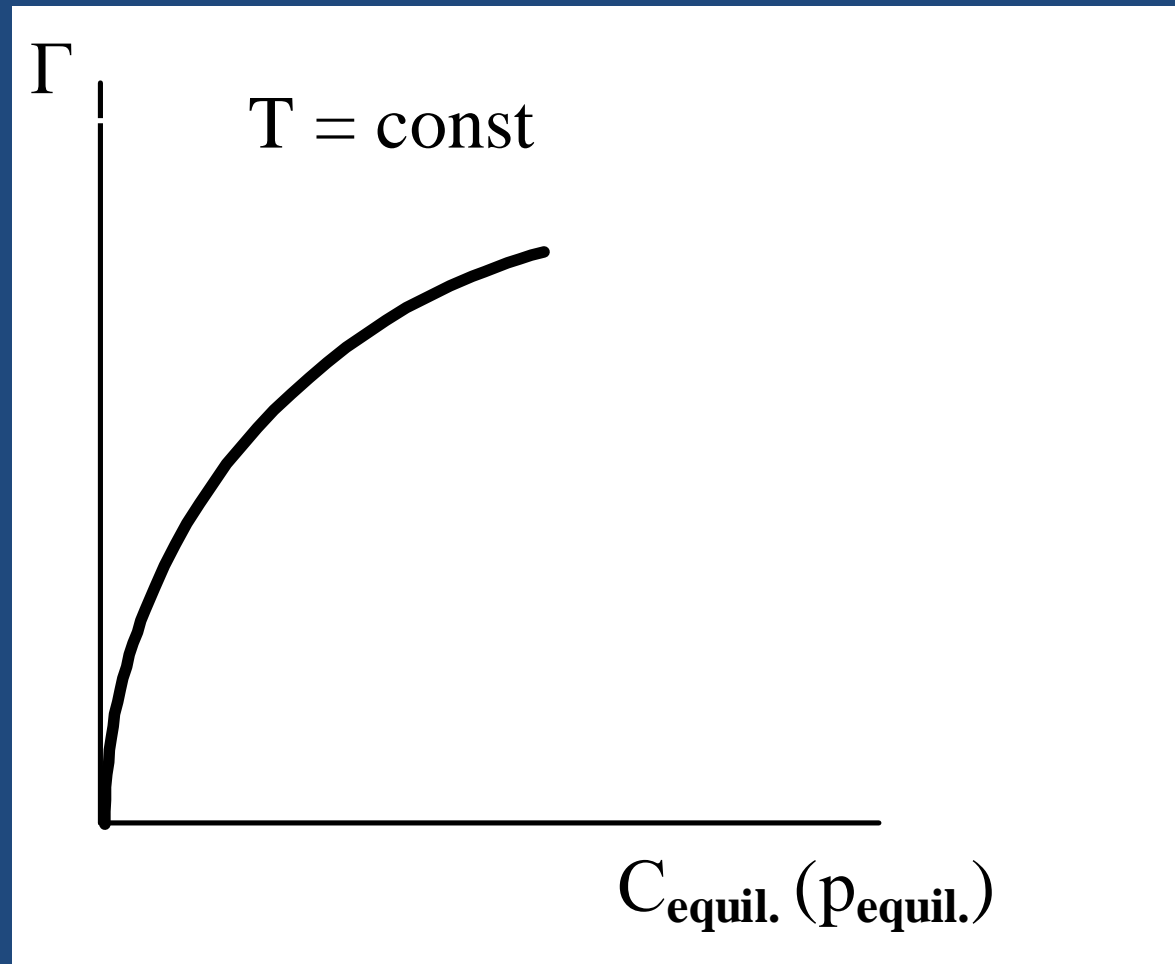
p is the equilibrium gas pressure in the system;

C is the equilibrium concentration;

K and $1/n$ are the constants.

Friendlikh's equation is the equation of a parabola and can't explain the almost linear increase of adsorption at low concentrations and the maximum adsorption value independent on the concentration.

Friendlikh's adsorption isotherm

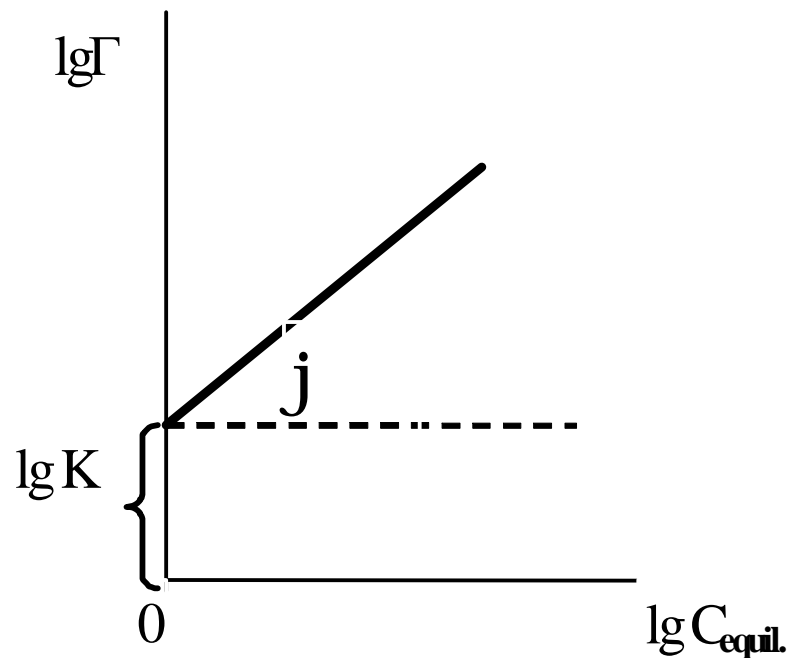


Friendlikh's equation can be used only for the interval of medium pressure and concentration.

Graphic estimation of constants in Freundlich's equation

the isotherm drawn in logarithmic coordinates:

$$\lg \Gamma = \lg K + 1/n \lg C .$$



The dependence of $\lg \Gamma$ on $\lg C$ is expressed by a straight line. The segment cut off by the line on the y-coordinate is equal to $\lg K$, and the tangent of angle (φ) of slope of the line to the x-coordinate is equal to $1/n$.

Medical-biological importance of surface phenomena and adsorption.

ü Water is the most frequently used solvent. It has great surface tension ($72,75 \text{ J/m}^2$ at 20°C) that's why with respect to it many substances are surface-active ones. The surface tension of biological fluids (e.g. blood serum) is less than that of water because of the presence of different SAS (acids of fatty series, steroids and so on) in biological fluids. These substances are accumulated (absorbed) spontaneously at vessel walls, cell membranes, which makes it easier for them to penetrate through these membranes.

ü Adsorption of substances and different gases plays a great role in the living processes. For example, due to great specific surface area of erythrocytes they are as quickly saturated with oxygen in lungs as liberated from excess of carbon dioxide. This is the reason of quick poisoning of organism by toxic fumes and gases. Medical substances are easily adsorbed on the erythrocytes surface and are transported by blood to organs and tissues.

ü Adsorption processes are used for the excretion of toxic substances from the organism. With this purpose blood, plasma and lymph are run through a layer of adsorbent. These processes are called hemosorption, plasmasorbption, lymphosorbption.