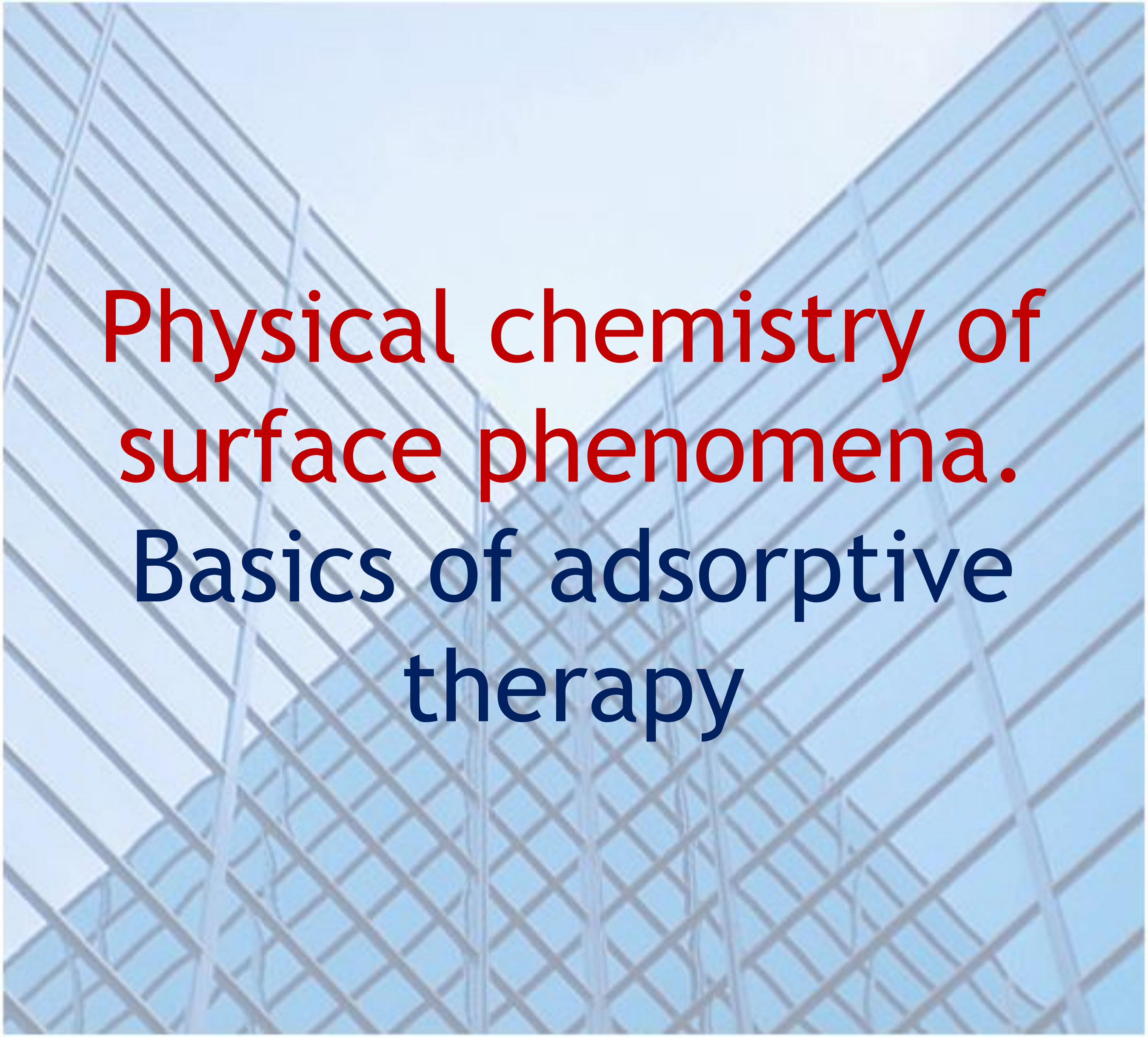
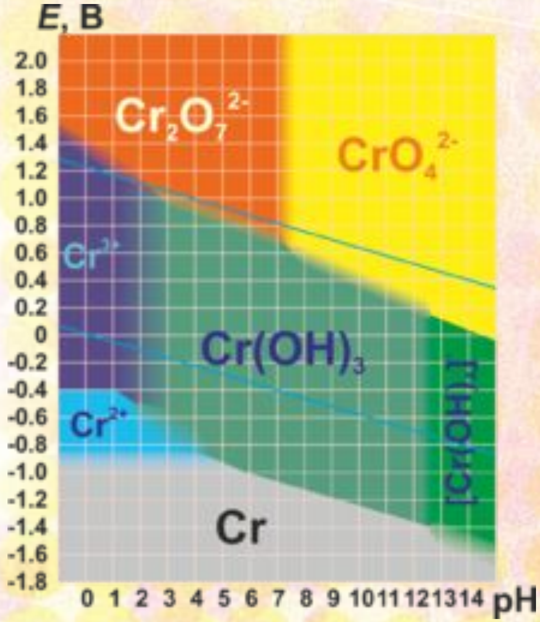


Physical chemistry of surface phenomena. Basics of adsorptive therapy

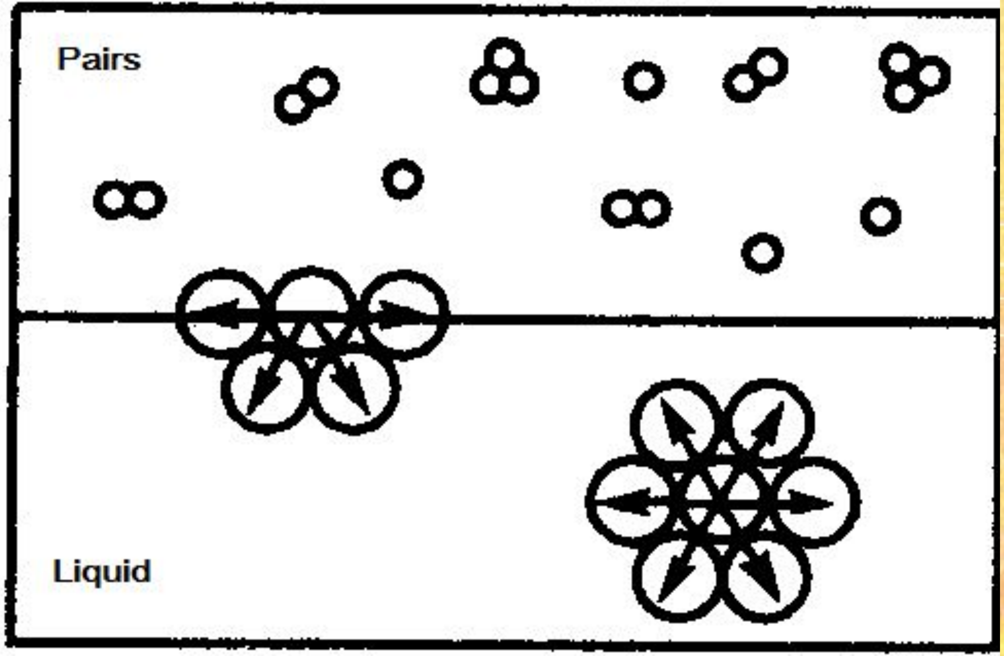
SURFACE PHENOMENA

are phenomena associated with the existence of interphase boundaries.



SURFACE PHENOMENA ARE STUDIED BY COLLOID CHEMISTRY

Surface phenomena



- Inside the fluid forces are balanced
- From the side of gas resultant is directed into the interface between the liquid and the liquid tends to decrease

Surface phenomena

- The increased surface area of the phase separation is associated with the transition of molecules from the depth of the phase on the surface. This work of dW is proportional to the square of the formed surface dS:

$$-dW=\sigma\cdot dS$$

σ- the coefficient of proportionality, called surface tension.

THE SURFACE ENERGY
THE SURFACE TENSION

Surface tension σ is the work required for the creation of 1 m^2 of surface

$[\sigma] = J/m^2$

Surface tension is the excessive energy, referred to a unit surface area of the phase separation $\boldsymbol{\sigma = E/S}$

Surface tension

Surface tension depends on:

- the nature of fluid
- $\sigma(H_2O)=72{,}8\ J/m^2$; $\sigma(serum)=45{,}4\ J/m^2$).
- temperature (↑t ↓σ , when $t_{boil.}$ $\sigma = 0$).
- pressure (↑p ↓σ).
- the concentration of the dissolved substance.

SORPTION

Medical & biological importance:

1. Assimilation of nutrients and drugs
2. Transfer of O_2 and CO_2 from the lungs to the tissues
3. The action of enzymes
4. Detoxification:
   a) Hemosorption - blood purification
   b) lymphosorption – lymph purification.
5. Absorption of toxic substances in the gastrointestinal tract (enterosorption).
6. Chromatography:
   - Separation of mixtures of aminoacids;
   - Cleaning of drugs;
   - Quantitative determination of vitamins, hormones;
   - Diagnosis of diseases

Sorption -change in the concentration of one or more components in heterogeneous systems

- **Sorption -** the process of absorption of one substance by another
- **Sorbent -** absorber
- **Sorbtiv (sorbate) -** absorbed substance
- **Adsorption -** absorption by sorbent surface
- **Absorption -** absorption by the entire volume of the sorbent

Adsorption

- ***<u>Adsorption</u>* is spontaneous change of component concentration in the surface layer compared to the volume of a phase**

Gibbs Equation

$$G = -\frac{a}{RT} \cdot \frac{d\sigma}{da}$$

G - the amount of adsorbed substance [mole/m^2]
a – equilibrium activity of the substances in solution [mole/l]
R - universal gas constant = 8,31 J/моль·(°K)

$\frac{d\sigma}{da}$ - surface activity of the dissolved substance.

$$G = -\frac{c}{RT} \cdot \frac{\Delta\sigma}{\Delta c}$$

G - the amount of adsorbed substance [mole/m^2]
c – the concentration of the substance in solution [mole/l]
R - universal gas constant = 8,31 J/моль·(°K)

$$G = -\frac{p}{RT} \cdot \frac{d\sigma}{dp}$$

G - the amount adsorbed substance [mole/m^2]
p – the equilibrium gas pressure, Pa
R - universal gas constant = 8,31 J/моль·(°K))

Surface activity

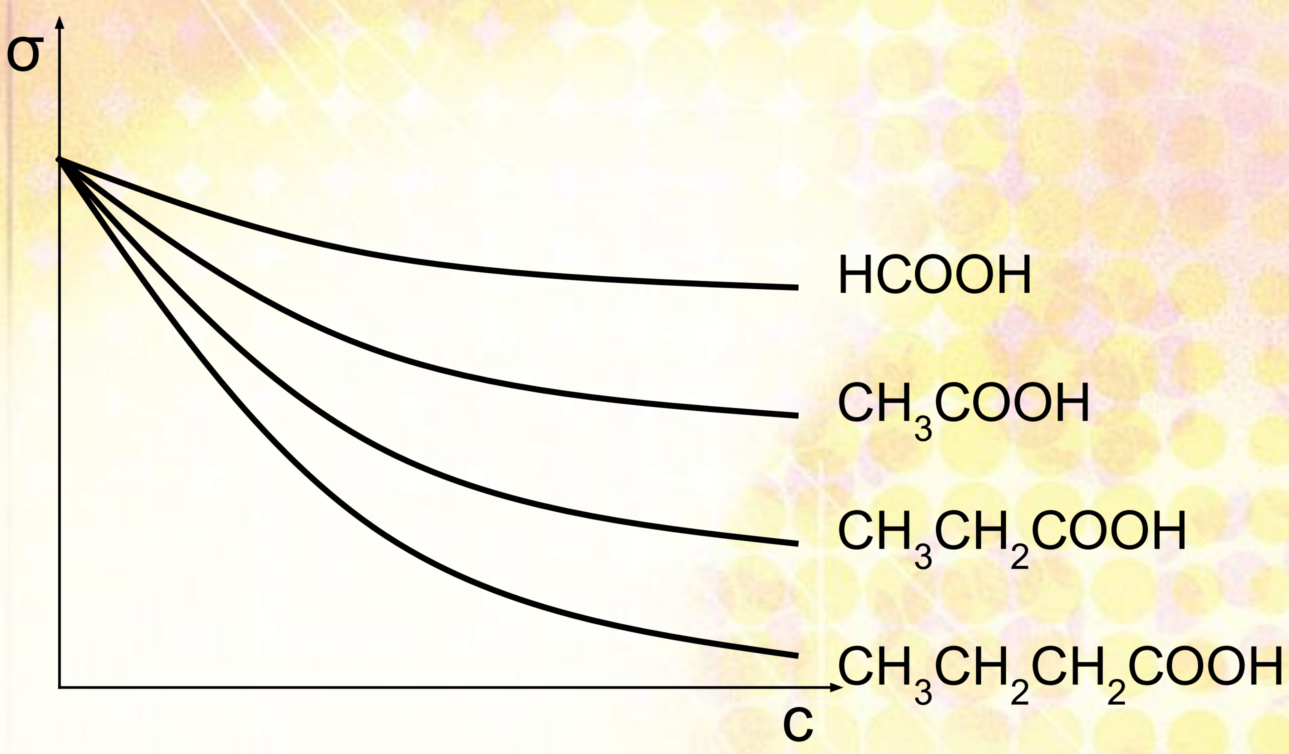
The ability of the solute to change surface tension is called **surface activity** (γ)

The measure of surface activity :

$$\gamma = -\frac{d\sigma}{dc}$$

Traube-Duclos rule:

When extending the chain-CH_2 - in homological series of surface activity increases in 3-3,5 times, respectively, increases the ability to adsorption.



SAS, SIS, SNS

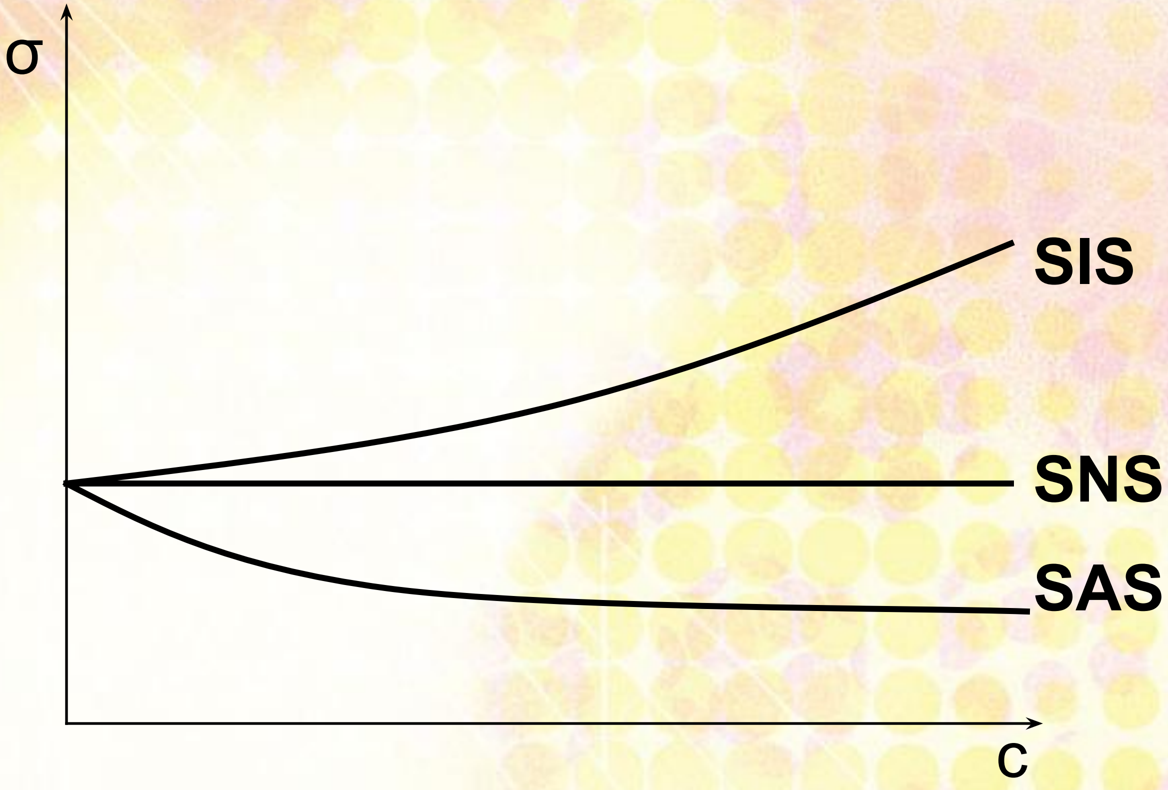
1. **Surface-active substances (SAS):**
   reduce σ solvent. σ solution < σ solvent; g> O.
   SAS: alcohols, organic acids, esters, proteins, cholesterol, fats, lipids, soaps.

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.

The isotherm of surface tension

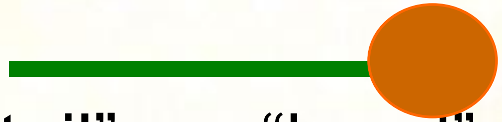
The dependence of σ on the concentration the dissolved substance at a constant temperature is called **isotherm of surface tension.**



The structure of SAS molecules:

SAS molecule consists of:

- non-polar hydrophobic hydrocarbon group (“tail”)
- polar hydrophilic group (“head”):
  $-OH$, $-COOH$, $-C(O)-O$,$-NH_2$; $-SO_3H$.

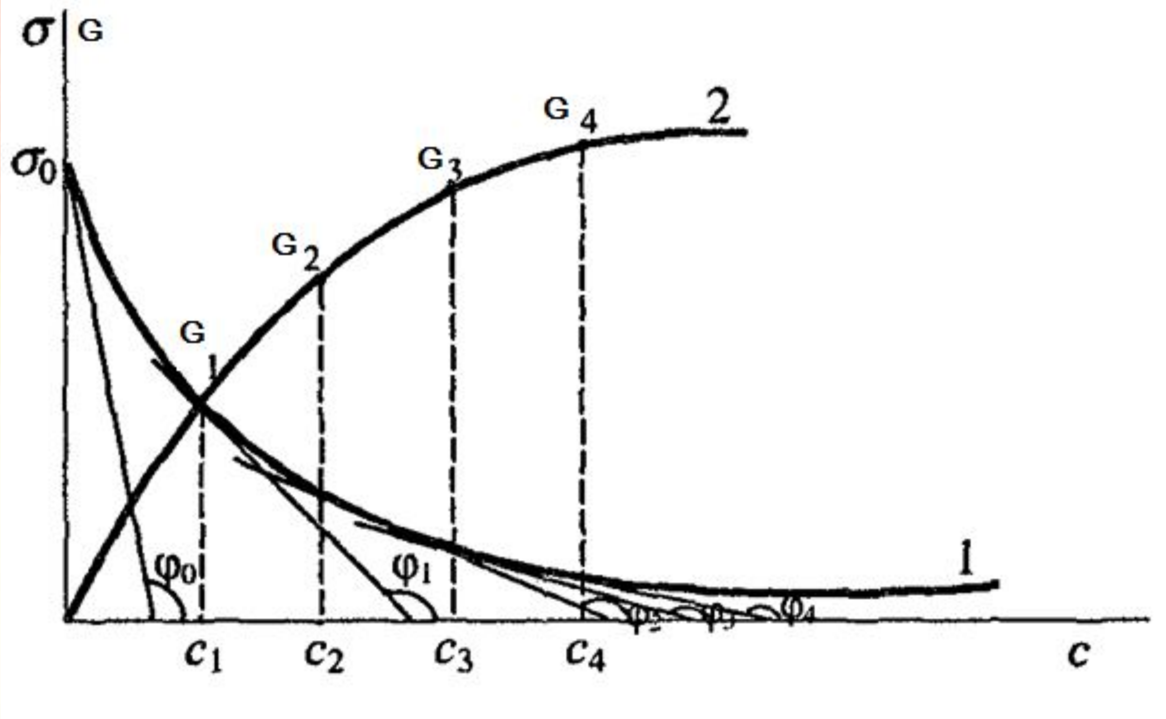


ADSORPTION ON THE SOLUTION-GAS BORDER

Calculation of the adsorption isotherm

$G = f(c)$

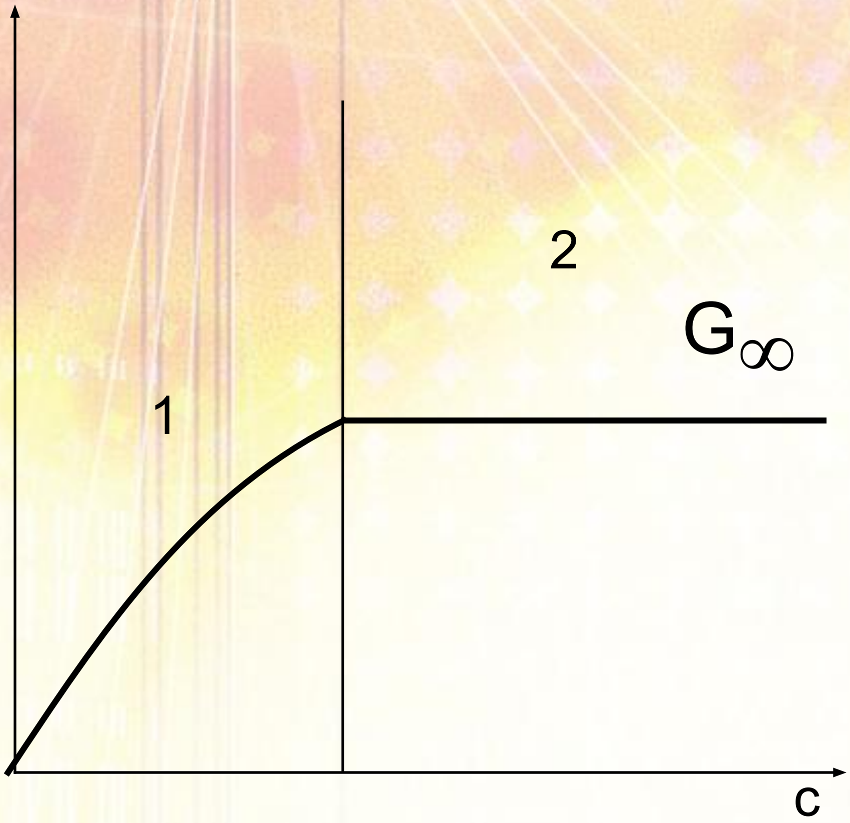
For the calculation of the adsorption isotherm you are to plot the dependence σ from c.



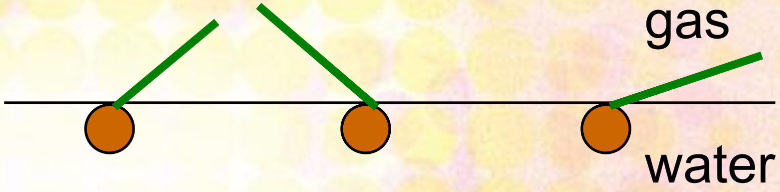
1-the isotherm of surface tension,

2-adsorption isotherm

Gibbs’ isotherm of adsorption

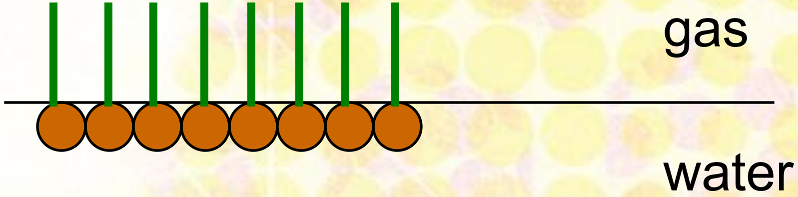


1. Low C



2. High C

«Langmuir’s palisade»



ADSORPTION ON THE SOLID-GAS BORDER

Adsorption by solids

The adsorption value depends on:

1. ***The size of the adsorbent surface***

*if S↑ surface then adsorption ↑****.***

2. ***Temperature*** (↑t ↓G).
3. ***Type of sorbent*** *affinity thereof to the solvent.*
   - *Hydrophilic.*
   - *Hydrophobic.*
4. ***Charge of the adsorbent and the adsorptive***.
5. ***Adsorptive concentration.***

Freundlich equation

$A = x/m = k \cdot p^{1/n}$ $G = x/m = K_F \cdot C^n$

x – the amount of substance of the adsorptive (mole)

m – mass of adsorbent

p – equilibrium gas pressure,

C – equilibrium concentration in the system

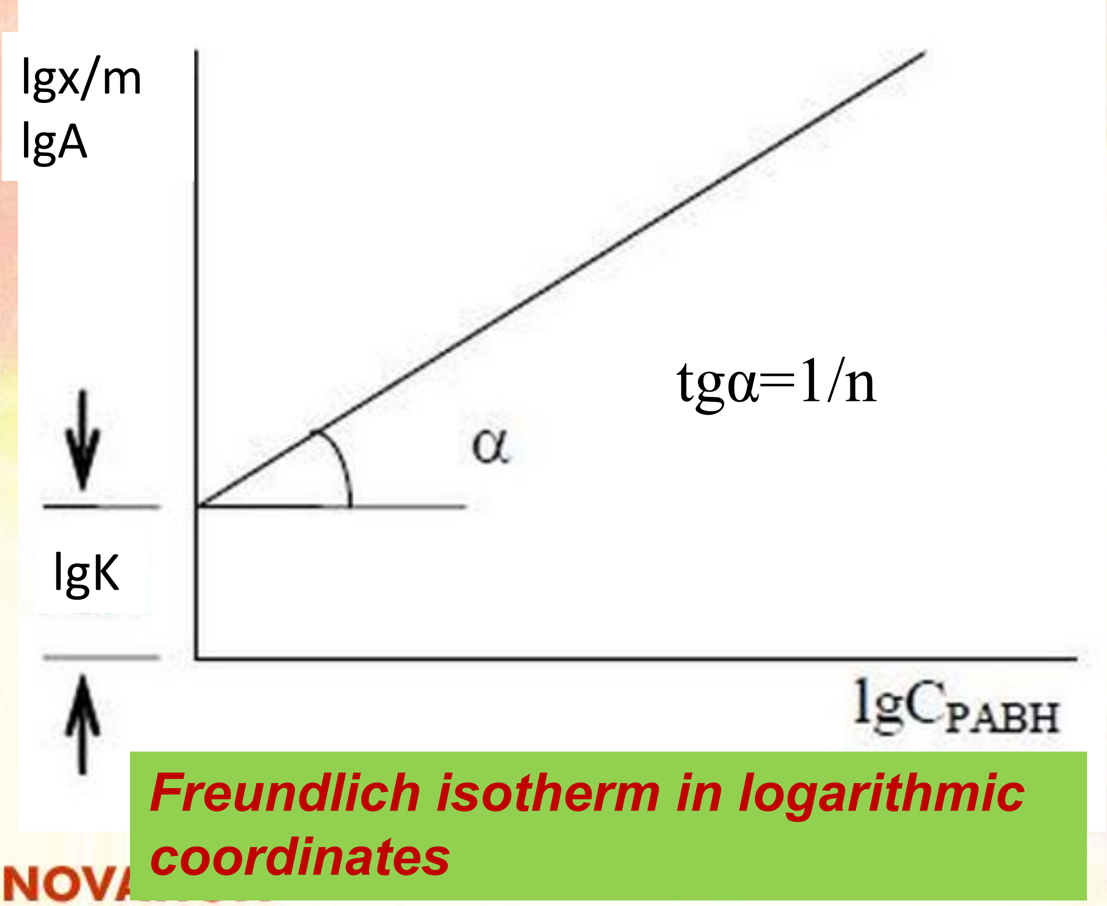
V adsorption = V desorption

к – Freundlich constant, к = A at p = 1

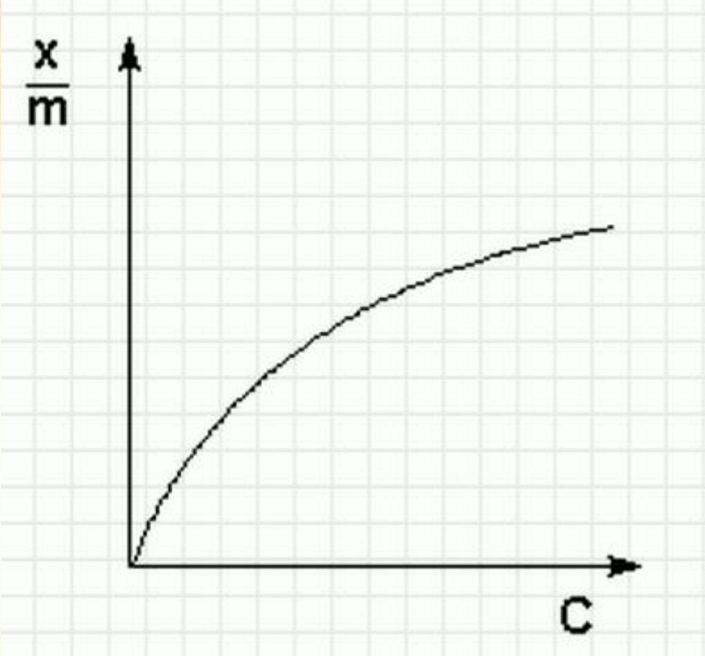
n – empirical constant.

Determination of the constants in the Freundlich equation

- ***$\lg A = \lg k + 1/n \lg c$***



Freundlich isotherm in logarithmic coordinates



Freundlich isotherm in conventional coordinates

The theory of Langmuir

1) On each absorption place on the surface of the adsorbent can be only one molecule or adsorption is localized on the adsorption centers.

2) Adsorption is monomolecular, i.e. is carried out only in one layer.

3) Adsorption surface is homogenious.

4) Between the adsorbed molecules there is no interaction.

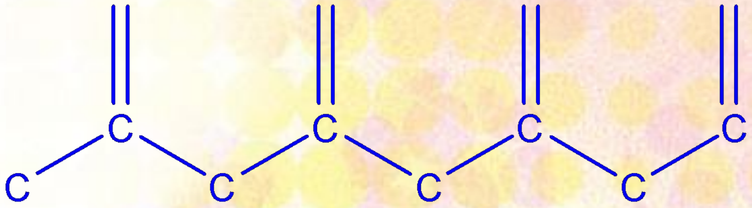
5) Adsorption is a reversible process.

The theory of Langmuir

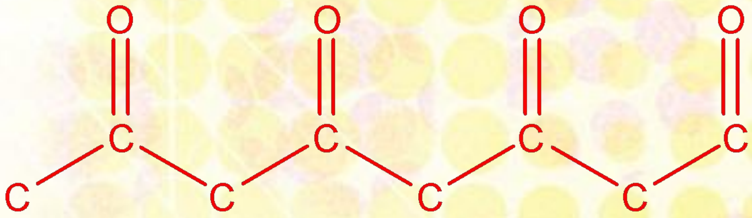
According to this theory localization adsorption can be represented of the quasichemical equation similar to the chemical reaction:

$$A + B \rightleftharpoons AB$$

Where A is adsorption center, B is molecule of substance AB is adsorption complex.



For example to the atoms of carbon, having free valences oxygen atoms can join



Langmuir equation

$$A = A_{\infty} \frac{\text{К}C}{1+(\text{К}C)} \qquad \text{for gases : } G = G_{\infty} \frac{\text{К}p}{1+\text{К}p}$$

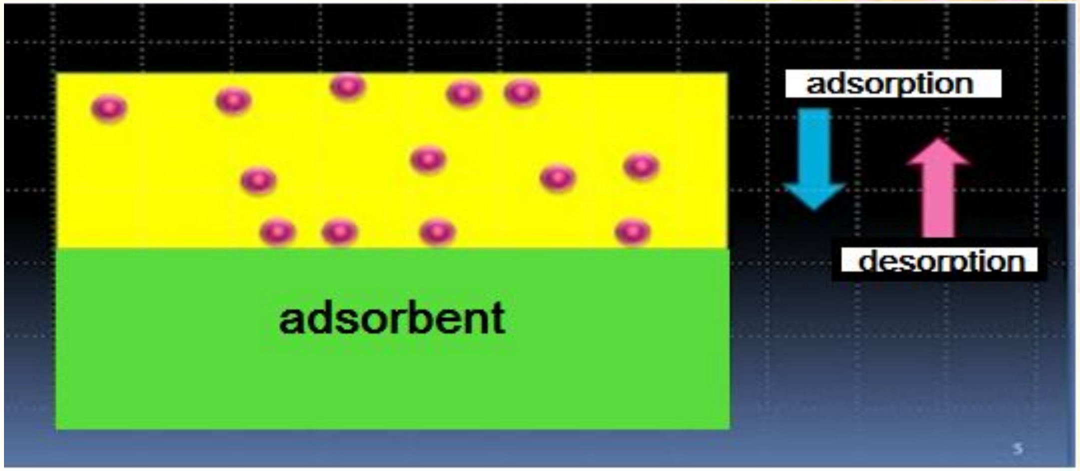
C – concentration

P - gas pressure

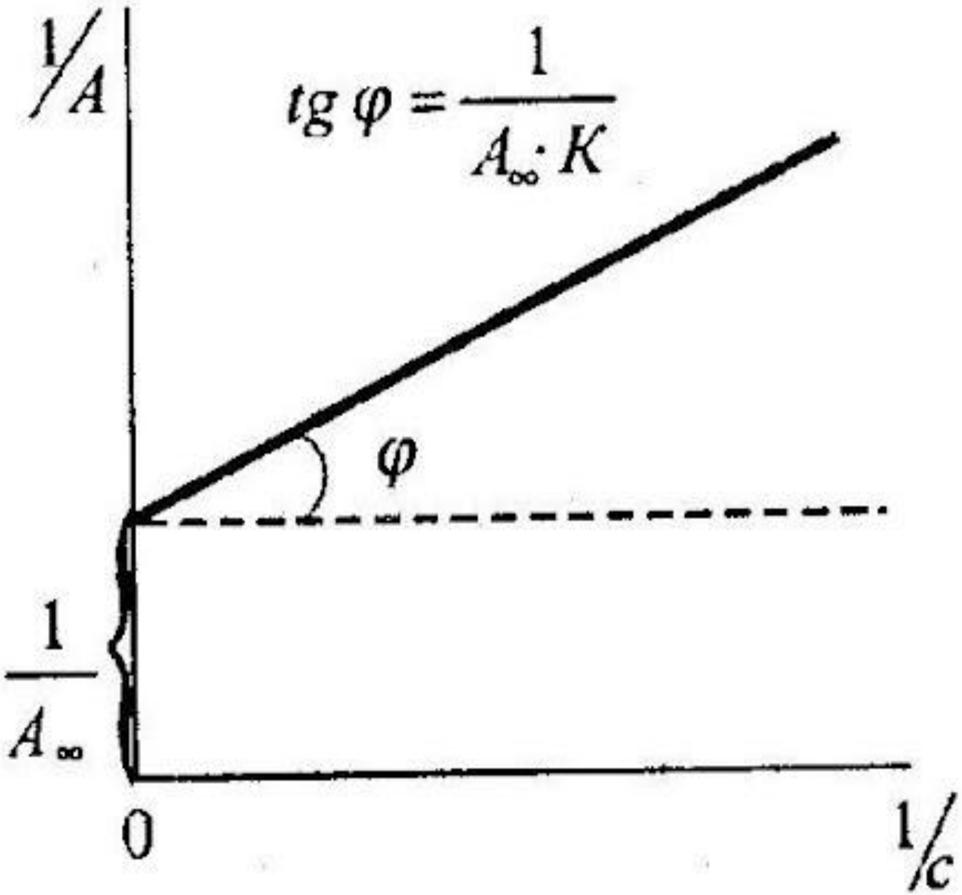
К - adsorption equilibrium constant $= \frac{\text{Кdesorption}}{\text{Кadsorption}}$

at C << К $A = A_{\infty} \frac{C}{\text{К}}$, linear dependence of G on C

at C > К $G = G_{\infty}$, further increasing the concentration does not affect the adsorption.



$$\frac{1}{A} = \frac{1}{A_\infty} + \frac{1}{A_\infty \cdot K} \cdot \frac{1}{c}.$$



To find the constants A ∞ and K linear formula of Langmuir equation is used. Substituting the experimental data graphically it’s easy to find the necessary constants.

- Langmuir theory is valid if monomolecular layer is formed.

Langmuir's isotherm of adsorption

$$G = G_{\infty} \frac{KC}{1 + KC}$$

At low concentrations $C << K$

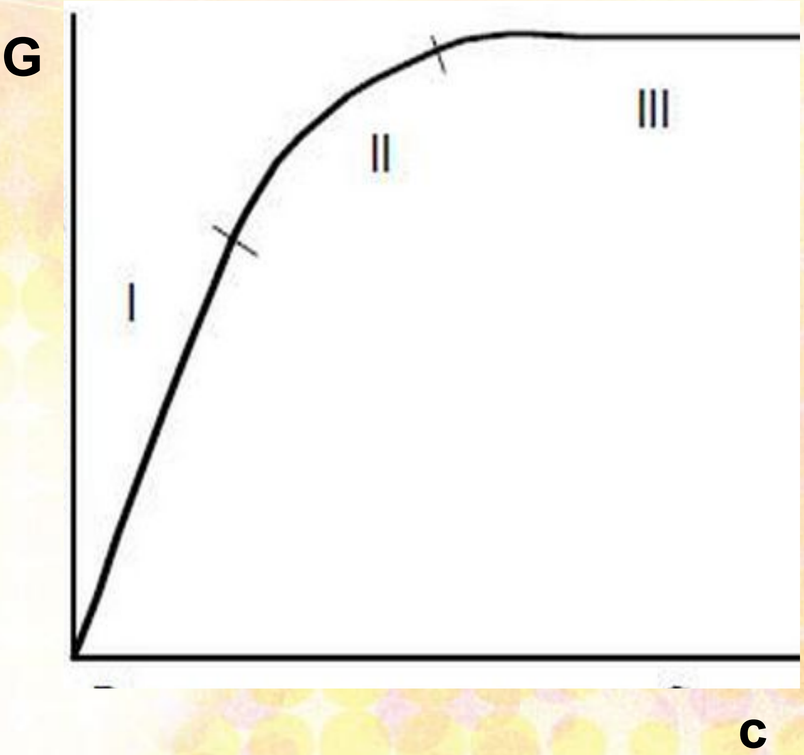
$$G = G_{\infty} \frac{K}{C}$$

At average concentrations $C = K$

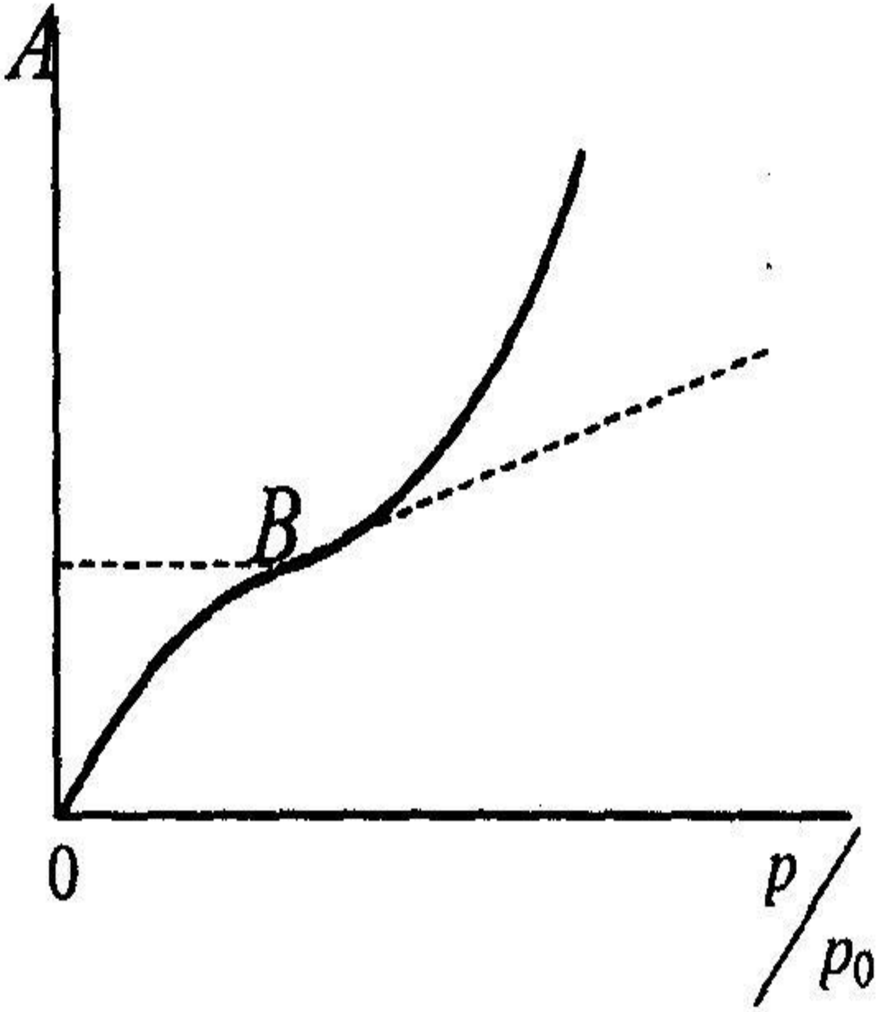
$$G = 1/2 G_{\infty}$$

At high concentrations

$$G = G_{\infty}$$



Theory of polymolecular adsorption BET (Brunauer, Emmett, Teller)



Many experimental evidence suggests that, after the monomolecular layer formation (point B) Adsorption continues to rise, due to the excess surface activity.

S-shaped polymolecular adsorption isotherm

ADSORPTION ON THE BORDER OF SOLID – SOLUTION

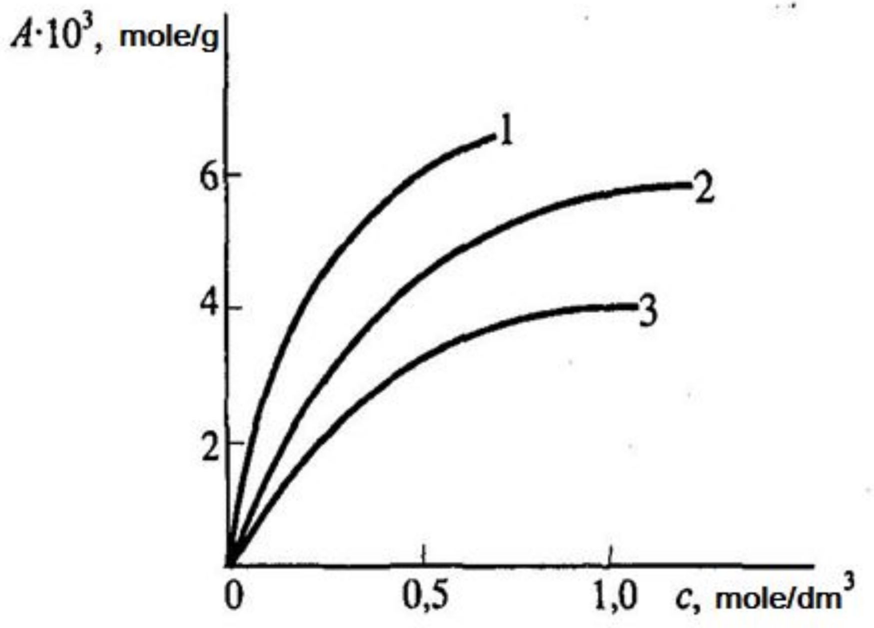
In the study of adsorption from solutions on solid adsorbents distinguish molecular adsorption (adsorption of nonelectrolytes or weak electrolytes) and the adsorption of electrolytes

Molecular adsorption

Experimentally determined value of the adsorption of knowing the initial concentration of the solution c_0, the volume of solution V and the adsorbent mass m.

$$A = \frac{(c_0 - c) \cdot v}{m}$$

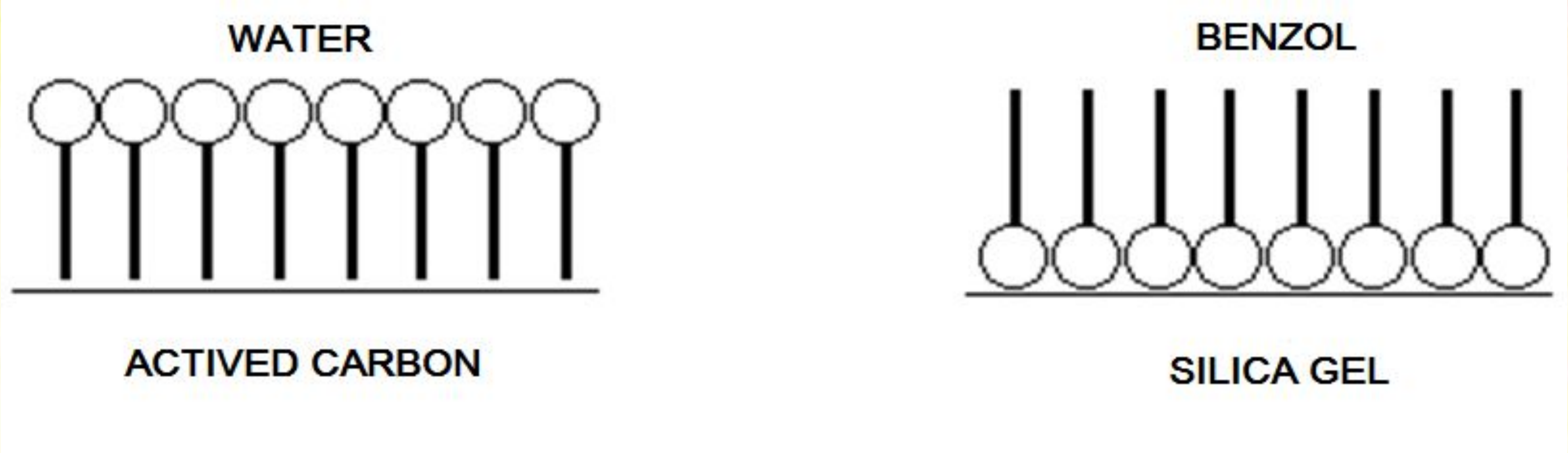
If you know the surface area of the adsorbent, the adsorption isotherm belongs to a given value:



Isotherms of adsorption on carbon from aqueous solutions of 1-phenol, 2-succinic acid, 3-benzoic acid

Molecular adsorption

So, in the adsorption of aliphatic carboxylic acids from aqueous solutions on a non-polar adsorbent - **activated carbon** - molecules are aligned by hydrocarbon radicals to an adsorbent, with adsorption of benzene (a nonpolar solvent) in the polar adsorbent - **silica gel** - orientation acid molecules will be reversed



Conclusion

From the above that is confirmed, that:

- For adsorption SAS from the nonpolar or low-polar solvents hydrophilic substances (silica, clays); must be used
- On the surfaces of hydrophobic (coal, graphite, talc) from aqueous solutions of SAS should be better adsorbed.

The ion exchange adsorption

The ion exchange adsorption - a process in which the adsorbent is added and the solution is exchanged between the equivalent amounts of similarly charged ions.

$RM_1 + M_2^+ \rightarrow RM_2 + M_1^+$ cation exchange

cationite

$RA_1 + A_2^- \rightarrow RA_2 + A_1^-$ anion exchange

anionite

To neutralize the excess acid in the gastric juice :

$$R–Kt^+OH^– + Cl^– \rightleftarrows R – Kt^+Cl^– + OH^–$$

Potassium ions: $R–An–H^+ + Na^+ \rightleftarrows R–An–Na^+ + H^+$

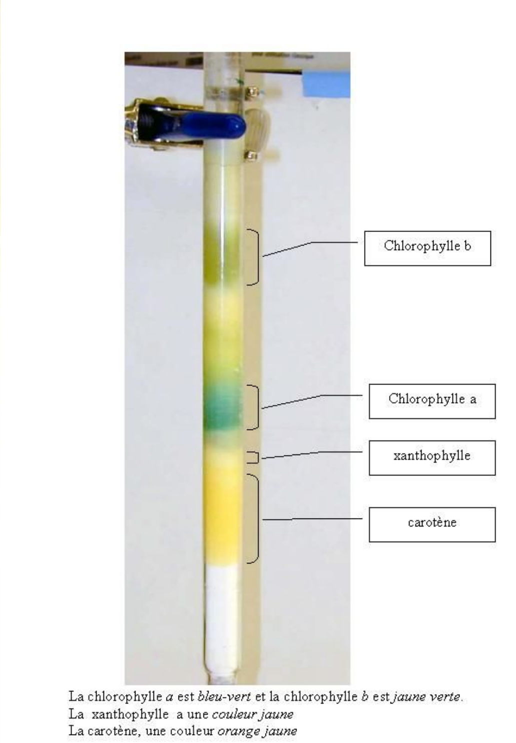
Chromatography

Chromatography is dynamic method of analysis based on multiply repeated processes of sorption and desorption.

Chromatography is physical chemical method used to separate substances

analytical objectives

formulations objectives



La chlorophylle *a* est *bleu-vert* et la chlorophylle *b* est *jaune verte*.
La xanthophylle a une *couleur jaune*
La carotène, une couleur *orange jaune*

Used for identification and quantitative determination of organic and inorganic substances

From the history of chromatography

Birthday of chromatography – 21.03.1903

The report of M.S. Tsvet "A new category of adsorption phenomena and their application to biochemical analysis"
His method of M.S. Tsvet called - "chromatography" (written by color)

Mikhail Semenovich Tsvet
(1872—1919)

Richard Kuhn (Institute of Basic Medicine , Heidelberg) (1938, Nobel Prize in Chemistry for the suggested color adsorption chromatography carotenoids and vitamins)
Alfred Vintershtayn (1915, Nobel Prize in Chemistry for his research of chlorophyll)
Archer Martin Porter , Richard Laurence Millington Singe (1938, first countercurrent extractor using water and chloroform to separate oligopeptides ; 1940. Using liquid-liquid chromatography for separation of amino acids ; November 19 , 1941. The article " A new form of use of the two liquid phases for chromatography " in «Biochemical journal»;1952 . Nobel Prize for the discovery of partition chromatography
Archer Porter Martin , Anthony James Trafford (50s first gas chromatograph)
Izmailov, Schreiber (1938g. first work on thin-layer chromatography)
Stahl (1956 Using thin-layer chromatography as an analytical method)

> *«No other discovery had such a huge long lasting effect in organic chemistry as the analysis using Tsvet’s adsorption chromatography»*
>
> *Carrere, 1947.*

Chromatographic methods are used for:

✔quantitative assessment of the basic substance in the bulk drug;

✔determination of impurities in bulk drug and medicinal forms;

✔the preliminary and confirming stages in the pharmaceutical, chemical and toxicological analysis;

✔ determining the purity of water and food;

✔studying the kinetics of chemical reactions;

✔analyzing oil, etc.

The principle of chromatographic separation of substances

Molecules of substances to be separated

The stationary phase

The mobile phase

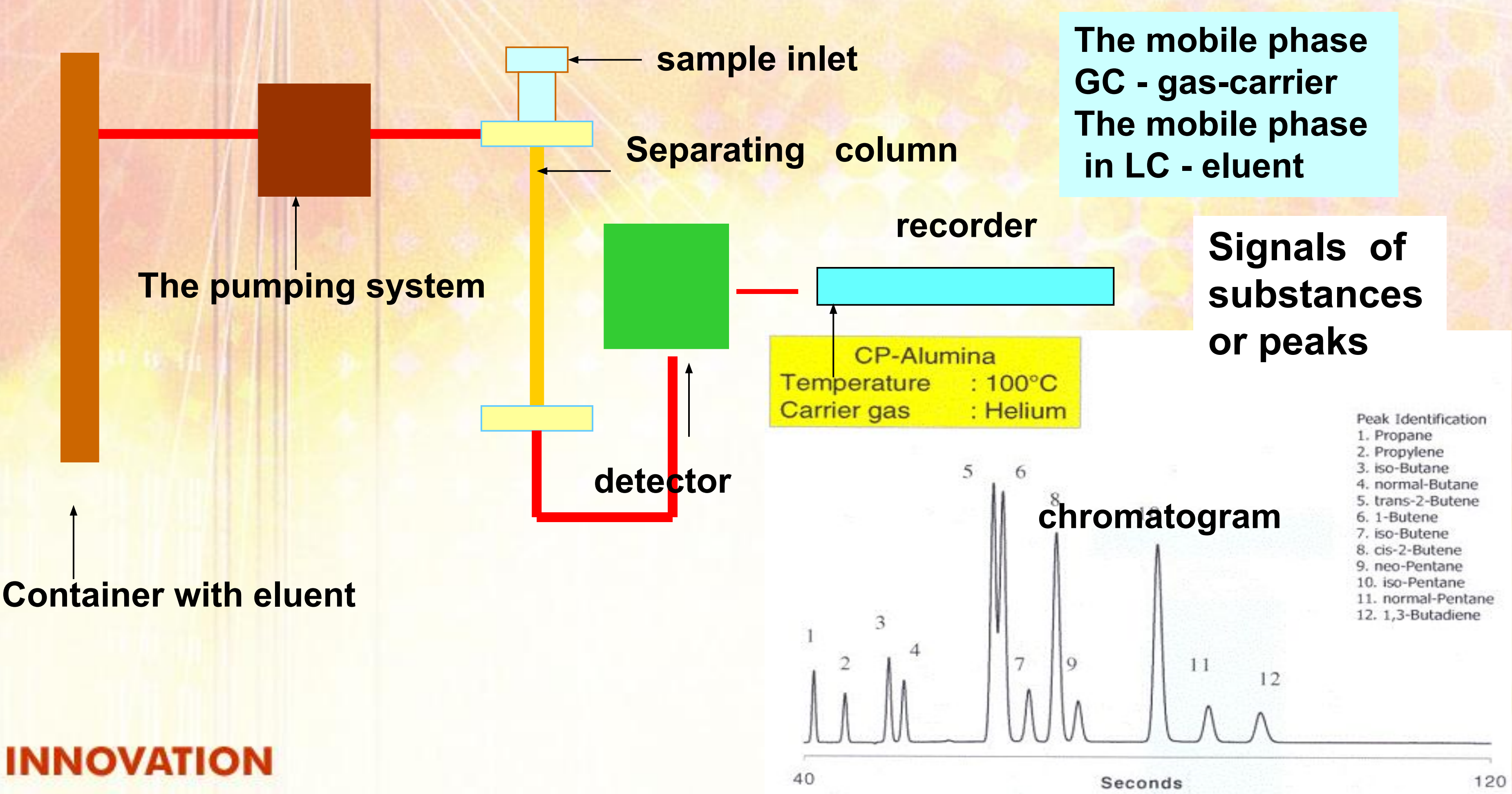
Separation effect is based on the fact that the compounds tested the distance at which separation occurs, with some inherent for this compound delay

Chromatographic process consists of a number of sorption and desorption, as well as the elution solution and that every time lead to a new equilibrium

Column chromatography

the stationary phase is in the column;
the technique used in gas and liquid chromatography

Schematic diagram of the chromatograph for column chromatography



sample inlet

Separating column

The pumping system

Container with eluent

detector

recorder

chromatogram

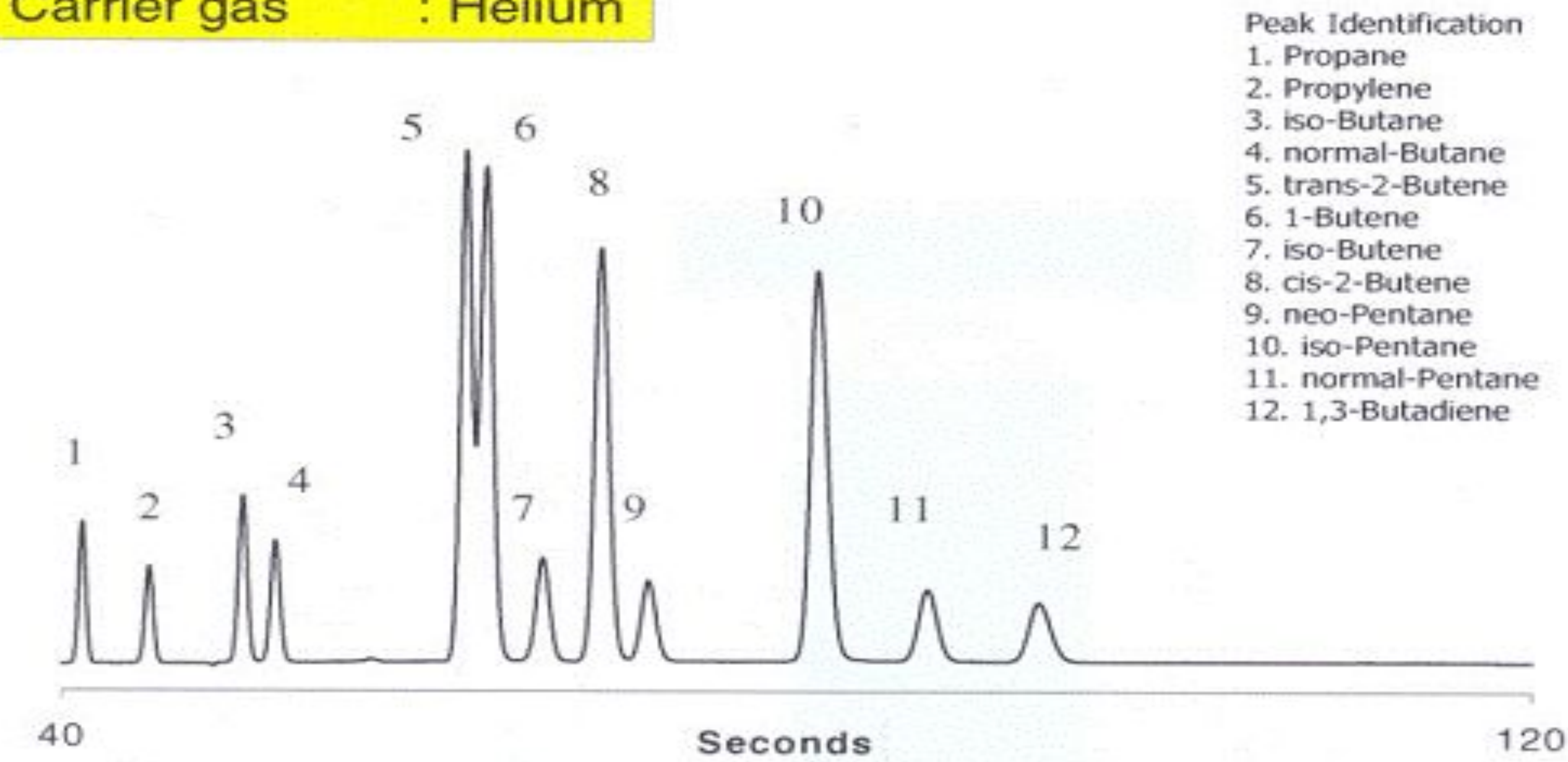
The mobile phase
GC - gas-carrier
The mobile phase
in LC - eluent

Signals of substances or peaks

Identification by GLC

For Identification of compounds in the mixture, its retention time compared with a retention time of standard sample

CP-Alumina
Temperature : 100°C
Carrier gas : Helium



HPLC Agilent Technologies

HPLC Milichrom

HPLC HP

GLC “Agilent Technologies”

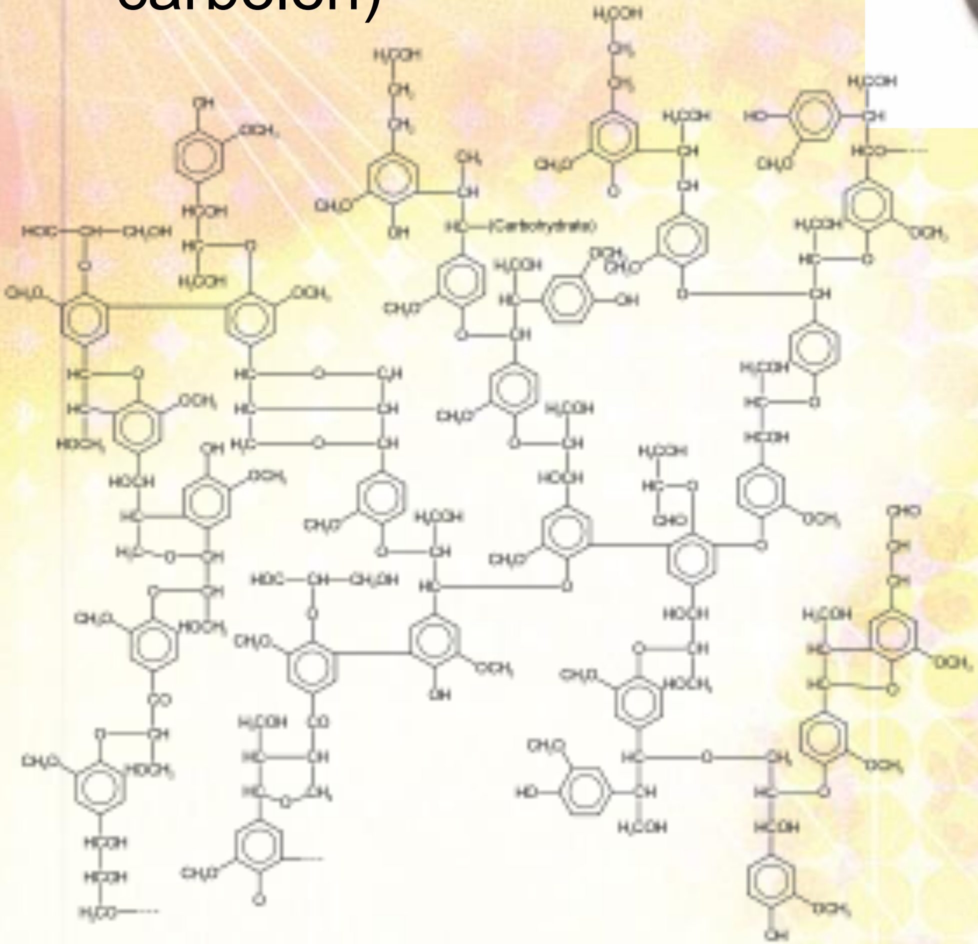
Enterosorption

It is method of treatment of various diseases, based on the ability of enterosorbents bind and excrete various exogenous substances, microorganisms and their toxins, endogenous intermediate and final products of metabolism that are able to accumulate, or to penetrate into a cavity of the digestive tract in the course of the illness.

Enterosorbents

Activated carbon (sorbex, carbolong, carbolen)

Polyphepan (lignin)



Enterosorbents

- Smecta

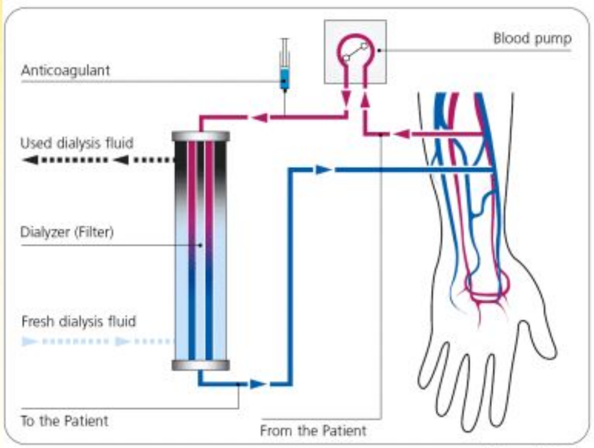
- Silicon organic sorbent Enterosgel

Enterosorption

Enterosorption is part of efferent therapy (from the Latin word efferens means output). Also **enterosorption,** this group includes hemodialysis, peritoneal dialysis, plasmapheresis, hemosorption and others.

Hemodialysis

Hemodialysis (from hemo-and διάλυσις - decomposition, office) is extrarenal method of blood purification during acute and chronic renal failure.

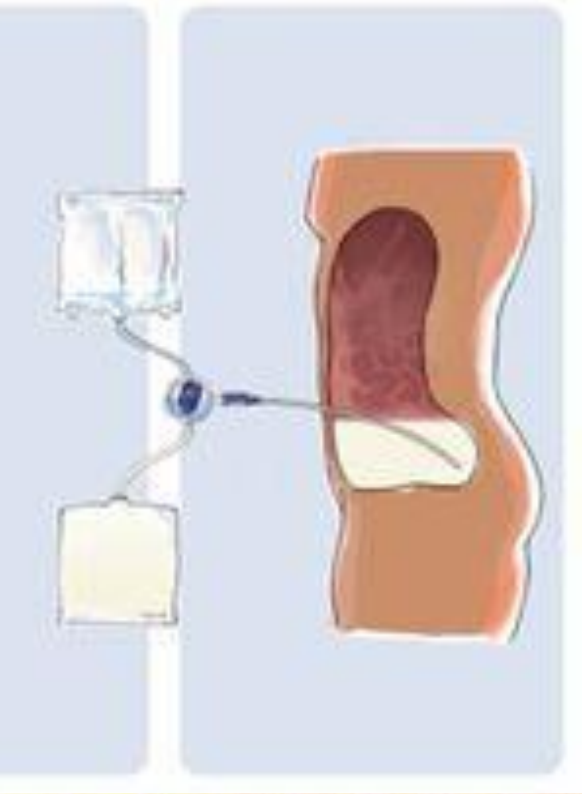


Hemodialysis

INNOVATION

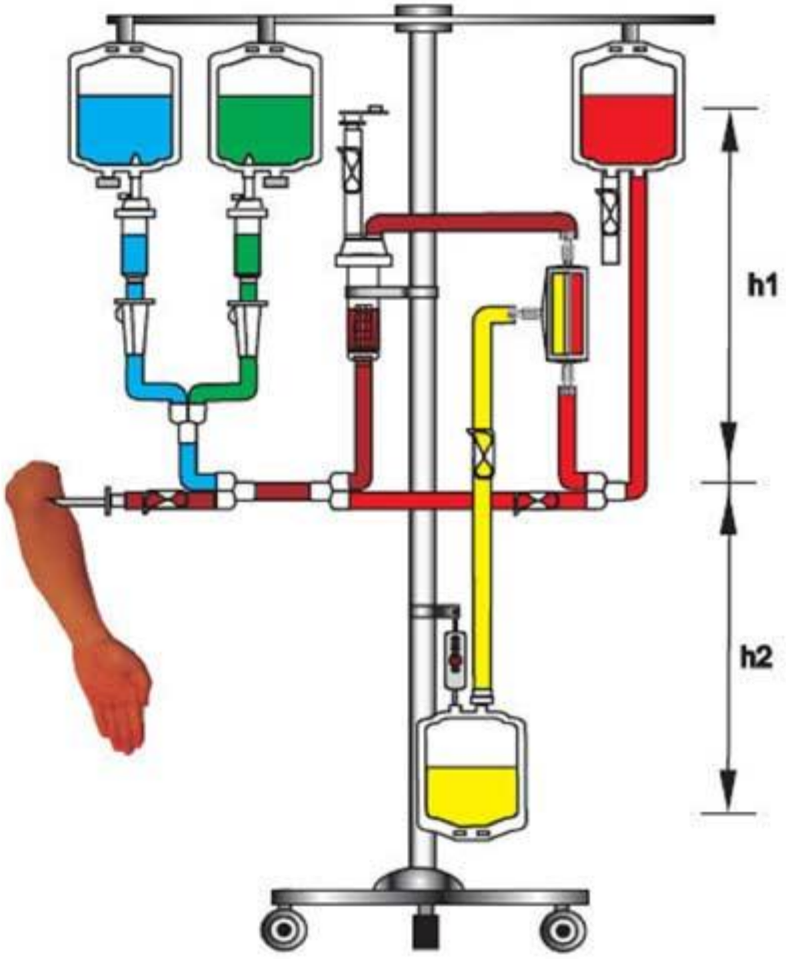
Peritoneal dialysis

- Peritoneal dialysis (dialysis Greek expansion, separation) is method of cleansing the blood of endogenous and exogenous toxins with simultaneous correction of water-salt balance by diffusion and filtration solutions of substances through the peritoneum as a natural semipermeable membrane.



INNOVATION

Plasmapheresis



- Membrane plasma filter contains a chamber for the flow of blood separated from the cameras for plasma collection by porous membrane. The membrane thickness of 10 micron has pores, diameter of which is about 0.5 microns, which allows you to freely pass through all the latest liquid blood components and detain all formed elements. Together with the liquid component of blood passes through the membrane pores and much of the toxines. Dirty plasma is filtered in a separate bag and removed, and clean blood cell mass is returned to the circulatory system.

Hemosorbtion

- **Hemosorbtion** (from the Greek. Haema blood + lat. Sorbere absorb) is a method of treatment aimed at removing from the blood of various toxic products and the regulation of hemostasis by contact with the blood outside the body of the sorbent.