Membranes and membrane technologies. History. Practical aspects.

SCIENCE PROGRESS LAST CENTURIES

Max Karl Ernst Ludwig Planck

1858-1937

- A great scientific idea is seldom introduced by the gradual persuasion and conversion of its opponents. In reality, what happens is that the opponents are gradually passing away. Only the growing generation uses new ideas.
- It means, the period of introducing new ideas is 40-50 years, i.e. activity of scientists. It is the same period from one scientific revolution to other.

SCIENCE PROGRESS NOW

The period from one scientific revolution to other is about 5 years and even less.

Why?

-Business and human needs;
- Social elevators, blurring boundaries between classes;
- Internet, digitalization of science.

Third millennium. Acceleration of scientific progress

Other political, economical and social reasons

Reasons caused by destruction

-
- Military conflicts with the use of modern weapons;
- Elimination of the consequences of military conflicts, man-made disasters, pandemics and natural disasters.

Reasons caused by creation

- Competitions between states and business companies;
- Government support;
- Positive image of science in society;
- Urbanization, raising the educational level of the population;
- Creation and development of scientific research centers;
- Large amount of scientific and popular science journals;
- Internationalization of science, opportunity for scientists to work in different countries. Now the scientists are citizens of the world.

Synthetic membranes and membrane separation in the third millennium

- Main scientific revolutions in this field occurred last century, all membrane separation processes are known. Now main efforts are focused on new membrane materials and improvement of known ones. Membrane processes are applied to new objects (fractionality of proteins or aminoacids from mixtures, recovery of RNA, dehydration of biofuel etc.)

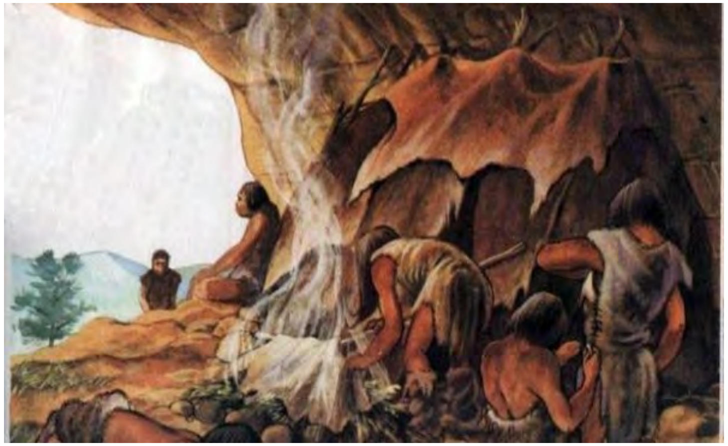
- Now biological membranes are in a main focus of attention. They are in the field of investigations of biologists.

- **In this lecture, we will consider the evolution of membrane materials and membrane processes for liquid separations, water decontamination and gas separation. We will also consider practical significance of scientific discoveries in this field.**

PROTOTYPES OF MEMBRANES. FIRST ATTEMPTS OF WATER DECONTAMINATION AND DISINFECTION

Prehistoric

It is difficult to assume the prototypes of membranes in prehistorical times.



Probably water was purified by means of settling, filtration through sand, finely dispersive rocks or coal from bonfires.

It is only assumption, since we have no proofs .

PROTOTYPES OF MEMBRANES. FIRST ATTEMPTS OF WATER DECONTAMINATION AND DISINFECTION

Ancient period

Clay plumbing of ancient Egypt

Wells of Ancient Greece

Plumbing of Ancient Rome

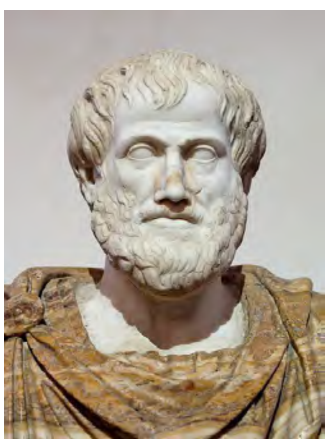
Filtration through textile

Centralized water treatment – settling.
Water treatment in certain households - filtration through sand, finely dispersive rocks, charcoal or dense textile.
Textile can be considered as a **prototype** of modern membranes. This method was already used in the III-II milleniums Before the Common Era.

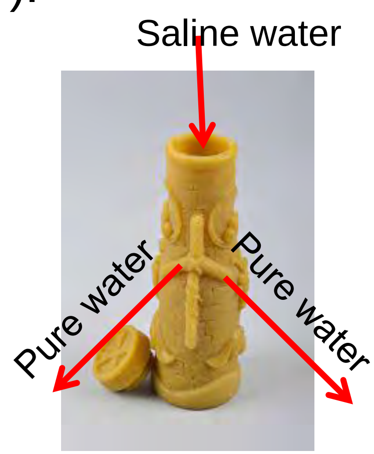
PROTOTYPES OF MEMBRANES. FIRST ATTEMPTS OF WATER DECONTAMINATION AND DISINFECTION

Filtration through textile allows one to remove only coarse particles. No removal of Pb^{2+} ions, which were in water due to lead pipes, was realized. It was the same regarding disinfection.

Cyrus king of Persia (559-530 BCE) supported a use of silverware by warriors to prevent the spread of infections. This disinfection method was available only for reach people. Moreover, a large concentration of silver ions is harmful for the humans. According to the modern standards for drinking water, the maximal allowable concentration of silver ions is 50 ppb (0.05 mg/dm^3).



Ἀριστοτέλης, 384-322 BCE



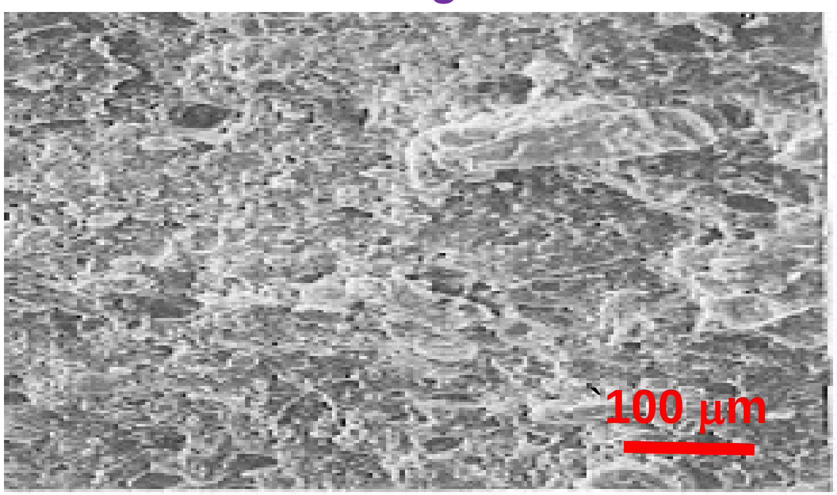
As a filter for desalination of sea water. Aristotle proposed a wax vessel (Aristotle, Meteorologica). Driving force of water leakage is gravitation.
Here the wax matrix is a prototype of modern membranes.

PROTOTYPES OF MEMBRANES. FIRST ATTEMPTS OF WATER DECONTAMINATION AND DISINFECTION

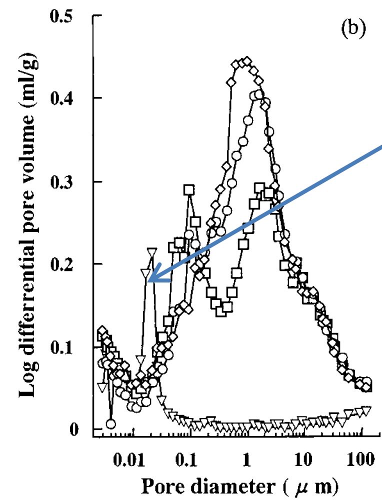
Was Aristotle right? Is the leakage of deionized water from the wax bottle possible?

Modern investigations of wax (H.Sato, Y. Miyagawa, T. Okabe et al. J. Pharmac. Sci. **1997. 86(8):** 929-934)

SEM image of wax



Differential pore size distribution

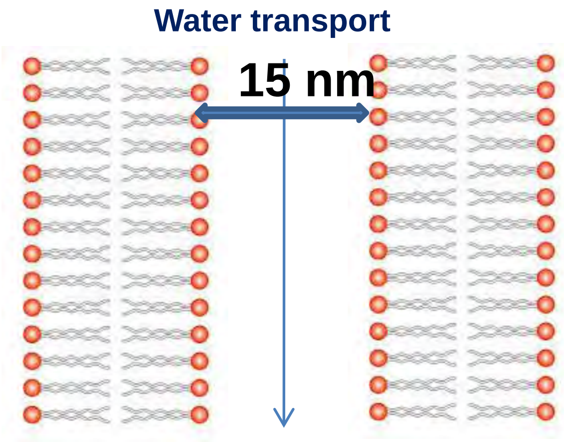


Pristine wax (15 nm of pore size)

PROTOTYPES OF MEMBRANES. FIRST ATTEMPTS OF WATER DECONTAMINATION AND DISINFECTION

Was Aristotle right? Is the leakage of deionized water from the wax bottle possible?

Wax consists of different lipids, which involve both hydrophobic and hydrophilic regions. Water is transported through hydrophilic pores.



As follows from pore size distribution, **partial rejection of Ca^{2+}, Mg^{2+} and SO_4^{2-} ions.** is possible similarly to ultrafiltration membranes. **Other advantages are disinfection, rejection of colloidal particles.**

Disadvantages : water leakage is too slow, singly charged ions remain in water.

EARLY MODERN ERA. XVIII CENTURY

Osmosis. "Membrane" term

Jean Antoine Nollet

1700-1770

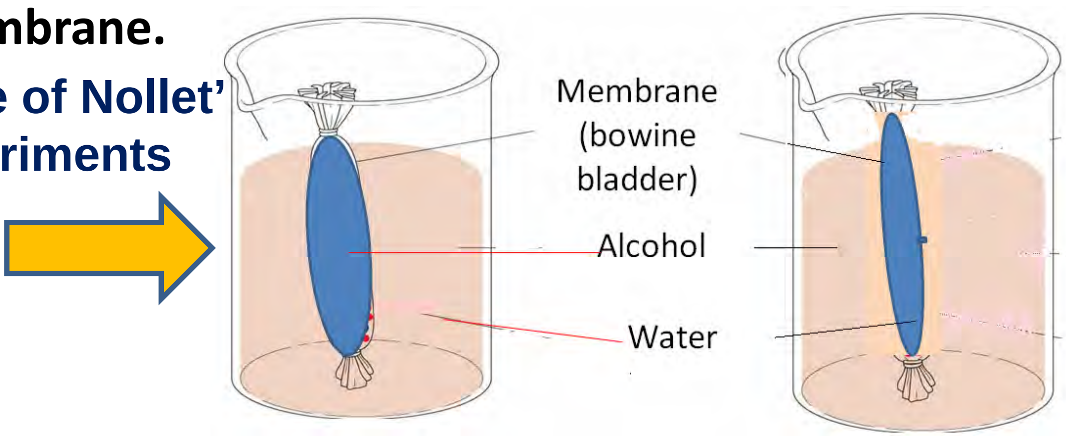
First time Nollet discovered osmosis *(ωσμυς pressure)*, he introduced a term of "osmotic pressure" (1748). Namely Nollet used a "membrane" term (lat. *membrana, i.e. shell, concha*).

Membrane is a thin film along perimeter between two spaces, which divides them from each other. Membrane for separation is a semipermeable, it allows penetration of only one kind of species and rejects other ones.

Osmosis – transport of liquid through the membrane.

Osmotic pressure is the excess hydrostatic pressure from a pure solvent, at which diffusion of solvent stops.

Scheme of Nollet' experiments



EARLY MODERN ERA. XVIII CENTURY

Rate of osmosis. “Membrane” term

René Joachim Henri Dutrochet;
1776—1847

René Dutrochet established that the rate of diffusion of different liquids through the membrane is proportional to their densities (experiments with ethanol, lavanda and olive oil).

He introduced the terms of “exoosmosis” and “endoosmosis”.

Exoosmosis

Plasmolysis

Endoosmosis

Turgor

MODERN ERA. XIX CENTURY

Osmosis pressure law

Jacobus Henricus van't Hoff

1852 - 1911

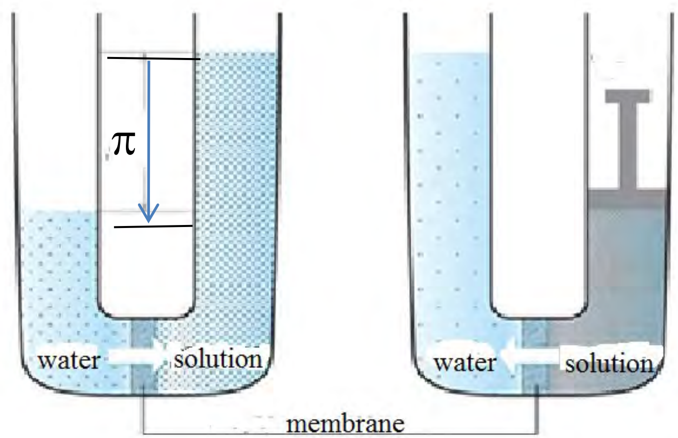
1901. Nobel prize in the field of chemistry for the discovery of laws of chemical thermodynamics and osmosis.

The osmotic pressure of a solution *(π)* is equal to the gas pressure that would be produced by the dissolved substance, being in a gaseous state and occupying a volume equal to the volume of the solution.

$$\pi = iCRT$$

R - gas constant, *i* - isotonical coefficient associated with the amount of ions produced by 1 molecule.

Forward osmosis   Reverse osmosis



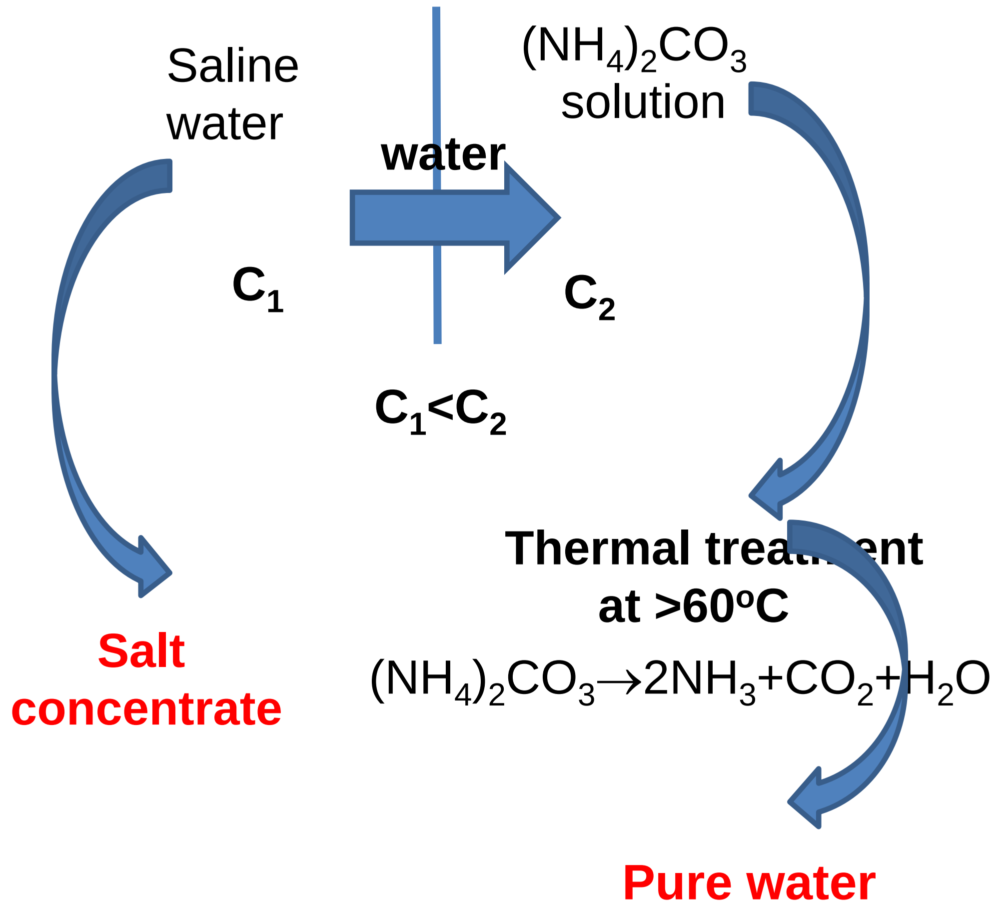
Osmotic pressure depends on the amount of the dissolved substance and independent on its nature and the nature of solvent.

MODERN ERA. XX CENTURY

Application of osmosis for water desalination

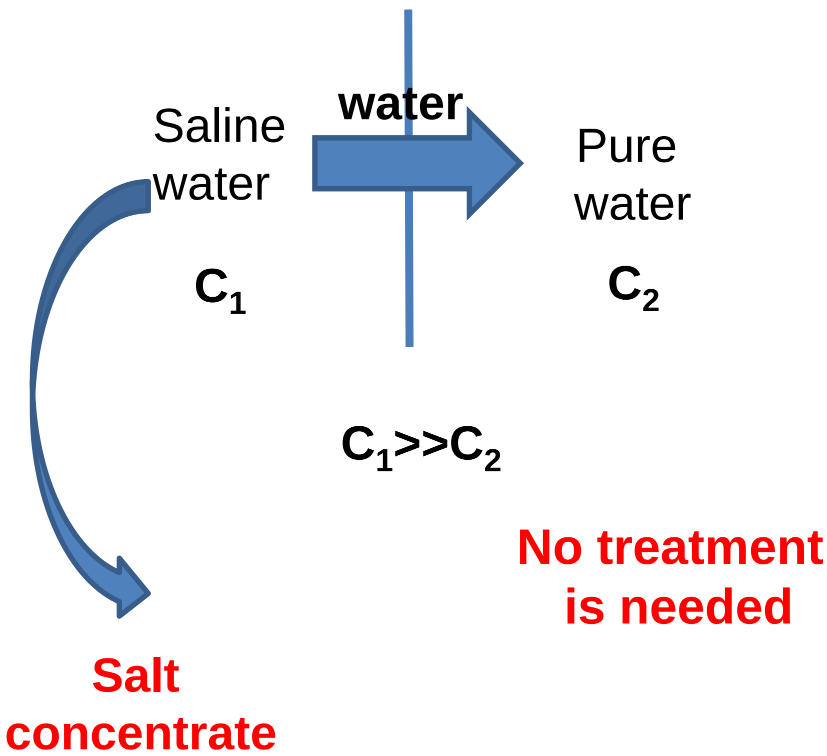
Forward osmosis

Driven force – osmotic pressure



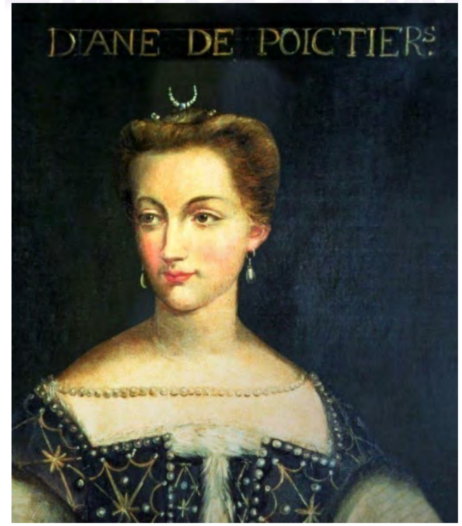
Reverse osmosis

Driven force – outer pressure



MIDDLE AGES. RENAISSANCE

***Ambroise Paré* (1510-1590)**



***Diane de Poitiers,* (1500-1566)**
Associated with Henri II Valois

Thomas Graham
1829 — 1901

Diana looked young until her death. According to one version, doctor Ambroise ***Paré*** made colloidal gold for her. In order to purify colloidal solution, ceramic or biological membrane (bowine bladder) was used. Namely gold poisoning caused her death. However, it is impossible to verify this version, since Diana's grave was destroyed more than 200 years ago during the revolution.

It is suggested officially, that first sol of gold was obtained iby Michael Faraday in 1857.Later sol was obtained and purified by **Thomas Graham.** Removal of additions was performed using a **parchment membrane. Graham is is considered the founder of colloidal chemistry.**

MODERN ERA

Membrane method for sol purification

Now sols of precious metal are also in a focus of interest. Sols are currently considered as nanoobjects. Main tasks:

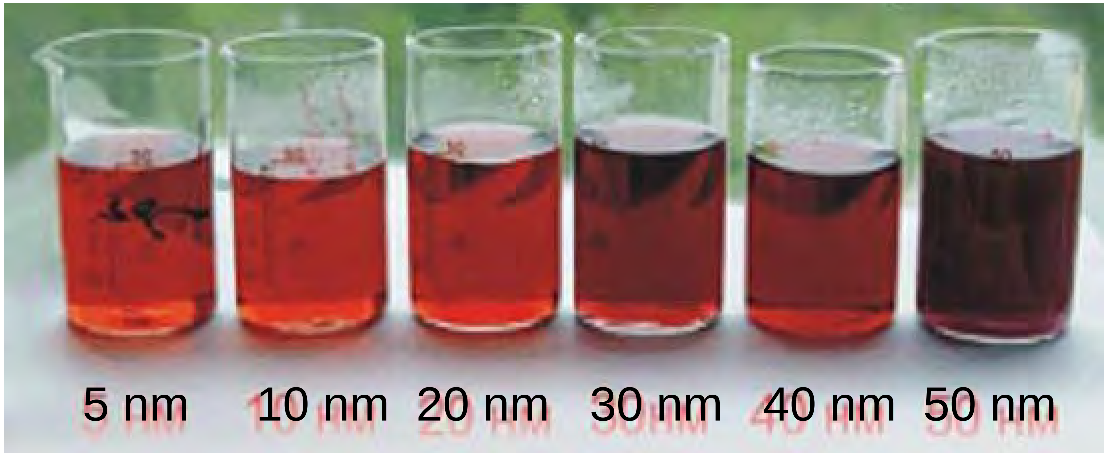
- obtaining nanoparticles of strictly predetermined size (Gaussian narrowing);.

- for medical application, a size of nanoparticles must be less than 10 nm (larger nanoparticles are cytotoxic);

-Deep purification of sol using membranes;

-- Stabilizing sol.

Gold nanoparticles. Size effect

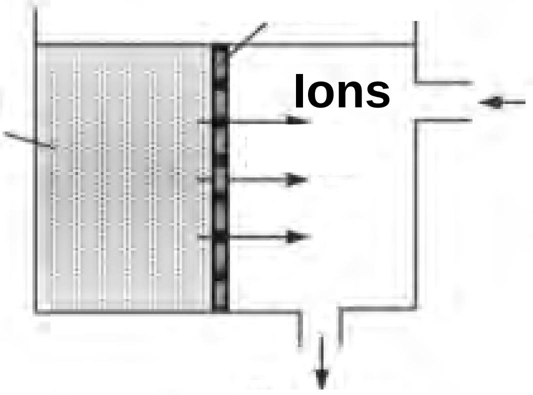


Tyndall conus

Increase of concentration gives the same effect

MODERN ERA

Dialysis for sol purification. Driving force is the concentration gradient



Dialysis (from the Greek diálysis — decomposition, separation), removal of impurities of low-molecular substances from colloidal systems using semipermeable membranes. The membranes allow the passage of small molecules and ions, but they reject colloidal particles and macromolecules.

Practical application of sols of gold nanoparticles

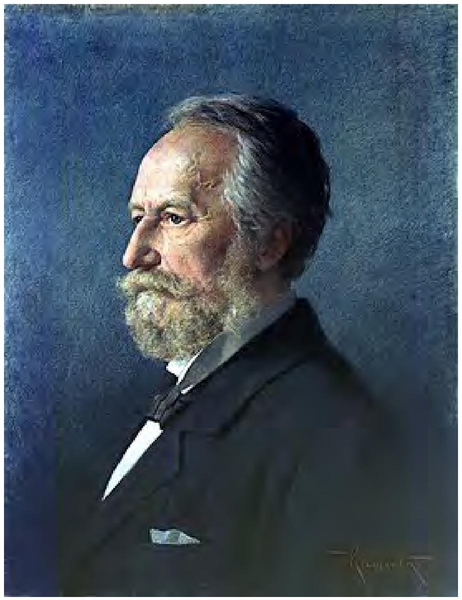
Medical application: contraventions of functions of the brain, impaired functions of the circulatory system, depressive states, drug addiction, chronic alcoholism, arthritis, contraventions of function of the endocrine secretion, contraventions of mechanisms of thermoregulation etc.

Cosmetics: shampoos, creams, hairsprays.

Electronics: spraying on components that cannot withstand the temperature of molten gold. they do not show the temperature of molten gold.

MODERN ERA

Development of the theoretical base of dialysis



Adolf Eugen Fick

1829 — 1901

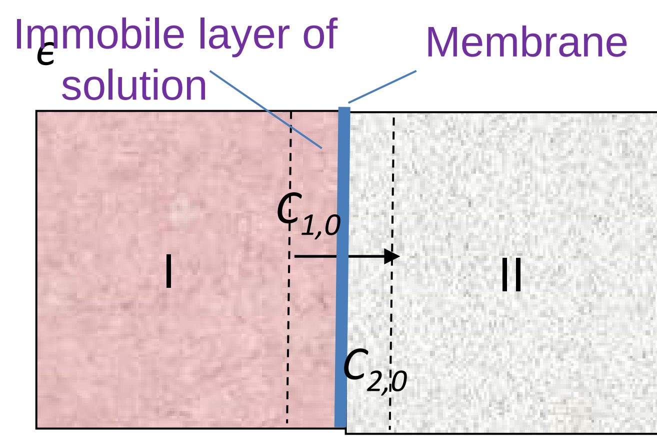
First Fick' law (1885) adapted to the ion transport through membrane: A flux through the membrane is proportional to the difference in concentrations of solutions on both sides of the membrane and inversely proportional to the membrane thickness.

$$J = D\frac{C_{1,0} - C_{2,0}}{l}$$

$C_{1,0}$, $C_{2,0}$ – concentration of solutions on both sides of the membranes in a **hydrodynamically immobile layers**.

D – diffusion coefficient of ions in the membrane,

l – membrane thickness.



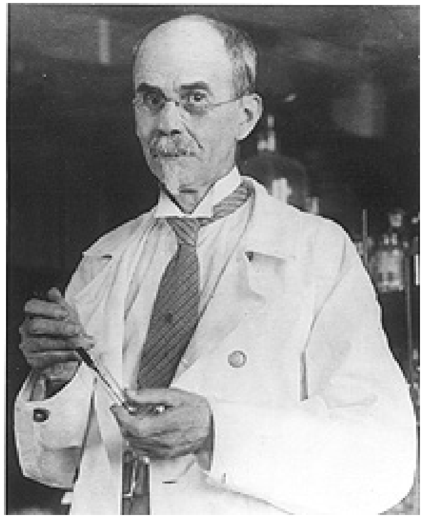
Dialysis is a too slow process. The ways to accelerate it:

- removal of species from the compartment II (combination of dialysis with adsorption),
- decrease of membrane thickness,
- increase of temperature (increase of diffusion coefficient).

MODERN ERA

Practical application of dialysis

- **Hemodialysis** (artificial kidney) is the process of removal of waste products and excess liquid from the body. The principle of hemodialysis is the retention of blood components by the membrane, urea passes to the physiological solution, which is on the other side of the membrane.



John Jacob Abel
1857-1938

1914. John Jacob Abel developed the first hemodialysis apparatus *(dogs were used for the experiments).*

1924– hemodialysis was used in Germany to purify human blood.

Problems:

1. Tromb formation after the contact of blood with membrane.

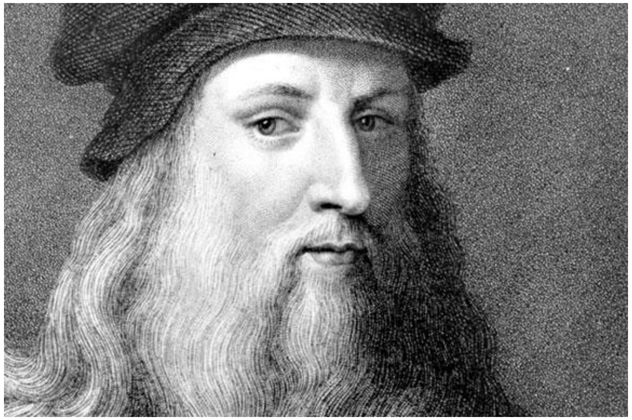
2. To prevent tromb formation, membranes are modified with heparin, which often causes allergic reaction.

3. Membranes are permeable towards some blood components,

Modern hemodialysis apparatus

MIDDLE AGE. RENAISSANCE

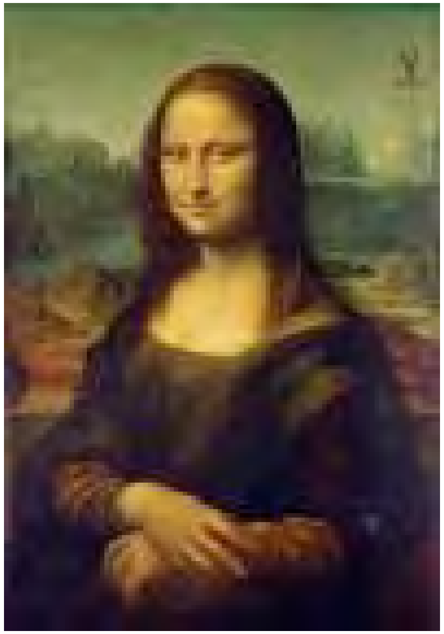
Development of the theoretical base of membrane processes



Leonardo da Vinci
1452-1519

Leonardo da Vinci is a foundator of hydrodynamics laws of which determine mass transport in membranes. He suggested an inversely proportional dependence of the rate of water flow (u) on the area of the cross-section of a pipe (A). In fact, it is a law of flow continuity.

However, Leonardo's authority is contested due to incomprehensible formulation.



La Gioconda

Now Benedetto Castelli is considered as an author of the law of flow continuity. He was a student of Galileo Galilei.

Benedetto Castelli (1577-1644)

MIDDLE AGE. RENAISSANCE

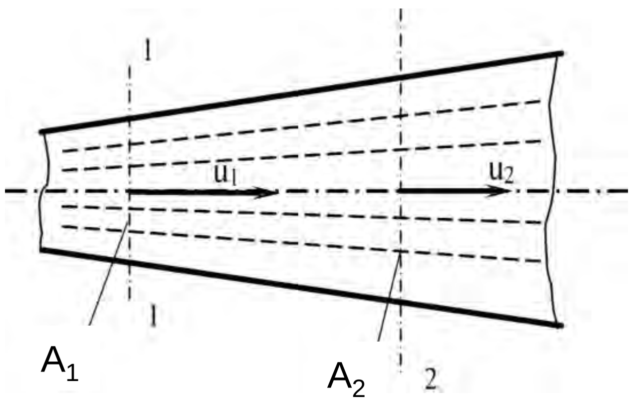
Development of the theoretical base of membrane processes

The law of the flow continuity is a special case of the law of mass conservation,

Its simplest formulation for hydrodynamics

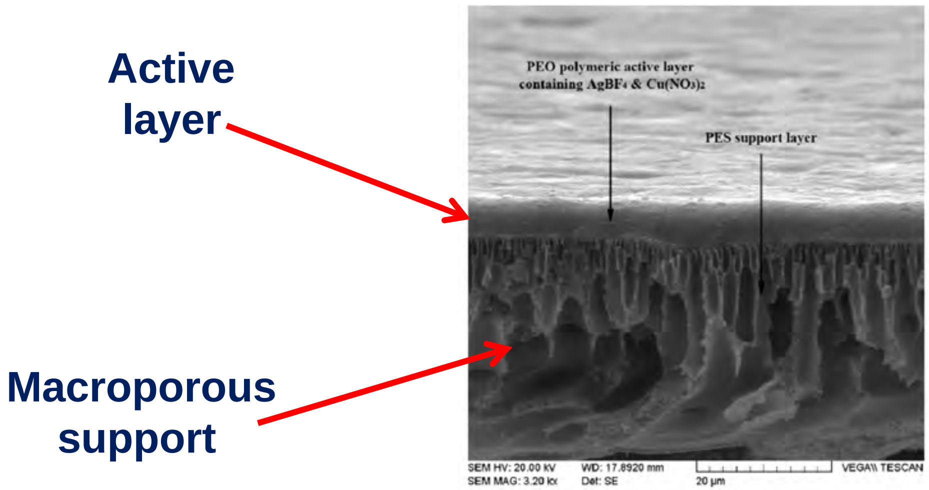
The amount of substance passing per unit of time through section 1, e. e. flux J_1 is equal to the amount of substance through section 2, i.e. flux J_2.

This law is important for asymmetric filtration membranes, which usually consist of macroporous support and active layer containing smaller pores. The fluxes throw the cross-sections of different regions are equal. It means, the amounts of substance at the “inlet” and “outlet” of the membraneare equal.



$$J_1 = J_2$$

$$\frac{u_1}{A_1} = \frac{u_2}{A_2}$$



The fluxes through each region of asymmetric membranes are similar.

EARLY MODERN

Development of the theoretical base of membrane processes

The law of energy conservation during stationary flow of an incompressible ideal fluid.

Daniel Bernoulli
1700-1782

Vertical flow

$$\frac{\rho u^2}{2} + \rho g h + p = const$$

I II III

Horizontal flow

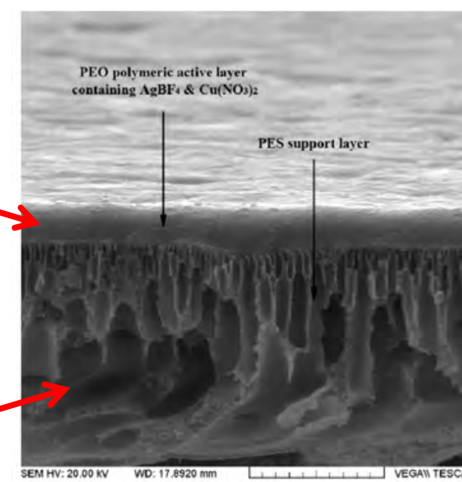
$$\frac{\rho u^2}{2} + p = const$$

I III

Term I – dynamic pressure, term II – hydrostatic pressure, term III – static pressure (pressure of molecules on pipe wall), ρ - fluid density, *h* – pipe height, *g* – acceleration of free fall.

For asymmetric membranes, the pressure in each region is a constant value.

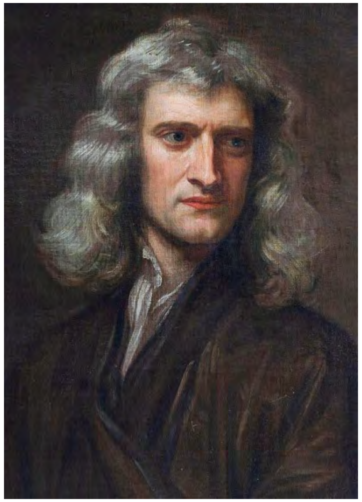
Active layer



Macroporous support

EARLY MODERN

Development of the theoretical base of membrane processes



Isaac Newton
1642-1727

Gottfried Wilhelm Leibniz
1646-1716

Basics of differential and integral calculus were developed. Foe instance, the expression for flux can be adapted to barometric filtration:

$$J = \frac{dV}{dt}\frac{1}{A}$$

V – cumulative permeate volume.
Representation form for differential like *dV/dt* has been proposed by **Leibniz.**

Newton' law of viscous friction for the moving layers of liquid

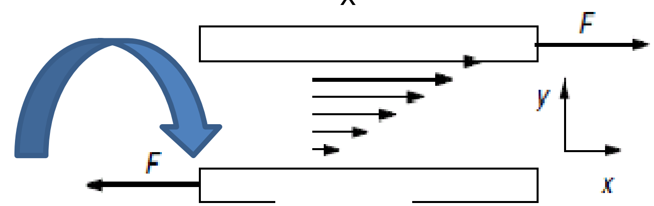
The force of viscous friction of moving layers of liquid *(F),* which are in contact with each other, is proportional to the velocity gradient. The proportionality factor is called "dynamic viscosity coefficient" (μ).

$$F = \mu \frac{du}{dy} A$$

Viscosity of liquids determines mass transport through membranes.

Profile of velocities

u_x=u



u_x=0

MODERN ERA. XIX CENTURY

Main law for the filtration through porous media

Henry Darcy
1803-1858

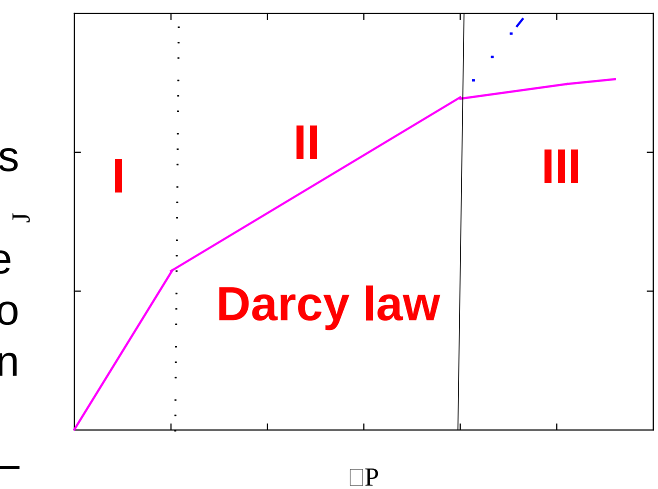
The law was obtained based on experimental data for rocks.

$$J = \frac{\Delta P}{\mu R}$$

R is the hydrodynamical resistance. The Darcy law is applicable for the filtration membranes.

II – region of Darcy law
I and III – deviations from Darcy law

Permeate flux through the filtration membrane vs pressure



Region of low pressure – penetration of the aqueous solution into hydrophobic pores.
Region of high pressure, slowdown of filtration – reversible membrane compression, transition from laminar flow to turbulent flow, growing of osmotic pressure, which acts in reversible direction of outer pressure.
Region of high pressure, acceleration of filtration – stretching of pores, leakage of modifier.

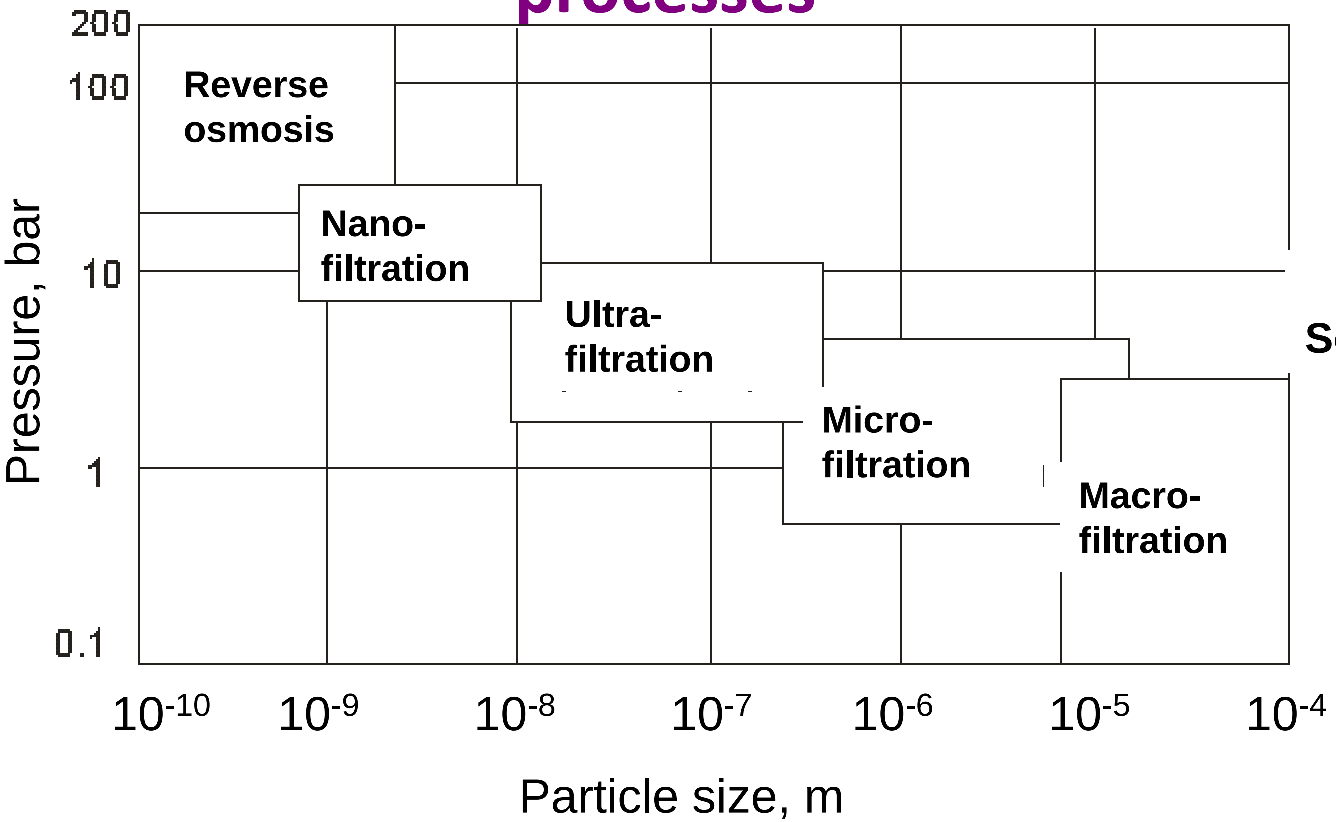
The behavior of one or other membrane strongly depends on its material.

MODERN ERA. XX CENTURY

Baromembrane separation

Despite considerable theoretical basis and experimental results, filtration processes were invented and commercialized, when suitable membrane materials were obtained.

Classification of baromembrane processes



Thickness of active layer

Macrofiltration

No active layer

Microfiltration

10-150 μm

Some membranes -0.1 μm

Ultra-, nanofiltration, reverse osmosis

0,1-10 μm

APPLICATION OF BAROMEMBRANE PROCESSES TO DIFFERENT SPECIES

Species	Size, nm	Method
Yeast, mushrooms	1000-10000	Macro-, microfiltration
Bacteria	300-10000	Macro-, micro-, ultrafiltration
Oil emulsions	100-10000	Macro-, micro-, ultrafiltration
Solid colloidal particles	100-1000	Micro-, ultrafiltration
Viruses	30-300	Micro-, ultrafiltration
Proteins, polysaccarides	2-10	Ultra-, nanofiltration
Enzymes	2-5	Ultra-, nanofiltration
Antibiotics	0.6-1.2	Nanofiltration, reverse osmosis
Organic molecules	0.3-0.8	Reverse osmosis
Inorganic ions	0.2-0.4	Reverse osmosis
Water	0.18	

Macrofiltration

Water jet pump

Schott filter

Paper filter or Shott filter
size of rejected particles up to 1.5 μm

MODERN ERA. XX CENTURY

Ultrafiltration

Background: Filtration of proteins and gum through animal membranes

Schmidt: Ann. Phys. Chem. 99, 337 (1856)

Filtration of blood plasma *in vivo*

Sanarelli: Cent. Bakt. Parasitenk., 467.(1891)

Filtration of enzimes

Levy: J. Infectious Diseases 2,1 (1905).

Heinrich Jakob Bechhold
1866-1937

1907. Development of ultrafiltration method.

1 stage. – Modifying filter paper with cellulose acetate. A series of membranes with graded porosity was obtained by H.J. Bechhold.

2 stage. - The technique for the determination of pore size (bubble method) has been proposed.

3 stage. -Considered a role of adsorption in filtration processes.

1926. Development of hermetic filter (membrane cartridge)

MODERN ERA. XX CENTURY
MICROFILTRATION

Richard Adolf Zsigmondy
1855-1929

1925 p. - Nobel Prize in Chemistry for establishing the heterogeneous nature of colloidal solutions and developing methods for their research (immersion microscopy).

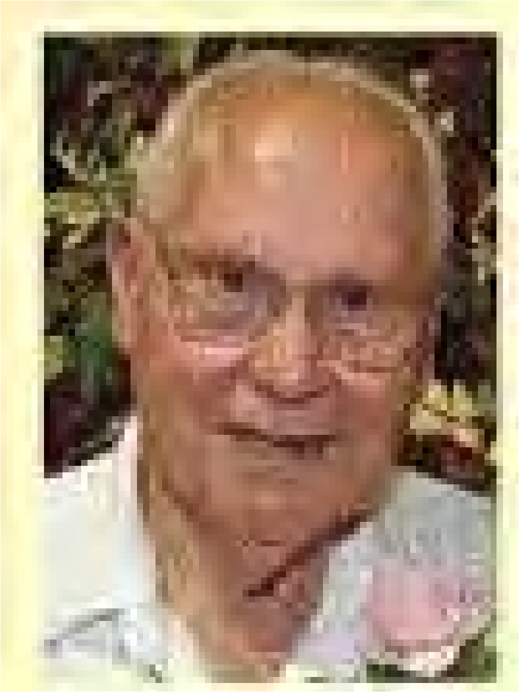
1918. Development of microfiltration method using nitrocellulose and cellulose-ester membranes

Zsigmondy R., Bachmann W.: 1918, „Ueber neue Filter," Z. Anorg. Allgem. Chem. 103: 119–128..

2021. US patent protects the invention.

The Membran-Filtergesellschaft Sartorius Werke company has been found, the company produces microfiltration membranes. This company is working now, its branches are in many countries.

MODERN ERA. XX CENTURY
REVERSE OSMOSIS



Charles E. Reid
1917-2000

1953. Main principles of reverse osmosis were formulated. It was shown that in order to obtain pure water from salt solutions, it is necessary to apply pressure to the system that exceeds the osmotic pressure.

C. E. Reid, E. J. Breto. Water and Ion Flow Across Cellulosic Membranes. J, Appl. Polym, Sci. 1959. 1(2): 133-143.

1960. Rapid development of reverse osmosis, since special membranes have been developed by Loeb and Surirajan.

Loeb S., Sourirajan S. *In:* Saline Water Conversion—II, ACS Publications. 1963. V. 28. P. 117-132.

Membranes were prepared based on cellophane and cellulose acetate, which were modified by silicone. Other commercial materials were also used. The membrane with the best characteristics produced 200-450 dm^3 m^{-2} of permeate per day under a pressure of 100-140 bar. A 5-.25% NaCl solution was desalinated. The final NaCl content was O.05%. Very high pressure is caused by non-porous active layer.

MODERN ERA. XX CENTURY
NANOFILTRATION

Two ways **to decrease pressure** for reverse osmosis processes.

- To **reduce a thickness of the active layer** (the value of minimal thickness is limited);
-- To **allow nanopores** (1-2 nm or a little bit larger), where double electric layers are overlapped.

1988. – Peter Eriksson (USA). ***P, Eriksson. Nanofiltration extends the range of membrane filtration. Environ. Progr. 1988. 7(1): 58-62.***

Andria Yaroschuk

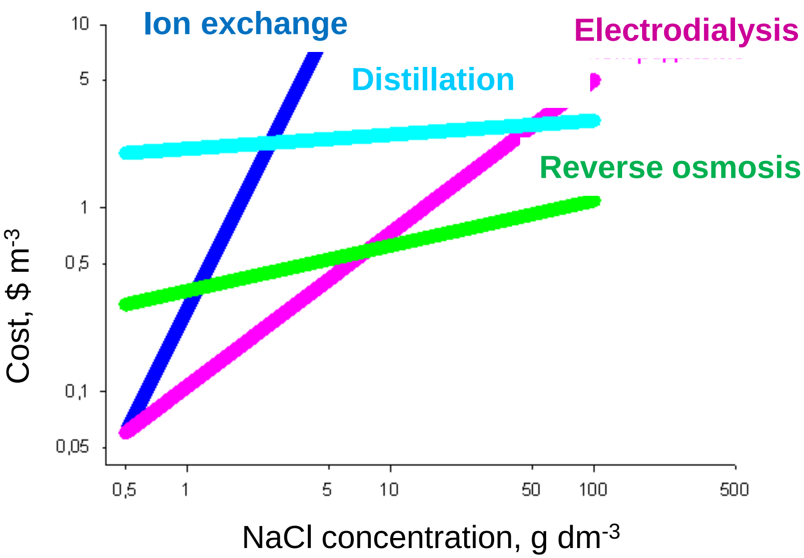
1970-1990. The theory was developed particularly in the Institute of Colloidal Chemistry and Chemistry of Water of the National Academy of Science of Ukraine.

A Yaroshchuk, E Staude. Charged membranes for low pressure reverse osmosis properties and applications. Desalination. 1992 86(2): 115-133.

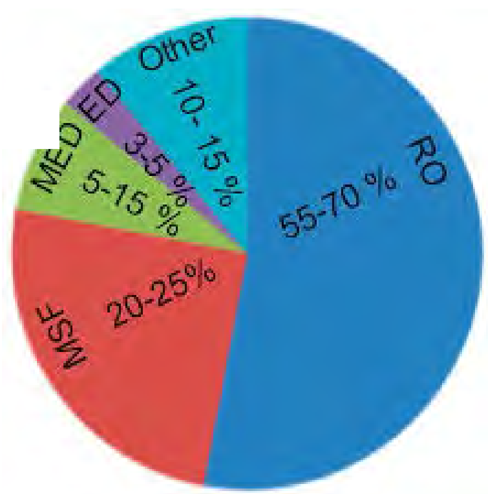
Nānofiltration allows us to remove hardness ions and heavy metals, arsenic compounds, phosphates, pesticides, and polysaccharides from liquids.

Problems: purification strongly depends on the composition of concentrate. Rejection ability of membranes is affected by adsorption.

Economical efficiency of different methods of water desalination



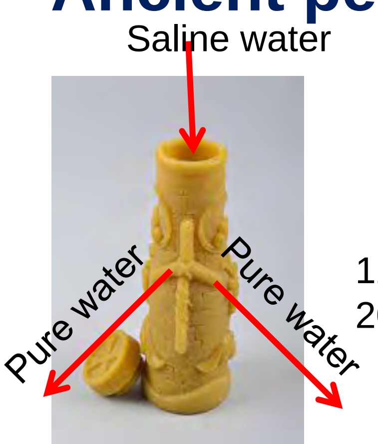
Contribution of various methods to global freshwater production



ED- electrodialys,
RO – reverse osmosis,
MED –multiple-effect distillation,
MSF – multi-stage flash distillation

WATER DESALINATION: FROM ARISTOTEL

Ancient period



Plant of sea water desalination, опріснення води, Ashkelon, Israel

127 millions m^{3}per year,
20 % of the country needs

Now

MEMBRANES
FOR GAS SEPARATION

MODERN ERA. XIX CENTURY

Diffusion through membranes. Different behavior of gases

John Kearsley Mitchell
1793-1858

The balloons made of caoutchouc, which were filled with different gases, decreased their volume with different rate depending on the gas. Hydrogen left balloon faster than air, but the fastest gas was CO_2.

Mitchell noted that CO_2 was adsorbed by the caoutchouc film. He suggested that pores of the film provide gas leakage.

Mitchell, J. K., On the Penetrativeness of Fluids, J. Roy. Inst., 4, 101-118; 5, 307-321 1831.

MODERN ERA. XIX CENTURY

Diffusion through membranes. Different behavior of gases

Thomas Graham

1829 — 1901

Thomas Graham used an apparatus to study the diffusion of gases .

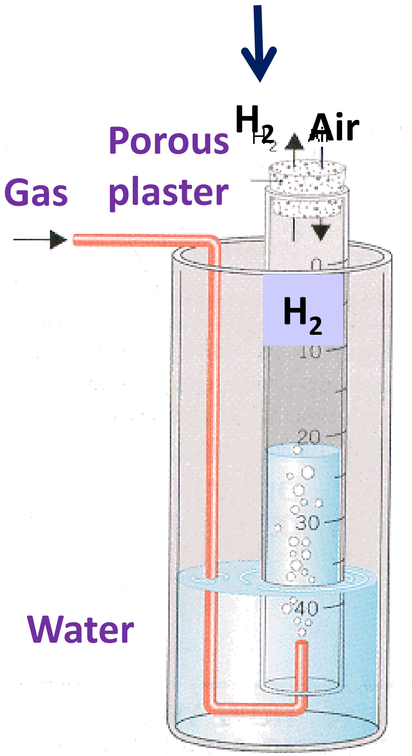
This apparatus consists of a glass tube sealed at one end with porous plaster.

When the tube is filled with H_2 gas, the level of water in the tube slowly rises.

This is due to the leakage of H_2 from the tube through the porous plaster. Hydrogen left the tube more rapidly than air can enter instead of it.

The rate of the change of the water level was studied. Based on these data, Graham estimated the rate, at which different gases mixed with air.

Gas (H_2) escape through porous material



MODERN ERA. XIX CENTURY

Illuminating gas – typical object for investigations

- **Illuminating gas was also an object of investigations by Graham. It is obtained by pyrolysis of coal or oil. Iluminating gas consists of H_2 (50 %), CH_4 (34 %), CO (8 %) and other combustible gases. In was developed by in the first half of the XIXth century by** *Friedrich Christian Accum* **(1760-1838). Iluminating gas was used for lighting in gas lamps and as fuel in XIXth and in the first half of the XIXth century.**

- **Illuminating gas in psychology – "gaslighting". This term is derived from the American movie "Gaslight" (1944).**

Purification of gas lamp in Westminster, London, 2011

Charles Boyer
as Gregory Anton/Sergis Bauer
Ingrid Bergman
as Paula Alquist Anton

MODERN ERA. XIX CENTURY

Diffusion of gases through membranes

- Graham also studied diffusion of illuminating gas through membranes (natural caoutchouc, guttapercha, platinum, palladium). Probably metallic particles were deposited chemically to natural or ceramic membranes (???).

- Faster diffusion of CO_2 and H_2 comparing other gases was found.

- Adsorption of hydrogen by Pt and Pd was suggested.

- Quantitative characteristics of membrane permeability with respect to oxygen, air, CO_2, CO, methane, etc. were determined. The rate of gas penetration is determined by pressure.

- Effusion was investigated. Effusion is a slow escape of gas through porous materials, molecules move in pores without collisions with each other. This is possible, when the pore diameter is much smaller than the length of the free path of the molecules. This distinguishes effusion from diffusion, when many molecules can penetrate through pores simultameously.

MODERN ERA. XIX CENTURY

Effusion of gases through membranes. Graham's law

Graham's law states that the rate of diffusion or of effusion of a gas (*Q*) is inversely proportional to the square root of its density (ρ) or molecular weight (*M*) at constant temperature and pressure.

$$Q \times \sqrt{\rho} = const$$

The constant is approximately similar for all gases

For two different gases:

$$\frac{Q_1}{Q_2} = \sqrt{\frac{M_2}{M_1}}$$

It means, the effusion rate is higher for lighter gas.

For instance, a balloon looses helium faster than air.

Further the theory of gas leakage through small pores was developed by Knudsen.

MODERN ERA. XIX CENTURY

Penetration of gases through membranes. Knudsen model

Martin Hans Christian Knudsen

1871-1949

Knudsen established that in pores with a pore diameter smaller than the length of the free path, the permeability cannot be described not only by the laws of viscous flow, but also by the laws of diffusion.

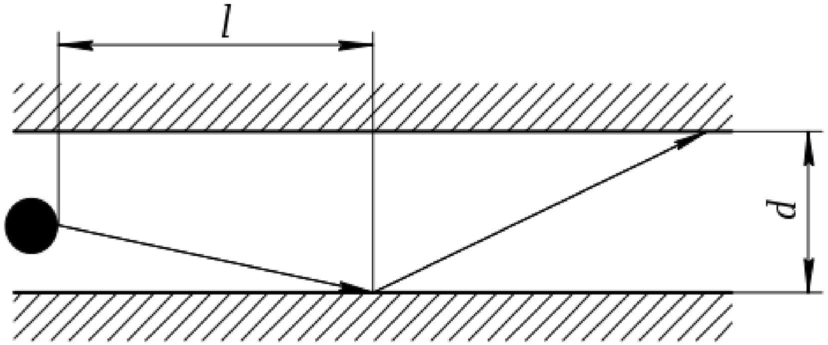
In order to describe permeability, the analogy with friction was used.

Now it is generally accepted that the Knudsen model is valid only in mesopores (2 nm<d<50 **nm). Though it is difficult to say about free path.**

In macropores (d>50 nm**), laws of molecular diffusion are valid. In micropores** (d< 2 nm) **, molecules interact with pore walls.**

MODERN ERA. XIX CENTURY

Penetration of gases through membranes. Knudsen model



The transition from ordinary diffusion in gases to Knudsen diffusion is characterized by a dimensionless parameter - Knudsen criterion (*Kn*):

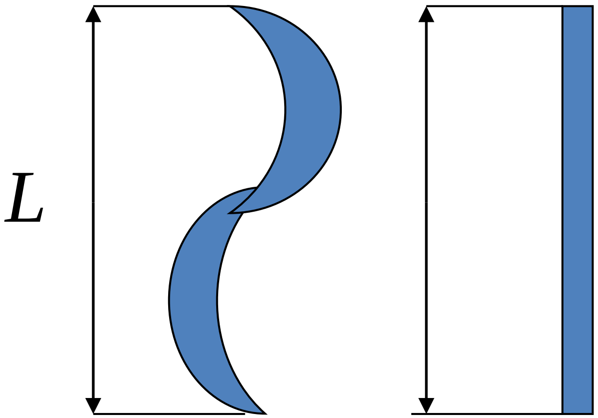
$$Kn = \frac{l}{d}$$

l – length of free pass,
d – pore diameter

***l* = 68 nm at 1 bar for molecules of O_2, N_2 and CO_2.**

***Kn*>>1 - the probability of collisions of gas molecules with pore walls significantly exceeds the probability of collisions of molecules with each other.**

Rate of gas through membrane *(Q)*



$$Q = \frac{\Delta P d^3}{6LP}\sqrt{\frac{2\pi RT}{M}}$$

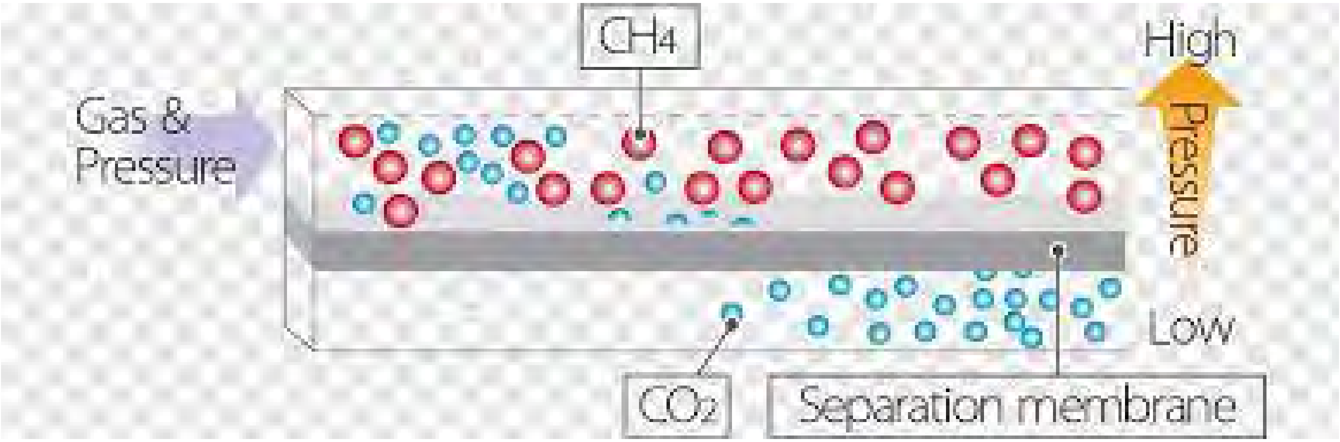
ΔP – difference of pressure between pore ends,
P - average pressure in a pore,
L – pore length

The *LP* parameter characterizes the tortuosity and narrowing-expansion of pores. The smaller this value, the higher rate of gas.

MODERN ERA. XX AND XXI CENTURIES

Practical application of Graham' and Knudsen' works

Development of membrane gas separation.



Driven force is the pressure gradient

The first membrane produced in industrial scale was made of poly(vinyltrimethyl)silane. The membrane was made in the middle of 1970 in the USSR. A thickness of dense layer was 0.2-0.4 µm, the overall thickness of the membrane was 100 µm.

Now the main producers of the membranes for gas separation are DuPont and Monsanto companies (USA).

MODERN ERA. XX AND XXI CENTURIES

Practical application of Graham’ and Knudsen’ works

Military needs.

- **Estimation of air leakage form spaceships and submarines. In order to remove CO_2 from air, special devices containing silicon membranes are used.**

MODERN ERA. XX AND XXI CENTURIES

Practical application of Graham' and Knudsen' works

Military needs

Atmolysis is the separation of a mixture of gases of different densities by multiple passing them through membranes.

1942.The multi-stage device for the separation of uranium isotopes was built in Oak Ridge (USA), Natural uranium is an isotopic mixture with 0.7% ^{235}U and 99.3% ^{238}U. Uranium is transformed into volatile UF_6, which is passed through the membranes. The diffusion rate of the ^{235}U isotope is higher only in 1.004 times comparing with ^{238}U. In order to obtain enriched uranium, membrane separation has to be repeated thousands times.

Gas centrifuge instead of membrane separation was used in the USSR.

The plant for uranium enrichment in Oak Ridge.

MODERN ERA. XX AND XXI CENTURIES

Practical application of Graham' and Knudsen' works

Oxygen concentrator

Membrane device is used for chirurgia. Oxygen diffuses through the silicone membrane into the blood. Oxygen dosing prevents protein denaturation and gas bubbles.

Especially the oxygen concentrator was important during COVID pandemic.

It is possible to increase O_2 concentration in air up to 33 % (I stage) and 91% (V stage). Graham obtained 46%.

It is possible to increase O_2 concentration in air up to 33 % (I stage) and 91% (V stage)). Graham obtained 46%.

CONCLUSIONS

Synthetic membranes and membrane separation in the third millennium

- Main scientific revolutions in this field occurred last century, all membrane separation processes are known. Now main efforts are focused on new membrane materials and improvement of known ones. Membrane processes are applied to new objects (fractionality of proteins or aminoacids from mixtures, recovery of RNA, dehydration of biofuel etc.)