

INTEGRATED SYSTEMS IN THE CHEMICAL PROCESS INTENSIFICATION

Igor N.Beckman

Chemistry Department, Moscow State University

Lecture

PLAN.

1. Introduction: New methods of chemical process intensification; combined use of equipment; improved plant design and process development.
2. Chemical functional materials and new technology.
 - 2.1 Chemical active filters.
 - Planar sorbents and catalysators.
 - Adsorption active filters for gas absorption and separation.
 - Catalytic active filters for gas conversion.
 - Regular structure apparatus.
 - Application (Environment, medica, technical)
 - 2.2. Swing adsorption.
 - 2.3. Membrane technology
 - Nonhomogeneous membranes
 - Non-steady-state regimes
 - Moving membranes
 - 2.4 Membrane catalysis
 - 2.5 Pump of heat
3. Integrated membrane systems
 - 3.1 Membrane technology and swing adsorption
 - 3.2 Permadsorbers
 - 3.3 Permabsorbers
 - Flowing;
 - Circulating;
 - 3.4 Selective membrane valve
 - Flowing;
 - Circulating;
 - 3.5 Permstractors
 - permstractor with flowing liquids
 - permstractor with supported liquids
 - Membrane extraction discs
4. Membrane reactors
 - 4.1 Chemical membrane reactor
 - Equipment for the performance of the membrane diagnostics
 - CMR with metallic membranes
 - CMR with ceramic membranes
 - CMR with glass membranes
 - CMR with polymeric membranes
 - 4.2 Plasma-chemical reactors
 - 4.3 Bio-reactors
 - 4.4 Membrane microfotoreactor
5. Combine equipment for new technology
 - Energetic save
 - Resource save
 - Little waste production.
6. Applications of new methods of chemical process intensification
 - In chemical industry
 - In biotechnology
 - In environment
7. Conclusion

ADSORPTION- OR CHEMICAL ACTIVE FILTERS AND THE REGULAR STRUCTURE APPARATUS

Possibility of differential design:

1. Apparatus design;

2. Tissue design;
3. Fibrous material design.

MATERIALS:

- Acids treatment basaltic fibres, tissue and felt;
- Active coal fibres, tissue and felt;
- Acid treatment glass fibres and tissue;
- Catalytic active basaltic fibres.

REGULAR STRUCTURES APPARATUS WITH PLANAR ADSORBENTS:

- Treatment of gaseous multicomponent waste;
- Removal H₂O, CO₂, SO₂, H₂S from air;
- Volatile organic compounds recovery from gaseous waste;
- Monitoring of pollutants in workplace air;
- Cleaning air from volatile hazardous metals (Sb, As, Cr) and their separation from polluted air resulting during incineration of municipal waste;

REGULAR STRUCTURES APPARATUS WITH PLANAR CATALYSTS:

- conversion of stereoisomers obtained in various incineration process to simple gases;
- transformation of organic compounds to gases may be important for energetic;
- thermo- and photodegradation of halogenated hydrocarbons
- production of methane and ethylene from agricultural and industrial wastes

A main advantage of active filters:

high removal efficiency, small volume, simple operation, excellent scale-up ability, no entertainment, flooding or channelling. Filtration through the active filters is a new process which combines adsorption, catalysis and filtration technology.

MEMBRANE METHODS OF GAS SEPARATION

1. Porous or non-porous (dense)
2. Active (membrane catalyst or ion- conductor) or chemical passive
3. Materials:

Inorganic membranes: Metal, alloy, ceramic, glass

Polymeric membranes: non-porous gas separation asymmetric composite membranes

4. Geometry of membrane: flat sheet or hollow fiber.

INTEGRATED MEMBRANE SYSTEMS

Liquid- membrane contactors:

1. Membrane permabsorber;
2. Selective membrane valve.

Condition of operation:

- 1) Flowing;
- 2) Circulating;

Selective flowing-liquid absorbent:

- 1) Non-specific in relation to the components of gas-separation mixture;
- 2) Solubility's of the gaseous components in a liquid could differ considerably;
- 3) Liquid could react with one or several of the gas components.

3. Perstractors with flowing liquids.

Liquid/liquid extraction processes for concentrating metal solutions from ppm-level to g/l-level with recycling of the concentrated metal solution and of the metal-free water.

Advantages:

High mass transfer, compactness, no fluid mixing.

1. Removal of toxic organic compound from waste water.
2. Removal of heavy metals from industrial waste or natural water.
4. Perstractors with supported liquid membrane technique for monitoring heavy metals (mercury and antimony) in natural water sources and biological solutions.

The main features of a new method are:

1. High extraction selectivity of the metal analysed (up to 10²-10³) due to proper choice of selective chelating agent and re-extraction phase content.
2. Concentrating of metal analysed in re-extraction solution by a factor of 10²-10⁴ due to "active" counter-current transport.
3. Volume of the probe analysed can be as small as 20-30 ml.
4. Cassette element design with thin channels for source and reextraction solutions that are separated by a porous hydrophobic support soaked with the solution of lipophylic chelating agent.

5. Membrane extraction discs for continuous monitoring of dissolved toxic metals.

- Hydrophobic membranes based from fluoropolymers;
- Acid-resistant macroporous spacers based on polyolefines of foam, sintered and non-wooven types;
- Defective lyophilic extragents for strontium and nicel extraction, of two classes: bis-(alkylcycloalkyl)-crownether and alkylene-bis-diphenylphosphine oxide with pendant aliphatic arm. Lyophilic alkylated hydroxyoximes for selective nikel extraction.

MEMBRANE CHEMICAL REACTORS

Membranes in chemical reactors:

- Equilibrium shift coursed by selective or preferential permeation of reaction products, leading to higher conversion in single pass or attaining a given conversion at less severe conditions of temperature and pressure.
- As reaction and permeation proceed simultaneously, the separation of products can be accomplished in the reactor unit.
- Selective permeation may prevent further reaction of a product and this may improve the yield of a desired component in a multiple reaction system.
- Ability to introduce a reactant in a controlled manner through a permeating membrane may allow the regulation of the reaction leading to better yield.
- Membrane may allow hot separation of products and eliminate the need for quenching a reaction to prevent back reaction.
- Membrane itself may act as a catalyst or catalyst may be impregnated on the membrane.
- The membrane reactor may be bifunctional and two complementary reactions may take place on either side of the membrane, the product of reaction on one side acting as a reactant on the other side, while the endothermicity of one reaction is compensated by the exothermicity of the other.

We are working in next directions:

- Construction of various new types of membrane reactors;
- Transport mechanism of fluids through active or passive membranes;
- Separation of mixed wastes;
- Steam reforming of methane;
- Water gas shift reaction;
- Dehydration of various hydrocarbons;
- Purification of tritium for thermomolecular energy installation;
- Radioactive waste management of nuclear power;
- Eir and water pollutants monitoring.

Membrane materials: metals (Pd, Pt, Ag, Fe, Ni, Cu), alloys, materials with coats and welds, ceramics, glasses (porous or dense)

Diffusants: hydrogen isotopes (protium, deuterium, tritium), air components, inert gases (stable and radioactive)

Diffusion methods: permeability method, sorption and desorption methods, thermodesorption spectroscopic analysis, frequency probing method, autoradiography method

Methods of membrane diagnostics: 1) Gas Diffusion Probe Method. 2) Auger Electron Spectroscopy. 3) Nuclear Gamma-Ray Resonance Spectroscopy Method (Mossbauer effect).

1. Intoduction.

It is well known that the chemical process intensification is novel design philosophy where significant reductions in plant scale can be achieved by matching the chemical, biological and/or physical requirements with the fluid dynamics of a process. Resultant benefice can include reductions in capital and operating cost, and/or significant improvements in efficiency process yield, waste production and inherent safety. Applications include implementation of continuous processes, compact heat exchangers and separators, modification of chemistry and improved plant layout and control.

Process intensification include:

- Compact reactors;
- Continuous processing;
- Compact separation methods;
- Reactors and separation systems optimisation;
- Novel chemistry;
- Combined use of equipment;
- Improved plant design and process development;
- Improved control systems (particularly for continuous processing);
- Achievement of significant process improvements through process intensification.

One would expect, that membrane reactor with chemical active and permselectivity walls, and/or circulate active carrier could play a great role in the chemical and biochemical process intensification.

In Russia carried out investigations to the prospects for use different type membrane reactor in chemical industry, biotechnology and environment. The emphasis is on the evolution of the new energetic- and resource save, safe and little waste production.

This lecture aims to discuss basic principles and potential application membrane reactors, MR, membrane integrated systems (permabsorber and permstractor), IMS, the adsorption or chemical active filters, MAF, with use the planar sorbents or catalysts and combine MR+IMS or MAF+IMS equipment was proposed. I shall consider of joint research completed in several organisations including Chemistry and Biological departments of Moscow State University and Membrane Centre of Institute of Petrochemical Synthesis RAS.

2. Chemical functional materials and new technology.

2.1 Chemical active filters.

Traditional adsorption apparatus using granulated sorbents are not efficient enough for the treatment of gases in order to separate the toxic components from the gaseous waste. Therefore chemical active filters have been used to this propose using mineral tissue (web) in the planar form. The advantages planar sorbent in comparison with the traditional (granular) sorbents:

- higher efficiency sorption;
- possibility of differential design of the sorption ensuring high technological flexibility;
- optimisation of the mass transfer and heat transfer in the sorption units (the chemisorption is connected with the release of heat which should be transferred out of the system).

Aim of our research was investigation of potential use of the new sorbents (adsorption or catalytic active filters) for cleaning industrial gases from hazardous pollutants (radioactive gases, organic contamination's and heavy metals).

Materials:

- Acids treatment basaltic fibres, tissue and felt;
- Active coal fibres, tissue and felt;
- catalytic active basaltic fibres.

Basalt planar sorbents were used for extracted of acid gases, hydrofoil organic and water vapours from polluted air or natural gas. Coal planar sorbents were used for sorption of hydrofolic organic vapours, radionuclides and vapours of volatile metals. Composite units containing planar sorbents made from different materials (coal and basalt).

We have made studies into regular structures apparatus with planar adsorbents uses for next aims:

- Treatment of gaseous multicomponent waste streams;
- Removal H_2O , CO_2 , SO_2 , H_2S from air;
- Volatile organic compounds (chlorinated micropollutants like dioxins and furanes, volatile ketone (MEK, MIBK), dioxins (PCDD stereoisomers) etc. recovery from gaseous waste;
- Monitoring of pollutants (benzene, xylol, dichlormethan, toluene, butanol, methanol) in workplace air;
- Cleaning air from volatile hazardous elements (I, Ag, Sb, As, Cr etc.) and their separation form polluted air resulting during incineration of municipal waste and in fire accidents;
- Removal from gaseous phases and storage of volatile heavy metals.

We have considered the potentiality of regular structures apparatus with planar catalysators uses for the performance of the next processes:

- conversion of dioxins stereoisomers obtained in various incineration process to simple gases;
- transformation of organic compounds to gases may be important for energetic.
- thermo- and photodegradation of halogenated hydrocarbons
- production of methane and ethylene from agricultural and industrial wastes

Pollutants removal from fluegas with active filters compared with conventional techniques the granular adsorbents has a main advantaged: high removal efficiency, small volume, simple operation, excellent scale-up ability, no entertainment, flooding or channelling. Filtration through the adsorption or catalytic active filters is a new, very selective separation process which combines adsorption, catalysis and filtration technology to produce an optimized hybrid process.

The prior analysis demonstrated that regular structures apparatus with planar adsorbents and/or catalysts hold the greatest promise for next application:

- environmental protection;
- energetic;
- chemical and petrochemical industry.

2.2. Swing adsorption.

2.3. Membrane technology

The entire history of membrane technology is a struggle for separation systems with high productivity, permselectivity, flexibility, and stability. This chapter gives some critical analyses of the existing methods aimed at controlling membrane gas separation processes. Several approaches are possible: selection of materials with heterogeneous spatial structure; employment of unsteady-state gas separation processes; use of mobile membranes, etc. Special consideration is given here to the problem of raising the selectivity of membrane systems.

2.3.1 Nonhomogeneous membranes

Composite materials are widely used today in membrane technology. A targeted search for such materials requires the development of a systematic approach to the construction of membranes that have a given efficiency and selectivity, using substances with known local diffusion properties. Here we regard the prospects for using the steric and chemical organization of a heterogeneous material to control the parameters of gas separation membranes.

For the mathematical description of diffusion in a heterogeneous medium one has to take into account several features of the system:

- The number of components in the medium
- The topology of the medium, i.e., the spatial arrangement of the discontinuity (layer, inclusions, dispersions of inclusions, etc.)
- Variations in the topology of the medium caused by external effects or by phase transitions
- Transport properties of the initial components of the medium
- The type of sorption isotherm for the diffusant in each of the components of the medium
- The nature of the interface between components
- The type of diffusion experiment, i.e., the set of initial and boundary conditions.

Defect Media. It is often implied that the nature of the interaction between a solute and the solvent is best investigated when the solute concentration approaches the infinite dilution limit. In this limit, solute-solute interactions can be neglected. However, for solid polymers specific sorption sites appear to exist and thermodynamic properties measured in the very low range of solute concentrations may not reflect the solute-solid polymer interaction at all. This is especially true at low temperatures because the fraction of solute molecules associated with such extra sites increases at temperature decreases.

Another aspect of the problem of solute trapping is related to the effect of such interactions upon the mobility of the solute molecules. It is clear that the solubility determined from the integrated flux measured in a permeability experiment will not, in general, be equal to the solubility that would be determined in an equilibrium situation, e.g., gas-polymer equilibration.

We now consider gas molecules that migrate in the polymer matrix via random walks that are interrupted by trapping into various imperfections (the point inclusions in a polymer-holes, cavities, or gaps between stiff chains) existing in a solid. The sample is believed to contain the penetrant in two energetically distinguishable sites: in the continuous phase of the polymer (i.e., "normal") and in inclusions (i.e., "trapped").

Certain types of energy diagrams for diffusion in a two-component medium are shown in Figure . The migration of the diffusant is determined by the positions of the two potential wells of types 1 and 2 relative to the zero level (i.e., by the energies G_1 and G_2) and also by the magnitude of the energy barriers on entrance to and exit from the potential well ($\Delta G_{11} = \Delta G_{11} D_1$ for a transition in the base matrix, ΔG_{12} for a transition from the base matrix to an inclusion, $\Delta G_{22} = \Delta G_{22} D_2$ for diffusion in an inclusion, and ΔG_{21} for exit from an inclusion to the base material of the specimen). A state with a lower free energy (Figure 5a) fills up with diffusant spontaneously (a "trap"). The transition to another phase may be hindered ($\Delta G_{12} - \Delta G_{11} = \Delta G_L$). The height of this barrier between two adjacent states (1-2) can be either higher or lower than the normal height in the case of undistributed diffusion (1-1). If the second (phase) has finite dimension, the transitions of 2-2 types should be considered as well (see the energy diagram in Figure 5b).

The gas solubility in a heterogeneous membrane (average concentration $\bar{C}(p)$) is defined by the formula

$$\bar{C} = \phi_1 C_1 + \phi_2 C_2$$

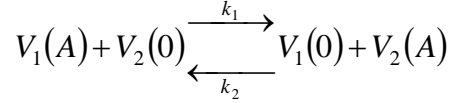
where $\phi_1 = \frac{V_1}{V_{\text{samp}}}$ and $\phi_2 = \frac{V_2}{V_{\text{samp}}}$ are the volume fractions of components 1 (the polymer) and 2 (inclusions or traps), respectively (V_{samp} is the sample volume, $V_{\text{samp}} = V_1 + V_2$).

There are several variants of the dual mode sorption model.

- 1) Dissolution in the continuous phase and in the inclusions is described by Henry's law: $C_1 = S_1 p_0$ and $C_2 = S_2 p_0$, where S_1 and S_2 are solubility constants and p_0 is partial pressure of penetrant at the membrane inlet (the Henry I-Henry II model).
- 2) Dissolution obeys Henry's law, and "hole-filling" obeys a Langmuir expression (the Henry-Langmuir model).
- 3) The model is given by superposition of Langmuir I and Langmuir II model).
- 4) Dissolution obeys Henry's law, and "hole-filling" obeys a Freundlich expression (the Henry-Freundlich model), etc.

Treatment of sorption in microvoid environments with typical void dimensions of truly molecular scale is provided by extension of Polyan's adsorption potential theory for surfaces to treat microporous materials. This treatment allows for energetic heterogeneity of the sorption "sites". Such an approach is more general than the Langmuir treatment, which assumes that the enthalpy of sorption in the microvoid that forms is essentially independent of the degree of site saturation. The superposition of Henry's law with Dubinin's isotherm leads to complicated situation.

The exchange of diffusant between the two types of potential wells is usually represented in the form



where $V_1(A)$ and $V_2(A)$ are the diffusant molecules in potential wells of types 1 and 2, respectively, $V_1(0)$ and $V_2(0)$ are vacant sites, and k_i is the rate constant for the passage of diffusant molecules from one energy state to another.

The equilibrium reaction constant for exchange of gas atoms between the components of a heterogeneous medium is

$$K = \frac{k_1}{k_2} = \frac{C_2(C_{1m} - C_1)}{C_1(C_{2m} - C_2)} = \frac{b_2}{b_1} = \frac{\theta_2(\phi_1 m_1 - \theta_1)}{\theta_1(\phi_2 m_2 - \theta_2)} = \frac{\tilde{\theta}_2(m_1 - \tilde{\theta}_1)}{\tilde{\theta}_1(m_2 - \tilde{\theta}_2)}$$

where $C_1 = \frac{n_1}{V}$ and $C_2 = \frac{n_2}{V}$ are the concentration of the gas atoms in sites 1 and 2, respectively;

$C_{1m} = \frac{n_{1m}}{V}$ and $C_{2m} = \frac{n_{2m}}{V}$, where $n_{1m} = m_1 N_1$ and $n_{2m} = m_2 N_2$ are the capacities of sites 1 and 2, respectively;

$\theta_1 = \frac{n_1}{N}$, $\theta_2 = \frac{n_2}{N}$, $\theta = \theta_1 + \theta_2$; $\phi_1 = \frac{N_1}{N} = \frac{V_1}{V}$, $\phi_2 = \frac{N_2}{N} = \frac{V_2}{V}$; $\phi_1 + \phi_2 = 1$; N_1 and N_2 are the number of states 1 and 2; b_1 and b_2 are Langmuir's sorption isotherm parameters of components 1 and 2. Each site contains up to m gas atoms, where m has values between 1 and ∞ . The total population (solubility) of the two-component system is $\theta = \frac{n}{N} = \frac{n_1 + n_2}{N_1 + N_2}$, and the mean population is $\tilde{\theta} = \phi_1 \tilde{\theta}_1 + \phi_2 \tilde{\theta}_2 = \theta_1 + \theta_2$. If $m_1 = m_2 = 1$, then

$$K = \frac{\theta_2(\phi_1 - \theta_1)}{\theta_1(\phi_2 - \theta_2)} = \frac{\tilde{\theta}_2(1 - \tilde{\theta}_1)}{\tilde{\theta}_1(1 - \tilde{\theta}_2)}$$

If $m_1 = m_2 \rightarrow \infty$, then

$$K = \frac{C_2}{C_1} = \frac{\theta_2 \phi_1}{\theta_1 \phi_2} = \frac{\tilde{\theta}_2}{\tilde{\theta}_1} = \frac{k_1}{k_2} = \frac{n_2 N_1}{n_1 N_2}$$

Mathematically a trapping effect has been introduced in Fick's law by adding reaction between mobile gas atoms and stable distribution of traps. The basic equation of motion is as follows:

$$\frac{\partial C_1}{\partial t} = \frac{\partial}{\partial x} (D_1 \frac{\partial C_1}{\partial x}) + \tilde{R}$$

where \tilde{R} represents the kinetics implied by process given by Relation 12.

In the partial immobilisation models, a diffusion coefficient is assigned to each of the penetrant populations. The unidirectional flux J_x is given by the linear combination of two Fick's-law contributions:

$$J_x = -D_1 \frac{dC_1}{dx} - D_2 \frac{dC_2}{dx}$$

where D_1 is associated with the population of component 1, and D_2 with diffusion of population of component 2.

Applying Fick's second law to j species ($j=2$ for dual sorption), we have

$$\frac{\partial^2 (\sum D_j C_j)}{\partial x^2} = \frac{\partial (\sum C_j)}{\partial t}$$

(where "Σ" means summation over all the species).

Some variants of the dual mode sorption models and their consequences are given in Table 1.

Let us consider the diffusion of gas in a solid formed as a mixture of two polymers, one of which is the continuous phase (phase 1) and the other one forms point inclusions (phase 2) capable of interacting with the diffusant (the Henry I [mobile]-Henry II [immobile] model). Let us suppose that point inclusions or isolated point defects with an unlimited capacity ($m_1 \rightarrow \infty$ and $m_2 \rightarrow \infty$) are randomly distributed in the bulk of the polymer membrane. In the course of their random motion, molecules of the diffusing agent are trapped by the defects and are excluded for a definite time interval from the diffusion process. This process, called gas diffusion with reversible trapping, can be described by the following differential equations:

$$\frac{\partial C_1}{\partial t} = D \frac{\partial^2 C_1}{\partial x^2} - k_1 N_2 C_1 + k_2 N_1 C_2 = D \frac{\partial^2 C}{\partial x^2} - k_1^* C_1 + k_2^* C_2$$

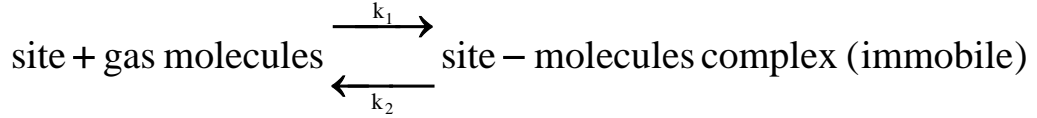
$$\frac{\partial C_2}{\partial t} = k_1 N_2 C_1 - k_2 N_1 C_2 = k_1^* C_1 - k_2^* C_2$$

where C_1 and C_2 are the concentrations of the diffusing agent in the diffusion channels and traps, respectively, and

$$k_1^* = k_1 N_2 \quad \text{and} \quad k_2^* = k_2 N_1$$

The first-order chemical reaction kinetics is used for describing the trapping of gas molecules by the matrix and subsequent release of the gas.

The trapping reaction is



A quasichemical equilibrium is shifted to the left-hand side at high temperatures, favoring movement of the gas to its mobile state and vice versa. The equilibrium constant of the trapping reactions is

$$K = \frac{k_1}{k_2} = \frac{n_2 N_1}{n_1 N_2} = \frac{\tilde{\theta}_2}{\tilde{\theta}_1} = \frac{\theta_2 \phi_1}{\theta_1 \phi_2}$$

or

$$K_H = \frac{n_2}{n_1} = \frac{k_1 N_2}{k_2 N_1} = \frac{k_1^*}{k_2^*} = \frac{C_1}{C_2} = K \frac{\phi_2}{\phi_1}$$

If $N_1 \approx N_2$, then

$$K_H = K \theta_2$$

The time dependence of the gas flow through the membrane containing a dispersion of defects of unlimited capacity is described by the following expression:

$$\begin{aligned} J_t &= -D \left. \frac{dC}{dx} \right|_{x=l} \\ &= \frac{C_0 D}{l} \left\{ 1 - \sum_{n=1}^{\infty} \frac{(-1)^n}{R_n} [(\alpha_1 - k_1^* - k_2^*) \exp(-\alpha_1 t) - \right. \\ &\quad \left. - (\alpha_2 - k_1^* - k_2^*) \exp(-\alpha_2 t)] \right\} \end{aligned}$$

$$\alpha_1 = 0.5(k_1^* + k_2^* + D\omega_n^2) - R_n$$

$$\alpha_2 = 0.5(k_1^* + k_2^* + D\omega_n^2) + R_n$$

$$R_n = [k_1^*k_2^* + 0.25(k_1^* - k_2^* + D\omega^2)^2]^{1/2}$$

$$\omega = \frac{n\pi}{l}$$

and C_0 is the gas concentration at the membrane inlet.

Figure 6 shows the permeability curves calculated from Equation 19 for the different values of the parameters k_1^* and k_2^* . The presence of point inhomogeneities in the structure is seen to increase the time before the flow can reach its steady state, as compared with diffusion in a homogeneous medium. As the capture constant increases, the time lag increases and the kinetic curve broadens and acquires a more asymmetric form.

Now we consider a concentration wave passing through defect media. The square concentration wave is sent to the membrane inlet, and the gas flux $J(t)$ is measured at the membrane outlet. Then the diffusion coefficient can be determined using a Fourier $J(t)$ transformation. As far the system of equations given by Expression 20 is linear, linear superposition of some of its solutions gives the problem solution.

Consequently, expanding the inert gas concentration into a Fourier series,

$$C = \sum_{n=1}^{\infty} A_n \exp(in\omega t) + A_0$$

and solving the problem for some harmonics, one can obtain the outlet in the form of a harmonic sum:

$$J = \sum_{n=1}^{\infty} B_n \exp(in\omega t) + B_0$$

where A_n and B_n are the concentration and outlet flux Fourier coefficients, accordingly. The solution for the first harmonic of the flux is described by the following expression:

$$J = DA_1 \left(\frac{Y^{1/2}}{\sinh Y^{1/2}} \right) \exp(i\omega t)$$

where $Y = \frac{i\omega l^2(k_1 + k_2 + i\omega)}{D(k_2 + i\omega)}$ and A_1 is the first harmonic of inlet concentration. Then $B_n = \frac{A_n D Y^{1/2}}{\sinh Y^{1/2}}$. The

diffusion coefficient can be determined using the Fourier transformation coefficients of the outlet flux and the inlet concentration ratio.

An important special case of the model is given when the trapping reaction has reached its thermal equilibrium. Differential Equation 17 reduces to the simple Fick's type, with D_{app} , which is smaller than D for undisturbed diffusion. If the local equilibrium is reached during the experiment ($k_1^*C_1 = k_2^*C_2$), the observed diffusion coefficients D_{app} may be related to the diffusion coefficient for the mobile gas, D , by the following: If $k_1^*C_1 = k_2^*C_2$, then (see Table 1, Case 2)

$$\frac{\partial C}{\partial t} = \frac{D}{(1 + K_H)} \frac{\partial^2 C}{\partial x^2} = D_{app} \frac{\partial^2 C}{\partial x^2}$$

where

$$D_{app} = \frac{D}{1 + K \frac{\phi_2}{\phi_1}} = \frac{D}{1 + K_H}$$

These results are derived by considering the equilibrium distribution of gas molecules between normal sites and traps. The expressions for the diffusion coefficient are correct if this equilibrium is established rapidly compared with the rate of diffusion of the gas out of the solid, and this condition is satisfied in many experiments.

The effective gas solubility in heterogeneous membrane is defined by

$$\bar{C} = \phi_1 \bar{C}_1 + \phi_2 \bar{C}_2 = \bar{C}_1 (\phi_1 + K \phi_2) = \bar{C}_1 \phi_1 (1 + K_H)$$

The permeability constant is given by

$$P = P_1 \phi_1 = D_1 S_1 \phi_1$$

because in dilute dispersions $\phi_2 \ll 1$ and $\phi_1 \cong 1$, $P \cong D_1 S_1$, i.e., when sorption centers of unlimited capacity are present in the membrane, the permeability constant in a defective medium is approximately equal to the permeability constant for an undisturbed matrix.

Dispersion Media. The main class of "microheterogeneous" structures is made up of dispersion media, i.e., solids containing a dispersion of inclusions of a specific shape and size. The thermodynamic and kinetic properties of the dispersed phase differ from those of the continuous base material.

The sorption process is assumed to be isothermal, and linear isotherms are assumed.

a. Gas permeability of material with inclusions of another polymer

The kinetics of gas diffusion into the plate containing inclusions (microspheres) obeys the following differential equations:

$$\frac{\partial C_1}{\partial t} = D_1 \frac{\partial^2 C_1}{\partial x^2} - 4\pi r_0^2 n_2 D_2 \left(\frac{dC_2}{dr} \right)_{r=r_0}$$

$$\frac{\partial C_2}{\partial t} = D_2 \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{dC_2}{dr} \right)_{r=r_0}$$

$$C_2 = K C_1$$

where C_1 is the continuous matrix (macropore) gas concentration, C_2 is the inclusion (micropore) gas concentration, D_1 is the matrix diffusivity, D_2 is the inclusion diffusivity ($D_2 \ll D_1$), r_0 is inclusion radius, n_2 is number of microspheres (inclusions) per unit sample volume, r is the distance from microsphere center, $K = S_2/S_1$, and x is the distance in a flat membrane.

The initial and boundary conditions are

$$C_1(x,0) = 0; C_2(r,0) = 0; C_1(l,0) = C_{10}; C_2(r_0,t) = K C(x, r_0, t);$$

$$\frac{dC_1(0,t)}{dt} = 0; \frac{dC_2(0,t)}{dt} = 0$$

where l is the thickness of the membrane.

The transmembrane flux of gas is

$$J_t = \frac{C_0 D_1}{l} \left\{ 1 + \frac{4\pi^2}{k\eta} \cdot \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{m^2 (-1)^m \exp(-\mu \xi_{mn}^2 \tau)}{\xi_{mn}^2 \left[\frac{\mu}{k\eta} + 1 + \cot g^2 \xi_{mn} - \left(1 - \frac{m^2 \pi}{k\eta} \right) \frac{1}{\xi_{mn}^2} \right]} \right\}$$

where ξ_{mn}^2 are the roots of the following transcendental equation:

$$\mu \xi_{mn}^2 + k\eta (1 - \xi_{mn} \cot g \xi_{mn}) = \pi^2 m^2$$

where $\mu = \frac{D_2 l^2}{D_1 r_0^2}$, $\eta = \frac{\psi D_2 l^2}{r_0 D_1} = \phi_2 \mu$, $\psi = 4\pi r_0^2 n_2 = 3\phi_2 / r_0$, $\phi_2 = \frac{V_{incl}}{V_{samp}}$, $V_{samp} = Al$ (volume of sample),

and $\tau = \frac{D_1 t}{l^2}$.

A phenomenological theory of transport in dispersion media was proposed by Maxwell to describe the electrical conductivity of dispersions and then adapted to the problem of thermal conductivity and diffusion (the history of the problem is given in Reference 28).

For a dispersion of inclusions of identical shape and size (modified by Maxwell formula),

$$\frac{P}{P_1} = \frac{\phi_1 + aP_2\phi_2/P_1}{\phi_1 + a\phi_2} \text{ and } \bar{\theta} = \bar{\theta}_{10}(\phi_1 + K\phi_2)$$

where

$$a = \frac{a_0}{\left(a_0 - 1 + \frac{P_2}{P_1}\right)}$$

a_0 being a geometrical factor depending only on the shape of the inclusion.

The value of a_0 is a measure of the distortions of the flow lines, i.e., the lines along which the product of the diffusion coefficient and the gradient of the diffusant concentration remains constant: for a given P_2/P_1 the smaller a_0 , the greater the distortion. For some simple forms of inclusions a_0 can be calculated analytically: e.g., $a_0=3$ for inclusions with a spherical shape and 2 for inclusions in the form of cylinder with its axis perpendicular to the diffusion flow, etc.

Equation 28 is valid for dilute suspensions ($\phi_2 < 0.3$); on changing to closet packing of the inclusions, additional terms must be introduced into formula 28. On the whole, Equation 28 is satisfied as long as the inclusions retain a definite shape and continuous diffusion flows along one of the components of the heterogeneous medium are possible. It should be noted that when there is phase reversal (i.e., when the matrix and the inclusion change roles), "hysteresis" of permeability may occur.

Using mathematical simulation methods to test known published models showed that there is a rigorous mathematical description only for cases of parallel diffusion and for diffusion in a lamellar medium. When extended inclusions of a specific shape and size are present, an analytical description is possible for certain simple forms (sphere, cylinder, spheroid), for which the "experimental" values of a_0 agree with the theoretical values and for $\phi_2 < 0.3$. As ϕ_2 increases, the description of the process by the analytical formula becomes worse, with P/P_1 approaching P_2/P_1 more rapidly than the ratio of the width of the inclusion to its length but also on the "distortion power" of the particular form of inclusion as regards the diffusion flow lines.

Numerical modeling methods can be used to find the values of a_0 for inclusions with the "exotic" shape of rectangular blocks, crosses, etc., for a lamellar medium with variable boundary, and also to study the evolution of a_0 by reversal of phases, which involves nucleation and growth of new phase, etc. In particular, the modelling method gives the value $a_0=1.55+0.15$ for an infinite block with a square cross section placed perpendicular to the direction of flow. This value is smaller than the value $a_0=2$ for a cylinder because a block with a square cross section distorts the diffusion flow lines considerably more severely. The common form of notation that we use here for the permeability of the main types of structure shows clearly the general character of the modified Maxwell formula (Equation 28), from which the other diffusion models arise as special cases when an appropriate choice of the geometrical form parameter a_0 ($a_0 \geq 1$) is made. The limiting cases are parallel diffusion ($a_0 = \infty$) and sequential diffusion ($a_0 = 1$).

A special class is formed by structures generated from dispersions of point inclusions as the volume fraction of the latter is increased (for brevity, we shall call such heterogeneous substances, the point inclusions are joined together in extended formations (clusters) and the dispersion is the clusters. In spite of the random nature of the cluster formation, this type of dispersion medium obeys strictly defined statistical rules and the evolution of the system can be quantitatively described in terms of percolation theory, using such concepts as the percolation threshold and the critical index. At a certain value of the volume fraction a continuous cluster is generated (there is "puncturing" of the membrane, accompanied by a sharp change in transport properties).

The dependence of the permeability on the volume fraction of the second component is shown in Figure 7 for various types of structures. The $P(\phi_2)/P_1$ curves lie between the two limiting cases: dissociative or parallel diffusion (the straight line, 1) and diffusion in a lamellar medium (Curve 2). Exceptions are provided by dispersion structures of the percolation type. The dependence of P/P_1 on the local transport parameters envisages an effect of the intercomponent layers on the transport (in this case a situation arises that requires the solution of the a "three-phase" diffusion problem for a two-component medium). Depending on the conditions at the boundary between the components, the $P(\phi_2)/P_1$ curve may pass below the straight line for the limiting case $a_0=1$, corresponding to a low permeability of the curve, or it may be completely within the permissible region (the permeability of the intercomponent layer lies between the corresponding values for the components of the medium, (Curve 4), or it may be situated above the limiting straight line for $a_0 = \infty$. The last situation arises when the permeability is high at the boundary (i.e., when $D_{12} \gg D_{11}$ and $D_{12} \gg D_{22}$, Curve 5), a maximum on the $P(\phi_2)/P_1$ curve being possible.

Effective medium percolation theory gives the following expression for the effective permeability P of a random mixture of particles of two differing permeabilities P_1 and P_2 :

$$\frac{P}{P_1} = 0.25 \left\{ 2 - \frac{P_2}{P_1} + 3\phi_2 \left(\frac{P_2}{P_1} - 1 \right) + \left[\frac{P_2}{P_1} - 2 - 3\phi_2 \left(\frac{P_2}{P_1} - 1 \right) \right]^2 + 8 \frac{P_2}{P_1} \right\}$$

where ϕ_2 is the volume fraction of component 2. The expression is independent of particle size.

Selection of the Material. We shall now turn to the problem of the membrane separation of a mixture of gases and assess the prospects for a directed choice of the structure of the heterogeneous medium in order to achieve the optimum efficiency and selectivity for the membrane.

Suppose that a mixture of two gases is supplied to the upstream side of a membrane, and suppose that the transport process of each of them through the membrane is characterized by its own set of parameters D , K , P/P_1 , and θ . These parameters are regarded as being dependent on the composition and topology of the membrane but independent of the composition of the gaseous mixture. We shall take as the selectivity factor the relationship

$$\alpha = \frac{P_{\text{eff}}^A}{P_{\text{eff}}^B} = \frac{\alpha_1 \chi^A}{\chi^B}$$

where $\chi^A = P^A / P_1^A$ and $\chi^B = P^B / P_1^B$ are the ratios of permeabilities of the first (target) and the second gases, respectively, and $\alpha_1 = P_1^A / P_1^B$ (P_1^A is the permeability of gas A in phase 1, and P_1^B is the permeability of gas B in phase 2).

The operational effectiveness of gas-separating system is characterized by two parameters: the efficiency (i.e., the permeability for the object component, χ^A), which determines the amount of product obtained, and the selectivity, which determines the purity of the product.

The effects of the local transport parameters of the heterogeneous medium on the flow of the object component χ^A and on the selectivity factor α are different: A decrease in D_2^A/D_1^A and K^A leads to reduction in χ^A and α , but a decrease in D_2^B/D_1^B and K^B increases α while leaving χ^A unchanged. Because the change in χ^A and α in heterogeneous structures of different types takes place differently, then, depending on whether the membrane works by purification or enrichment, these parameters will have the optimum values for quite different spatial organizations of the material. It follows from Equation 30 that α is function of six parameters (if the topological factor α_0 is taken as one of them). We shall therefore restrict ourselves to a few examples.

The first two examples are taken from Reference 36, in which measurements were made of the gas permeability of PVTMS (Component 1)- PDMS (Component 2) block copolymers of various compositions; PVTMS represents poly(vinyltrimethylsilane), and PDMS represents polydimethylsilane). We shall discuss Kr-Xe and H₂-Xe gas mixtures. For a Kr-Xe mixture the experimental separation factor ($\alpha=0.56$) is close to the value calculated (0.61) for the parallel diffusion mechanism. However, there is considerable discrepancy between the experimental and calculated values of χ^A (2.04 and 10.4, respectively). This might be explained by an extra resistance to transport at the boundaries between the components of the block copolymer. In this case the membrane used in the experiment is close to the optimum from the point of view of concentrating the Kr. In using a membrane for Xe purification, the membrane efficiency can be increased (by a factor of 5) if a structure that ensures a parallel diffusion mechanism is created.

For a H₂-Xe mixture the theoretical value of the efficiency with respect to the target gas (H₂) is slightly dependent on the structure of the membrane and is close to the experimental value (evidently, for hydrogen, resistance to diffusion at the boundary between the components does not play a significant role). However, the theoretical analysis shows that the membrane structure used in the experiment was not the optimum as regards selectivity; in this case a lamellar membrane should be used.

The effect of the structure on the gas-separation parameters χ^A and α is conveniently studied using topology-property diagrams. To construct such diagrams (Figure 8), the reciprocal of the geometrical factor α_0 is plotted along the abscissa, with χ^A and α as the ordinate.

These diagrams first of all, enable the geometrical factor α_0 to be estimated from gas permeability data. The value α_0 can be determined experimentally by measuring either the efficiency of the membrane or the separation factor. The agreement between the α_0 values found by different methods indicates the absence of resistance at the boundary between the components. The discrepancy between the values of α_0 obtained from χ^A and α (in Figure 8 the range of uncertainty for α_0 is shaded) is large for the Kr-Xe mixture (Figure 8a), far larger than the corresponding range for the H₂-Xe mixture (Figure 8b).

Such diagrams can be thus be used for diffusion-structure analysis, i.e., to determine the topological characteristics of a membrane used in a separation process. On the other hand, they can be used to select the optimum structure for a gas-separating membrane because, for known transport properties of the individual components, they display clearly the properties of heterogeneous structures. In the case shown in Figure 8a, selection of structure enables, primarily, the membrane efficiency to be controlled, is only altering it by an order of magnitude; the selectivity, however, is only altered by a factor of 1.5. Figure 8b illustrates the reverse case - the structure of the membrane controls mainly the selectivity while the efficiency remains almost constant.

Local and non-steady-state separations factors. The complex nature of gas diffusion in real polymeric materials was exhibited in the experiments with radioactive isotopes and by using autoradiographic techniques.[37-40] For example, nonuniform distribution of radioactive gas on both the upstream and downstream surfaces of a membrane was demonstrated by this method in the research of the Rn diffusion through the polypropylene films with spherulite structure [38].

Description of the permeation process through heterogeneous polymers requires introduction of the concept of local solubility and diffusivity spectra. The spectra have asymmetric shape and change during the course of the diffusion process development.

This feature of heterogeneous gas-separation membranes should be considered by using the concept of local coefficient productivity spectrum (i.e., the spectrum of fluxes through separate parts of the membrane) and the local separation factors. In order to check this assumption, a mixture of tritium and radon was passed through a membrane of polypropylene. Recording of each gas is carried out separately by using photographic plates that are sensitive either to β - radiation of tritium or to α - radiation of radon. The autoradiogram was photometered on a scanning microphotometer and a kind of topographical map was obtained, $I(y,z)$ [Figure 9] [38,39]. A map of the inert-gas distribution obtained in this way at the output of a polypropylene membrane (Figure 9a) allows us to determine the spectra of the local diffusion coefficients and solubility constants of the inert gas in the membrane material (see Figure 9b).

It is seen from the maps that the film is significantly nonuniform for the diffusion process of both tritium and radon. There are regions of two kinds: with abnormally low concentration of diffusant (boundary of spherulite). There is a certain correlation between the distribution functions of tritium and radon on the membrane surface, but there are substantial differences (Figure 10a). They are determined by the different value of solubility and diffusion of these gases in particular morphological formations of polypropylene. These differences become more evident by introducing the concept of the local separation factor spectrum.

In accordance with Fick's law for each diffusant,

$$J(y, z, t) = -D \frac{dC}{dx} \approx -DS \frac{I_{in}}{I_{out}}$$

Then the local non-steady-state separation factor is

$$\alpha_{loc}(y, z, t) = \frac{P_A}{P_B} \frac{I_{in}^A / I_{out}^A}{I_{in}^B / I_{out}^B} = \alpha_{ss}^{A/B} \rho$$

where

$$\alpha_{ss}^{A/B} = \frac{P^A}{P^B} \quad \text{and} \quad \rho = \frac{I_{in}^A / I_{out}^A}{I_{in}^B / I_{out}^B} \propto \alpha_{loc}$$

Relative density of the darkening is easily determined from the autoradiography data. A typical $\rho(y)$ curve for the tritium-radon-polypropylene system is shown in figure 10b. In the vicinity of a spherulite center, the ρ parameter is seen to increase (at the spherulite boundary $\rho=1$). Figure 10b gives the curve of the distribution function of $\rho(y)$ over the membrane surface, measured for different diffusion times ($t=\tau_L T_2$ and $t=2\tau_L T_2$, where $\tau_L T_2$ is the time lag of tritium diffusion over the whole membrane, measured from the permeability kinetic curve). It is seen that $\alpha_{loc}=f(t)$, and, as the steady-state permeability mode is approached, the $\alpha_{loc}(y,z)$ spectrum becomes more uniform.

The use of heterogeneous membranes thus requires introduction of the notion of non-steady-state local separation factor.

Table 2 lists the interrelations between the local and overall (i.e., measured for the whole membrane surface), steady, and integral (i.e., measured by the amount of the passed gas) and differential (i.e., measured by the gas flow through the membrane) selectivity factors.

2.3.2 Selective permeation of gases in non-steady-state conditions

At present, membrane separation of gas mixtures is performed exclusively at steady-state conditions. The effectiveness of the gas separation process in this case is determined mainly by the transport characteristics of the membrane material. In order to reach high productivity and selectivity, it is necessary to control separately the effective diffusion coefficient (the selection of a polymer, chemical or structural modification of the diffusion medium, etc.) and the solubility coefficient (introduction of chemically active centers, mobile penetrant carriers, etc.).

The permeability coefficient of the j th gas component in the membrane is given by

$$P(j)=D(j) \times S(j)$$

where $D(j)$ is the diffusion coefficient in the membrane and $S(j)$ is the solubility coefficient of the j th gas component.

For a given membrane material, the productivity can be altered over a wide range by changing the thickness and the area of the membrane or by going to a more favorable geometry. The steady-state separation factor for two species is the product of the diffusion coefficient and solubility coefficient ratios, i.e.,

$$\alpha_{ss} = \frac{D^A S^A}{D^B S^B}$$

For many pairs $D^A/D^B > 1$, yet $S^A/S^B < 1$, which often leads to less efficient separation than desired. Once the membrane material is fixed, the selectivity characteristics are also essentially fixed, the selectivity characteristics are also essentially fixed when steady-state operation used. This chapter points out that transient operation of the membrane can be used to alter the selectivity characteristics [1]. Cases will be examined where great improvements in selectivity can be realized; however, this is always accompanied by a loss of productivity.

Steady-state and transient membrane operations. For a flat membrane with a constant diffusion coefficient and Henry's coefficient for each gas, i.e., D and S , the total amount of gas permeating the membrane in time t at steady-state is

$$q_{ss} = AtD(C_H - C_L)/l = AtDS(P_H - P_L)/l$$

where p_H and p_L are the upstream and downstream gas pressures, A is the membrane area, l is the thickness of the membrane, and C_H and C_L are the upstream and downstream gas concentrations. The steady-state transport of a gas through a membrane responds to D and S independently.

Different experimental permeation schemes are in use [2,3]. Typical experimental curves are demonstrated in Figure 1a-d: (a) the integral method; (b) the differential method; (c) the impulse method; (d) the differential impulse method. In the time-lag-type experiment (integral method), the amount of gas passing through the membrane ($C_H=C_0$, $C_L=0$) is measured continuously over time (see Figure 1a):

$$\begin{aligned} q &= DAC_0 \left[\frac{t}{\ell} - \frac{\ell}{6D} - \frac{2\ell}{D\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp \left\{ - \left(\frac{n\pi}{\ell} \right)^2 Dt \right\} \right] = \\ &= AC_0 \left[4\sqrt{\frac{Dt}{\pi}} - 2\ell \sum_{n=0}^{\infty} (2n+1) \operatorname{erfc} \left\{ - (2n+1) \sqrt{\frac{\ell^2}{4Dt}} \right\} \right] \end{aligned}$$

The differential method is based on measurement of the change in the gas flux through the membrane (Figure 1b):

$$\begin{aligned} J(t) &= \frac{DAC_0}{\ell} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp \left\{ - \left(\frac{n^2 \pi^2 Dt}{\ell^2} \right) \right\} \right] = \\ &= \frac{2AC_0 \sqrt{D}}{\sqrt{\pi t}} \sum_{n=1}^{\infty} \exp \left\{ - \frac{(n-0.5)^2 \ell^2}{Dt} \right\} \end{aligned}$$

When the pulsed version of the permeability method is employed, a square concentration pulse to the membrane inlet and the pulse distortion occurring in the diffusion process is measured [4-6]. If the square pulse duration is Δt , the time dependence of gas flux at the membrane outlet (Figure 1c) is expressed by the equation

$$J(t) = J_{ss} \left[f(u) - \mathcal{F} \left(u - \frac{D\Delta t}{\ell^2} \right) \right]$$

where $J_{ss} = \frac{DC_0A}{\ell}$, $u = \frac{Dt}{\ell^2}$, and $C_0 = p_H S$; $\gamma = 0$, for $u \leq \frac{D\Delta t}{\ell^2}$, is the ascending part of the curve; $\gamma=1$, for $u > D\Delta t/\ell^2$, is the descending part of the curve.

$$\begin{aligned} f(u) &= 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\{-n^2 \pi^2 u\} = \\ &= \frac{2}{\sqrt{u\pi}} \sum_{n=1}^{\infty} \exp\left\{-\frac{(n-0.5)^2}{u}\right\} \end{aligned}$$

The membrane productivity decreases with decreasing time duration. Compared with the traditional versions of the permeability method, the pulsed version requires less time for the experiment and allows higher resolving power and dynamics [8]. The differential gas-pulse method [3] is based on the interruption of the steady-state flow of the inert gas, creating a series of subsequent pulses that are delivered at the membrane input (Figure 1d).

The method of concentration waves is based on study of the passage of harmonic oscillations of the penetrant concentration through the membrane. For example, if the gas concentration at the membrane inlet changes according to the sinusoidal law

$$C_H = 0.5C_0(1 + \sin(\omega t))$$

(where ω is frequency of concentration oscillation at the membrane input), then the sinusoidal oscillation occurs at the membrane outlet at the same frequency, although with smaller amplitude and with a phase shift (Figure 2).

Under non-steady-state conditions, the flux changes at the membrane outlet follows the expression [8]

$$\begin{aligned} J_t &= \frac{DAC_0}{2\ell} \left\{ \sin(\omega t) + 2\omega \sum_{n=1}^{\infty} (-1)^n x \right. \\ &x \left(\frac{(n^2 \pi^2 D / \ell^2) \left[\cos(\omega t) - \exp(-n^2 \pi^2 Dt / \ell^2) \right]}{n^4 \pi^4 D^2 / \ell^4 + \omega^2} + \right. \\ &\left. \left. + \frac{\omega \sin(\omega t)}{n^4 \pi^4 D / \ell^4 + \omega^2} \right) \right\} \end{aligned}$$

Periodic oscillation occurs with respect to the basic level

$$J_P = \frac{DAC_0}{2\ell} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left(-\frac{n^2 \pi^2 Dt}{\ell^2}\right) \right]$$

At long times, the steady-state condition is attained and is maintained with periodicity:

$$J_{ss} = A_{\omega} \sin(\omega t + \delta)$$

where the amplitude A_{ω} is given by

$$A_{\omega} = \frac{\frac{DAC_0}{\ell} \left(\ell \sqrt{\frac{\omega}{D}} \right)}{2 \left[\sinh^2 \left(\ell \sqrt{\frac{\omega}{2D}} \right) + \sin^2 \left(\ell \sqrt{\frac{\omega}{2D}} \right) \right]^{1/2}}$$

the phase shift δ is given by

$$\delta = \arcsin \left[\frac{\cos(\tilde{z}) \sinh(\tilde{z}) - \sin(\tilde{z}) \cosh(\tilde{z})}{\left[2 \left[\sinh^2(\tilde{z}) + \sin^2(\tilde{z}) \right] \right]^{1/2}} \right]$$

$$\text{and } \tilde{z} = \ell \sqrt{\frac{\omega}{2D}}$$

$$\text{At high } \omega, \quad \ell \sqrt{\frac{\omega}{2D}} > \frac{\pi}{2} \quad \text{and } \delta \approx \ell \sqrt{\frac{\omega}{2D}} - \frac{\pi}{4};$$

$$\text{at low } \omega, \quad \delta = \frac{\omega \ell^2}{6D}.$$

As compared with the classical version of the permeability method, the method of concentration waves exhibits additional degrees of freedom: the time for the output to move toward the periodic steady-state condition, the equilibrium position, the oscillation amplitude, and the phase shift [1,8,9]. An additional degree of freedom results from the possibility of performing the experiment at various frequencies. Figure 3 exemplifies frequency characteristics (amplitude and phase) of the membrane at various values of the diffusion coefficient. It seen that, with an increase of frequency ω , the amplitude of the outcoming wave decreases (the lower the value of D , the faster the drop in amplitude), while the phase shift passes through a minimum (with further increase of frequency, oscillation takes place). The amplitude-phase diagram is given in Figure 3c. Thus, the membrane can be considered as filter of low frequencies, and the greater the diffusion coefficient, the wider the band of filtration.

Another approach is to pulse the upstream pressure in a square wave form as illustrated in Figure 4. It should be noted that transient and non-steady-state operation of membranes may be more efficient if the membrane used is not uniform but has a certain special inhomogeneity. Hence, the following section is devoted to transport in such media.

Separation of gas mixture in non-steady-state conditions. In contemporary membrane technology, gas mixtures are separated exclusively under steady-state conditions. The results are analyzed by means of Formula 2 in Table 2, i.e., the separation factor is defined as $\alpha_{ss}=P_A/P_B$. Under steady-state conditions it is impossible, by definition, to separate a mixture of gases A and B for which $P_A=P_B$. Such a mixture can, however, be separated if one makes use of the unsteady-state separation mode.

a) The permeability metod.

The time dependence of gas flow through the membrane is described by equation 5. In the case of studing the permeability of two gases in a homogeneous medium, the unsteady-state separation factor is determined by equation

$$\alpha_{ss} = \frac{D^A S^A \left\{ 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp \left(- \frac{n^2 \pi^2 D^A t}{\ell^2} \right) \right\}}{D^B S^B \left\{ 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp \left(- \frac{n^2 \pi^2 D^B t}{\ell^2} \right) \right\}}$$

Thus, in contrast to the steady-state separation factor, the non-steady-state separation factor depends on the time of diffusion. According to Equation 34, at short diffusion times larger separation factors are reached unlimitedly high selectivity factor values, although at the expense of the separation process productivity. Therefore, under real conditions, one should select the time interval of sampling that provides a compromise between the membrane throughput and the selectivity.

b) Pulsed variants of the permeability method.

Let us consider the passage of a square concentration pulse consisting of a binary gas mixture through the membrane [1,9,41]. In this case, the membrane acts as a kind of chromatographic column. At the membrane outlet, separation of the mixture components takes place. Figure 11 shows, as an example, the results for concentration pulses of various time durations of a two-component (A and B) gas mixture (50:50) through the membrane. Let the permeability coefficients of gases A and B in the membrane be equal, $P_A=P_B$, whereas the diffusion coefficients of these gases in the polymer are different, $D_A=10D_B$. Figure 11 shows that that, at short times, component A is the main species present, at moderate times, a mixture of the components is observed, and at long times, the component B predominates. Figure 11 also shows that the peak resolution decreases with increasing pulse time duration. Thus, the separation efficiency of the membrane cell can be controlled by selecting the pulse duration and adjusting the time

intervals within which the choice of the output gas is enriched with "fast" or "slow" gas mixture components is performed.

For quantitative description of the membrane separation process under pulse conditions, we introduce the term of differential unsteady-state separation factor:

$$\alpha(t) = \frac{J^A(t)}{J^B(t)} = \frac{J_\infty^A F^A}{J_\infty^B F^B} = \alpha_{ss} K_\alpha$$

$$F_i = f_i(u) - \gamma f_i\left(u - \frac{D\Delta t}{\ell^2}\right)$$

where $\alpha_{ss} = S^A D^A / (S^B D^B)$ is steady-state separation factor, $K_\alpha = F^A / F^B$ is the selectivity parameter, and $\alpha(t) = \alpha_{ss} K_\alpha$ is differential unsteady-state separation factor.

It is clear that, at $\Delta t \rightarrow \infty$, $K_\alpha \rightarrow 1$ and $\alpha(t) = \alpha_{ss}$, i.e., at longer time durations of the concentration pulse at the inlet, the non-steady-state separation factor turns into the steady-state one. It should be noted that α_{ss} is defined by the ratio of the permeability coefficients $P^A = S^A D^A$ and $P^B = S^B D^B$, whereas the K_α parameter is defined by the diffusion coefficients alone.

Figure 12 shows the dependence of the selectivity parameter K_α on the pulse time duration and the time or selection of gases at the outlet from the membrane. A possibility of the inversion of selectivity parameter in the course of the experiment is obvious. It is seen that, at long time durations of the pulse and short measurement times, $K_\alpha \gg 1$ (i.e., the outgoing flux is enriched with the "fast" component), whereas at short pulses and long diffusion times, $K_\alpha \ll 1$ and the mixture is enriched in the component with the lower coefficient.

Thus, it follows that the pulsed version of the permeability method allows us to separate gas mixtures that cannot be separated under steady-state conditions [42].

c) Method of concentration waves.

Now we consider the passage of the concentration wave through the membrane, where the wave consists of the mixture of two gases, A and B [9].

At the membrane inlet, the following equation holds:

$$C^A = \frac{C_0^A}{2} [1 + \sin(\omega t)] \text{ and } C^B = \frac{C_0^B}{2} [1 + \sin(\omega t)]$$

Then the flux at the membrane outlet is

$$J_T = J^A + J^B$$

after the periodic steady-state condition is attained, and the oscillation amplitude is [43]

$$\begin{aligned} A_w &= A_w^A \sin(\omega t + \delta^A) + A_w^B \sin(\omega t + \delta^B) = \\ &= A_w^{AB} \sin(\omega t + \delta^{AB}) \end{aligned}$$

where $(A_w^{AB})^2 = (A_w^A)^2 + (A_w^B)^2 + 2A_w^A A_w^B \cos(\delta^B - \delta^A)$ and

$$\delta^{AB} = \arctan\left(\frac{\delta^B - \delta^A}{A_w^A + A_w^B \cos(\delta^B - \delta^A)}\right)$$

and where A_w^A , A_w^B and δ^B , δ^A are estimated by Equation 10b.

Figure 13 illustrates the amplitude-frequency characteristics of the membrane for the mixture of gases A and B at various values of D^A/D^B (the composition of the mixture at various values of A/B=50:50). Calculations were performed for $P^A = P^B$. It is seen that the oscillation amplitude of the gas mixture at the membrane outlet at decreasing wave frequency ($\omega \rightarrow 0$, $A_w^{AB} / A_w^A \rightarrow 2$) will be determined by both components of the gas mixture. With

increasing frequency ω , the term $A_w^{AB}(\omega) / A_w^A$ passes through a minimum, and at $\omega \rightarrow \infty$, $A_w^{AB} / A_w^A \rightarrow 1$. The minimum point of the curve of the dependence of $A_w^{AB}(\omega) / A_w^A$ on ω is due to the fact that the phase shift between the

output oscillation of components A and B, $\Delta\delta^{AB} = |\delta^A - \delta^B| \rightarrow \pi / 2$, results in a decrease of the total value of the output oscillation amplitude. At sufficiently high frequency ω , the amplitude $AB\omega$ for the component with the lower diffusion coefficient is small and the total amplitude of the output oscillations, $A\omega$, is determined mainly by the amplitude for the mixture component with a high diffusion coefficient.

Figure 14 illustrates the dependences of the flux at the membrane outlet of the gas mixture components for which the permeability coefficients differ by the factor 10 ($D^A=10D^B$). It is seen that, when the frequency increases from 5 to 60 rad/s, the oscillation amplitude for the component with lower D drops abruptly, whereas for the component with a higher D the amplitude decrease is negligibly small.

Thus, filtration of the output oscillations from the signal of the component of low D is attained by changing the frequency of the input oscillations of the concentration wave.

d) Separation of gases by heterogeneous membrane under non-steady-state conditions. We shall assume that the diffusion process of gas A in polymeric solids obeys the classical mechanism of diffusion. In the course of gas B motion the molecules are trapped by defects, i.e., gas B diffusion is submitted to one of the variants of dual mode sorption theory.

As previously mentioned, under steady-state conditions the Henry I (mobile)-Henry II (immobile) model predicts the equality of gas fluxes through defects and homogeneous media (Table 1, Case 2). Therefore, the stationary separation factors for defects and for a defect-free medium are identical. However, the non-steady-state separation factor depends on the duration of diffusion, t , on the gas-defect interaction parameters k_1 and k_2 , and on the membrane composition, ϕ_1 and ϕ_2 . Several examples of time dependences for α are given in Figure 15. For Henry I-Henry II models, the selectivity factor does not depend on the gas concentration.

In some other variants of dual mode sorption theory (Henry-Langmuir, Langmuir-Langmuir, etc.) the separation factor depends on the gas concentration. In the real situation, gas A and B can interact with membrane defects. Then the non-steady-state selectivity factor depends on the duration of the diffusion, the gas mixture composition, the gas-defect interaction parameters, the membrane composition, and temperature in a complicated manner.

e) Examples of gas separation in non-steady-state conditions.

Membrane separation process using a steady cycling operation attracted a great deal of interest, documented by the articles by Barrer [42,43], Beckman [10, 44,45], Paul [1], and Higuchi [46]. Paul [1] reported that considerable improvements in separation efficiency may be achieved by steady cyclic pulsing of the gas pressure on the upstream side of the membrane (integral version of the permeability method). The effectiveness of the pulsed scheme of operation depends on the relative time scale of the pressure and the relaxation time scale of the membrane-gas system - i.e.,

$\tau_1^B = \frac{\ell^2}{6D^B}$ [1,44,48]. If D and S are constants for all species, the system behaves in a linear fashion and there is no

enhancement if permeate collect continuously. To realize the benefits of this method of operation, the permeate must be collected alternately in at least two receiving vessels. The productivity of a membrane for given species has a drastic minimum in q_t/q_{ss} at small values of W. Because of this minimum, improved separation factors may be realized. The recovery of helium from natural gas was used as an example of a separation type that can advantageously employ pulsed-membrane operation.

Higuchi and Nakagawa [46] have reviewed a number of examples of gas separation in non-steady-state conditions. Non-steady-state flux ratios of oxygen to nitrogen in the poly(dimethylsiloxane) membrane were theoretically investigated as a function of time. In a time-lag-type experiment, the flux ratios for O_2 to N_2 in PDMS membrane, $J(O_2)/J(N_2)$, at $t/l_2=600$ s/cm², is estimated to be 215300, although the flux of O_2 is 10^9 times lower than that at steady state. The value $\alpha(t)=J(O_2)/J(N_2)$ increases with a decrease in time (at $t \rightarrow \infty$, $\alpha_t \rightarrow \alpha_{ss}=1.944$). The permeation time needed for such non-steady-state operation is generally too short to be utilized practically for conventional permeation conditions. If the upstream pressure is varied with period of $T=T_1+T_2$, $T_1=0.15$ s and $T_2=15$ s for the present model membrane with $l=0.01$ cm, the ratios of the permeated amounts of oxygen and nitrogen, $qO_2(T_1, \infty)/qN_2(T_1, \infty)=259.9$ and $qO_2(T_2, \infty)/qN_2(T_2, \infty)=1.944$.

Another attractive application of non-steady-state operation has also been examined by Higuchi and Nakagawa [46]. The separation of isotopic compounds is generally regarded to be difficult due to their similar chemical and physical properties. The model calculations are performed on the conditions of $D(^{235}UF_6)=1.00429 \times 10^{-5}$ cm²/s, $D(^{238}UF_6)=1.00000 \times 10^{-5}$ cm²/s, and porous membrane. The flux ratio of uranium-235 to uranium-238 in the non-steady state is calculated to be 1.144 at $t/l_2=800$ s/cm², which is higher than the ideal separation factor (1.004299) at steady state.

If the objective is to obtain 5% concentration of ^{235}U , it should be repeated 900 times at the steady state. If the uranium enrichment is performed by non-steady-state membrane methods, the required number of repetitions is only 29.

Experimental testing of the pulse method is exemplified by separation of a He-CO₂ gas mixture on a polymeric poly(vinyltrimethylsilane) (PVTMS) film (l=147 μm) [10,44]. The permeability coefficients of He and CO₂ in PVTMS are approximately equal whereas the diffusion coefficients differ by factor 74 (see Table 3). The model experiments were performed using films of this polymer on a gas mixture comprising 47% He and 53% CO₂.

The amplitude-frequency characteristics for He and CO₂ are adduced in Figure 16 [44]. At frequencies above 0.77 rad/s, the oscillation amplitude $A_{CO_2}^{CO_2} < 1\%$ of the minimum value, whereas the amplitude of the output oscillations of He, $A_{He}^{He} < 20\%$. Figure 16 illustrates the dependence of the input and output signals of the He-CO₂ gas mixture on time with the frequency of inlet oscillations ω being equal to 0.628 rad/s. It is seen that under these conditions the detector records only the signals coming from He.

The application of non-steady-state boundary conditions provides active control over the process of gas transfer into the membrane. It is shown that non-steady-state boundary conditions also allows us to achieve a considerable increase (by factor of several orders of magnitude) in the separation factor α (He-CO₂) using a relatively nonselective poly(vinyltrimethylsilane) membrane.

The CONCENTRATION WAVES METHOD is based on the passage of harmonic oscillation of penetrant concentration through a polymer membrane. Being compared with the classical version of permeability method of concentration waves provides additional degrees of freedom: the time of establishment of the periodical steady state, the equilibrium position, the amplitude and phase shift of the passed wave. By increasing the oscillation frequency, the passed wave amplitude decreases and the phase shift passes its minimum value and then is subject the periodic oscillations.

The characteristics of the concentration waves passage through the material can be interpreted in form of the amplitude-phase diagram, where the amplitude value corresponds to the vector length, and the phase shift corresponds to the slope angle. The diagram does not depend upon the parameters of the gas transport in the membrane in case of an "ideal" Fick's diffusion in homogeneous media (Curve 1).

The existence of two independent diffusion paths in the membrane makes influence upon the form of the amplitude-phase diagram (Curve 2-5). At low frequencies the mass transfer occurs by the both diffusion paths. At higher frequencies the wave occurs through that path that makes the most contribution into the total flux, and the second path becomes "invisible".

Another way of the concentration wave method data interpretation is the Lissageou figures construction, where the passed wave amplitude is fixed on the ordinate axis, and the initial wave amplitude is fixed on the abscissae axis. In the case of homogeneous media Lissageou figure has linear form and does not depend upon the oscillation frequency.

When the parallel diffusion mechanism by two independent paths is realized in the membrane, the form of Lissageou figures becomes elliptical and the absolute values of the major and the minor ellipse axes depend upon the oscillation frequency.

The amplitude-phase diagrams of concentration waves passed homogeneous media and media with two independent diffusion paths. Curves: 1-homogeneous media. 2-parallel diffusion.

DIAGNOSTICS OF GAS SEPARATION MEMBRANES USING INERT GAS PROBE TECHNIQUE

Principles of the inert gas probe technique. The inert gas probe technique suggested in this paper is based on the measurement of radioactive inert gases which have been inserted at the input of the membrane. Various inert gases, e.g. radionuclides of Xe-133, Kr-85 and Rn-222 were advantageously used by the authors. The application of this technique consists in inserting trace amounts of radioactive inert gas at the input membrane placed in a standart equipment for gas separation. Several methods of the application of inert gas probe technique have been applied for the diagnostics of polymer membranes.

Method and their application. 1. Gas permeability method with autoradiographic detection [1,2]. The trace amount of the inert radioactive gas is inserted at the membrane input and after establishing the steady state of the inert gas flow the diffusion process is stopped by freezing, the membrane is put in between two photographic plates to obtain autoradiographs. A map of the inert gas distribution obtained in this way at the output of the polypropylene membrane is shown in Fig.1a. From the differences of the map obtained at the membrane input and output, resp. the spectra of local diffusion coefficients and solubility constants of the inert gas in the membrane material can be determined (see Fig.1b). From the spectra in Fig.1b we have concluded that the temperature treatment of the membrane in the air at 80-100oC lead to an increased appearance of higher values of diffusion coefficient D, probably due to the development of microcracks.

2. Pulse method for the gas permeability measurement [3,4] is based on the measurement of an inert gas concentration pulse passed on the inserted in the form of an infinitely thin pulse at the membrane input, and the time T necessary for attaining the maximum flux at the membrane output is determined. The appearance of a deviation of T from the standart T_{st} value can be considered as a signal of a damage of the membrane separator. In Fig.2a the results of this method in investigation of polyvinyltrimethylsilane is demonstrated.

3. Differential inert gas pulse method is based on the interruption of the steady flow of the inert gas creation of a series of subsequent pulses which are inserted at the membrane input. The response curves obtained at the PVTMS membrane output are demonstrated in Fig.2b.

4. Double pulse method for the gas permeability measurement. Two subsequent radioactive inert gas rectangular pulses are inserted at the input of the membrane (the time interval between the pulses being equal to their widths) and the passage of the pulse at the output response is measured (see Fig.3). The single peaked response curve (curve 1, Fig.3) corresponds to the perfect state of the membrane, splitting of the single peak to a double peak (curves 2-6, Fig.3) indicates the appearance of a microcracks of the membrane.

The principles and application of several experimental techniques for diagnostics of polymer gas separation membranes bases on the diffusion of radioactive inert gases are outlined. By means of these techniques the quality and operation properties of the membranes can be investigated continuously in the course of the operation of the membrane separator. DIFFUSION METHODS IN THE DEFECTOSCOPIC STUDY OF SELECTIVE MEMBRANES Operation properties of selective polymer membranes are determined by the structure of the material and the quality of its surface layers. Deviations from the required chemical composition, density fluctuations and the presence of microdefects lead to a decrease in the operation efficiency of the polymer membranes. As changes of transport properties of the membranes, taking place in the course of their operation, can lead to a discontinuity in the membrane functioning, accidents with serious consequences can happen, especially in the medical application of membrane separators. For this reason, methods for checking quality of the membranes during their operation and investigating changes in their transport properties have been developed. Methods discovering the early stages of the membrane erosion are of special importance. By using information obtained by these methods, the membrane separators can be repaired in time and accidents can be prevented. In this communication the principles of the methods for checking the operation and transport properties of selective membranes are given, and the possibilities of these methods are demonstrated.

Principle of methods. The pulse method for the gas permeability measurement [1] is based on the measurement of a gas concentration pulse passed through the membrane. The gas mixture to be separated or a special gaseous probe are inserted at the input of the membrane in time t_0 . The expression for the gas concentration pulse of a rectangular shape passing through the membrane is given by the authors in another contribution to these Proceedings [2].

For cases when for the normalized flux we have $J_m/J_\infty < 0.3$ ($J_\infty = C_0 D/l$), the diffusion coefficient can be determined as

$$D = J_m \ell^2 / 5.922 J_\infty \Delta t$$

If an infinitely thin gas pulse $\Delta t \rightarrow 0$ is inserted at the input of the membrane, the output gas flux can be expressed by Eq.(1)

$$J(t) = 2C_0 D \Delta t \ell^{-1} \sum_{n=1}^{\infty} (-1)^{n+1} n^2 \pi^2 D \ell^{-2} \exp\left\{-\left(\frac{n\pi}{\ell}\right)Dt\right\}$$

which can be written in the form normalized with respect to the peak area as

$$f(t) = 2 \sum_{n=1}^{\infty} (-1)^{n+1} n^2 B \exp(-n^2 B t)$$

$$\text{where } B = \frac{\pi^2 D}{\ell^2}.$$

The time T which is necessary for attaining the maximum flux on the membrane output ($T = t_m - t_0$) is related to the parameter $U = D/L^2$. The diffusion coefficient D can be determined from Eq.(3)

$$D = \frac{\ell^2}{10.9T}$$

In this way, any change of the diffusion coefficient, caused e.g. by changes of the membrane structure, the deposition of substances at the membrane input, variations of the membrane thickness, etc., lead to variations of T (with respect to the standart value T_{st} determined previously). The appearance of the deviation ΔT can be considered as a signal of a signal of the defect of the membrane separator. The sign plus or minus of the deviation $\Delta T = T - T_{st}$ gives the first information about the cause of the defect. If ΔT exceeds the limit ΔT_{lim} , repair of the membrane separator should be undertaken. The main advantage of this method consists in its simplicity. Another independent method of investigation of the operation ability of the membrane separator is based on the on the measurement of the gas pulse height [1]. The diffusion coefficient can be expressed by Eq.(4)

$$D = \frac{0.2442J_m \ell}{C_0}$$

where $C_0 = \Gamma p$; Γ is the solubility constant of the gas in the material of the membrane, p is the partial pressure of the gas at the membrane input. The parameter J_m (height of the pulse) can be advantageously used for the characterization of the "rapid" membranes (small thickness, higher operation temperatures), where the parameter T can hardly be evaluated with a sufficient accuracy because of the apparatus inertia.

The simultaneous evaluation of J_m and T is of special interest, as both the kinetic parameter (D) and the thermodynamic parameter (T) of the membrane system may be determined simultaneously. Moreover, the accompanying processes, such as the gas trapping in the polymer matrix, can be quantitatively estimated by means of this method: the rate constant of the reaction can be obtained by analyzing the shape of the output gas pulse.

Application of methods. Several examples of the application of the pulse gas method for gas permeability measurement are given below. Let us suppose that isolated point defects arise, randomly distributed in the bulk of the polymer membrane. In the course of their random motion, molecules of the diffusing agent are trapped by the defect and excluded for a definite time interval from the diffusion process. This process, called "gas diffusion with reversible trapping", can be described by the following differential Eqs.(5)

$$\frac{\partial C_1}{\partial t} = D \frac{\partial^2 C_1}{\partial x^2} - k_1 N_2 C_1 + k_2^* C_2$$

$$\frac{\partial C_2}{\partial t} = k_1 N_2 C_1 - k_2^* C_2$$

where C_1 and C_2 are the concentrations of the diffusing agent in the diffusion channels and the traps, resp.; k_1 and k_2 are the rate constants of the gas trapping and release, resp. ($k_2^* = k_2 N_2$); N_1 and N_2 are the concentrations of the diffusion channels and traps, resp. ($N_1 + N_2 = N$), the equilibrium constant of the trapping reactions $K = k_1/k_2$ (the 1st order chemical reaction kinetics is used for the description of the trapping of gas molecules by the matrix and subsequent release of the gas). As seen from Fig.1, isolated point defects in the membrane cause a significant distortion of the gas pulse shape. It follows from Fig.1 that for low concentration, N_2 , of the point defects the position of the peak maximum does not change, but "tags" appear on the curves. The parameters k_1 and k_2 , which can be determined by analyzing the curve shape, characterize the non-homogeneity of the polymer membrane. The position of the peak maximum is shifted towards a higher time in cases of increased defect concentration. The effective diffusion coefficient, evaluated from Eq.(6), decreases as a result of the defect formation in the membrane. The effective diffusion coefficient can be evaluated as

$$D_{\text{eff}} = \frac{D}{1 + K \frac{N_2}{N}}$$

The effect of the polymer membrane structure can lead to the formation of channels where molecules of the diffusing agent can penetrate. In this case the transport of the gas in the defective membrane can be described by the multichannel diffusion mechanism. In Fig.2 we demonstrate changes of the shape of the gas pulse after a passage through the polymer membrane where a diffusion mechanism via two channels is supposed. As follows from Fig.2, the position of the peak maximum is shifted towards a lower time and the height of the peaks increases when the concentration of the structure damage is more intense. (The relation $D_1 = 2D_2$ between the two diffusion coefficients in the channels was supposed).

The changes of the defect state of the polymer materials or by an increase in thickness of the membrane) can be investigated by means of the pulse method using a special gas probe. Radioactive nuclides of inert gases, such as Rn-222, Kr-85 or Xe-133, are advantageously used as gas probes for the defect state of a polymeric membrane. The high sensitivity of detection of radioactive nuclides makes it possible to use very low concentrations of the gases, so that no influence on the diffusion of the gas mixture to be separated can be supposed. In the Fig.3, the results of the application of an inert gas probe in the investigation of the changes in the polymer material are demonstrated. Curve 2 represents the original pulse of the inert gas (Rn-222), curves 2 and 3 represent the distorted pulses of the gas after the passage through either a stable or an unstable polymer membrane.

Conclusion. By means of this method the quality and operation properties of the membrane can be investigated continuously in the course of the operation of the membrane separator. The height and width of the gas pulse, as well as the inert gas used as the probe can be varied during the defectoscopic investigation of the membrane. Even a mixture of

inert gases can be used as the probe of the defect state of the material. The evaluation of the results shown in Fig.3 is described elsewhere (1,3).

2.3.3 Moving membranes

Application of moving membranes allows one to accomplish spatial separation of gas-mixture components [45,47-49]. In the course of an experiment, one can use a diffusion cell separated into two chambers by a moving polymeric membrane (Figure 17). The velocity of the membrane motion is selected such that the mobile component of the gas mixture should have enough time during the membrane passage through the diffusion cell to pass almost completely through the membrane, whereas the slow component does not have enough time to diffuse into the membrane very deeply and is carried along with it into the neighboring cell. In this case, separation is achieved owing to the difference in the values of the unstead-state selectivity factor.

3. Integrated membrane systems

3.1 Membrane technology and swing adsorption

3.2 Permadsorbers

3.3 Permabsorbers

When the experiment is conducted according to another scheme (Figure 8), the polymeric gas-separation membrane stays immobile, but a specific selected liquid flows through the diffusion cell [45, 50-53]. The following versions are possible in selection the liquid:

- 1) The flowing liquid can be nonspecific with respect to the separated gas mixture.
- 2) The solubility constants of the gas-mixture components in the absorption medium differ considerably.
- 3) The liquid is capable of chemical interaction with one or several components of the gas mixtures.

In the course of separation, the gases pass through the membrane, dissolve in the liquid absorbent, and are carried along into the desorber. To describe the work of such a device one must make use of the separation factors listed in Table 2.

In the membrane module with the flowing liquid membrane, the productivity and selectivity obviously will depend on the transport parameters of the gases in the absorption liquid, on the time it takes for the liquid to pass from the diffusion cell, to the desorber, as well as on the time of passage through the desorber.

1. Membrane absorber-desorber.

The membrane permabsorber (MPA) consist of two cell (absorption cell and desorption cell) and the liquid specifically selected as an agent for extraction that circulates between them (Figure 18) [52]. The gas mixture passes over the polymeric membrane in the absorption cell. The most permeable component of the gas mixture diffuses selectively through the nonporous polymeric membrane into the flowing liquid under it, is absorbed by this liquid, and is transferred to the desorption cell. Degassing of the liquid occurs in the desorption membrane cell. Degassing of the liquid occurs in the desorption membrane cell through the nonporous polymeric membrane, leading to highly concentrated gaseous products. There are two operating conditions of the membrane device: a **flowing device**, and a **circulation device**, where the liquid is continuously circulated in the system.

To facilitate practical calculations, we shall perform a simplified analysis of the work of a membrane permabsorber consisting only of one absorber module and one desorber module. An analytical solution of this problem for the steady state can be obtained on the following assumptions: (1) gas diffusion coefficients in the liquid are much greater than those in polymeric membranes; (2) distribution of penetrant concentration over the polymeric membrane is linear; (3) the flow-rate profile of the liquid is uniform; (4) diffusion of the liquid component through the polymeric membrane does not affect the penetrant gas transfer coefficient; (5) absorption of the in the liquid follows Henry's law; and (6) the membrane in the absorber and desorber modules are rectangular and of equal surface area.

With these assumptions, the work of a membrane absorption-desorption gas-separating system is described by the following equations:

$$G_a \frac{d\theta_{\ell a}}{d\xi} = 1 - \theta_{\ell a} \quad (0 \leq \xi \leq 1)$$

$$G_d \frac{d\theta_{\ell d}}{d\xi} = -\theta_{\ell d} \quad (1 \leq \xi \leq \eta)$$

$$\theta = \frac{C}{C_0}, G = \frac{S_\ell \vartheta l_1 l_{ma}}{S_{ma} D_{ma} h_a} = \frac{S_\ell \vartheta^*}{Q_{ma}}, G_d = \frac{S_\ell \vartheta^*}{Q_{md}},$$

where

$$\eta = \frac{h_a + h_d}{h_d}, \xi = \frac{y}{h_a}, C_0 = S_\ell p_0, \text{ and } A = hd,$$

and where p_0 is the partial pressure of the

partial pressure of the penetrant (atm), $Q_m = ADS/lm$ is the productivity ($\text{cm}^3(\text{STP})/[\text{s}\cdot\text{atm}]$), v^* is the volume flow rate of the liquids (cm^3/s), v is the linear rate of the liquids in a membrane absorber (cm/s), l is the membrane thickness, h is the membrane length, d is the membrane width, C is the gas concentration, y is the coordinate in the direction of moving liquids, and the subscripts are as follows: a, absorber; d, desorber; l, liquid absorbent; m, membrane.

The solution of the ordinary differential Equation 40a and 40b has the following form:

$$C_{\ell a} = C_0 (1 - K_a \exp(-\xi / G_a))$$

$$C_{\ell d} = C_0 K_d \exp(-\xi / G_d)$$

where K_a and K_d are constants determined from the boundary conditions.

One can identify two principal types of membrane perabsorbers: the **continuous-flow**-membrane perabsorber fresh liquid is fed into the absorber module. It carries the penetrant, which has passed through the membrane, into the desorber module and is then discharged out of it (Figure 18a). The boundary conditions in this case are $\xi=0$, $\theta_{\ell a}=0$ and $\xi=1$, $\theta_{\ell d}=\theta_{\ell a}$.

Applying these conditions to Equations 40, we get

$$K = \frac{C_0 - C(0)}{C_0}$$

$$K_d = \left(1 - \frac{C_0 - C(0)}{C_0}\right) \frac{\exp\left(-\frac{1}{G_a}\right)}{\exp\left(-\frac{1}{G_d}\right)}$$

where C_0 is the penetrant concentration at the membrane absorber inlet and $C(0)$ is the background concentration of the liquid.

Then the concentration profiles along the direction y are

$$C_a = C_0 \left[1 - \left(\frac{C_0 - C(0)}{C_0}\right) \exp\left(-\frac{\xi}{G_a}\right)\right] (0 \leq \xi \leq 1)$$

$$C_d = C_0 \left[1 - \left(\frac{C_0 - C(0)}{C_0}\right) \exp\left(-\frac{\xi}{G_d}\right)\right] \frac{\exp\left(-\frac{\xi}{G_a}\right)}{\exp\left(-\frac{\xi}{G_d}\right)} (1 \leq \xi \leq \eta)$$

The local flux of the penetrant (i.e., the flow at point y) from the desorber is

$$j(y) = -D_{md} \frac{dC_{md}(x, y)}{dx} \Big|_{x=0}$$

$$J = A \int_1^{\eta} j(\xi) d\xi = \frac{AS_{\ell} \ell_{\ell d} \mathcal{P} p_0}{h_d} \left\{ 1 - \left[\frac{C - C(0)}{C_0} \right] \exp\left(-\frac{1}{G_0}\right) \left[1 - \exp\left(-\frac{1}{G_d}\right) \right] \right\}$$

If $\mathcal{G}^* \rightarrow 0, J \rightarrow 0$. At small \mathcal{G}^* values, $J \approx \mathcal{G}^*$, the flow linearly increases with increasing volumetric flow rate of the liquid. With large \mathcal{G}^* values $J \rightarrow 0$.

The total, steady, differential selectivity factor is determined by the formula [52]

$$\alpha^{A/B}(\mathcal{G}^*) = \frac{Q_d^A}{Q_d^B} = \frac{S_{\ell}^A \left[1 - \exp\left(-\frac{1}{G^A}\right) \right]^2}{S_{\ell}^B \left[1 - \exp\left(-\frac{1}{G^B}\right) \right]^2}$$

where the limits are

$$\lim_{\mathcal{G}^* \rightarrow 0} \alpha^{A/B} = \frac{S_{\ell}^A}{S_{\ell}^B} \text{ and } \lim_{\mathcal{G}^* \rightarrow \infty} \alpha^{A/B} = \frac{S_{\ell}^B}{S_{\ell}^A} \left(\frac{Q_m^A}{Q_m^B} \right)$$

Now we shall briefly discuss the results of mathematical simulation of the membrane absorber operation. Figure 19a shows the distribution profiles for penetrant concentration along the direction x , calculated for different contact time values of the absorbent moving at a linear rate v_y along the membrane, $T=y/v_y$, $D_{ma}/l^2=1$, and $D_l/l^2=10$. It is seen that, with a constant v_y , the concentration profile $C(x)$, even in the steady state, is not linear and the penetrant distribution across the layer of the liquid (in the direction x) is not uniform. From Figure 19a it also follows that, as the flow rate of the liquid increases, the penetrant concentration in it drops. Note that, when calculating the curves shown in Figure 19a, we assumed $S_m=S_l$. If $S_m \neq S_l$, then at $x_{ma}=1$ a concentration jump will be observed at the interface.

Figure 19b describes the distribution of the average concentration of the penetrant in the liquid along the direction y . At sufficiently high y values the concentration is seen to become constant.

Proceeding from these facts, one can expect that the separation process of a binary mixture will be characterized by a total separation factor (Figure 20). With a constant absorber length ℓ , the plot of $\alpha(y)$, calculated from Equation 4 in Table 2, is seen to have a clearly defined maximum (a situation similar to the pulsed gas-separation mode, but here the role of pulse duration is played by the flow rate of liquid). On the other hand, the total separation factor $\alpha(y)$ depends on the rate of absorbent motion: there exists a rate at which the separation factor reaches maximal value.

It is important to emphasize that in the example given $P^A=P^B$, i.e., the separation of gases is impossible under steady-state conditions; the liquid is also nonspecific- $S^A_l=S^B_l$, $D^A_l=D^B_l$, i.e., one cannot separate these gases by the absorption method. However, separation of such a mixture proves to be possible in a membrane absorber (because of the difference in the diffusion coefficient values for different gases in the polymeric membrane: $D^A_{ma} \neq D^B_{ma}$ (at the optimum value of the extractant rate of motion v_y , $\alpha=1.92$).

The dependence of normalized productivity and selectivity factors, for gases A and B in membrane absorber, via flow rate of the liquid are shown in Figure 21. One may see (Figure 21A) that the maxima of productivity for gases A and B are situated at different flow rates of the absorbent although $Q^A_m=Q^B_m$. The position of the maximum in the case of continuous-flow membrane absorber is determined by the solubility coefficient of gas in liquid. It is obvious that by varying the flow rate of the liquid one can invert the selectivity factor in a continuous-flow membrane absorber.

In a circulatory-membrane permabsorber [52,53] the extractant, after leaving the detector, is again fed to the absorber inlet (Figure 18b). The main advantage of this modification is that the extractant continuously circulated between the absorber and the desorber and is not consumed.

In this case the boundary conditions are as follows: $\theta_{\ell a}(1) = \theta_{\ell d}(1)$ and $\theta_{\ell a}(0) = \theta_{\ell d}(\eta)$. Then

$$K_a = \frac{1 - \exp\left(\frac{\eta - 1}{G_d}\right)}{\exp\left(-\frac{1}{G_a}\right) - \exp\left(-\frac{\eta - 1}{G_d}\right)}$$

$$K_d = \frac{[\exp\left(-\frac{1}{G_a}\right) - 1] \exp\left(\frac{\eta}{G_d}\right)}{\exp\left(-\frac{1}{G_a}\right) - \exp\left(\frac{\eta - 1}{G_d}\right)}$$

The total flux of the penetrant at the desorber outlet

$$J = \frac{AS_{\ell} \ell_{\ell} \mathcal{G} p_0}{h_d} K_d [\exp\left(-\frac{1}{G_d}\right) - \exp\left(-\frac{\eta}{G_d}\right)]$$

with $G_a = G_d = G$ and $h_a = h_d$, the flux is

$$J = \psi \frac{\left[1 - \exp\left(-\frac{1}{G}\right)\right]^2}{1 - \exp\left(-\frac{2}{G}\right)}$$

$$\psi = \frac{AS_{\ell} \ell_{\ell} \mathcal{G} p_0}{h} = S_{\ell} p_0 \mathcal{G}^*$$

If $\mathcal{G}^* \rightarrow 0$, then $J \rightarrow 0$. At small \mathcal{G}^* values, $J \approx \mathcal{G}^*$, i.e., the flow linearly increases with increasing volumetric flow rate of the liquid. With large \mathcal{G}^* values, $J \rightarrow 0.5 Q_m p_0$. The limits for the selectivity factor are

$$\lim_{\mathcal{G}^* \rightarrow 0} \alpha^{A/B} = \frac{S_{\ell}^A}{S_{\ell}^B} \quad \text{and} \quad \lim_{\mathcal{G}^* \rightarrow \infty} \alpha^{A/B} = \frac{Q_m^A}{Q_m^B}$$

The maximum productivity to be achieved in circulatory membrane absorber is one half of the membrane productivity for the gas under investigation (Figure 21a).

Comparison of the different versions of membrane absorber operation shows the productivity of the circulatory membrane absorber to be $1/(1 - \exp(-2/G))$ times greater than that of a continuous-flow absorber. Here lies the second advantage of circulatory mode.

The total, steady, differential separation factor in circulatory MPA is determined by the formula

$$\alpha^{A/B}(\mathcal{G}^*) = \frac{S_{\ell}^A \left[1 - \exp\left(-\frac{1}{G^A}\right)\right]^2}{S_{\ell}^B \left[1 - \exp\left(-\frac{1}{G^B}\right)\right]^2} x \frac{1 - \exp\left(-\frac{2}{G^B}\right)}{1 - \exp\left(-\frac{2}{G^A}\right)}$$

where the limits are

$$\lim \alpha^{A/B} = \frac{S_\ell^A}{S_\ell^B} (\text{selectivity of absorption liquid})$$

$$G^* \rightarrow 0$$

$$\lim \alpha^{A/B} = \frac{Q_m^A}{Q_m^B} (\text{selectivity of membrane})$$

$$G^* \rightarrow \infty$$

Varying the flow rate of the absorbent, one can change the separation factors of separation (Figure 21b). $\hat{\Delta}$ $\zeta\grave{a}\grave{a}\grave{e}\grave{n}\grave{e}\grave{i}\grave{n}\grave{o}\grave{d}\grave{e}$ $\grave{i}\grave{o}$ $\grave{n}\grave{e}\grave{i}\grave{o}\grave{i}\grave{n}\grave{o}\grave{d}\grave{e}$ $\grave{a}\grave{a}\grave{e}\grave{a}\grave{a}\grave{e}\grave{y}$ $\grave{n}\grave{a}\grave{e}\grave{a}\grave{e}\grave{o}\grave{d}\grave{e}\grave{a}\grave{i}\grave{n}\grave{o}\grave{u}$ $\grave{r}\grave{a}\grave{a}\grave{a}\grave{o}$ \grave{e} $\grave{n}\grave{o}\grave{d}\grave{a}\grave{i}\grave{o}\grave{n}\grave{y}$ \grave{e} $\grave{i}\grave{n}\grave{o}\grave{i}\grave{y}\grave{i}\grave{n}\grave{o}$ $\zeta\grave{a}\grave{a}\grave{e}\grave{p}$.

The experimental results of biogas separation by circulatory MPA are shown in Figure 22, with achievement of separation factor values for the gas pair CO₂-CH₄ of up to ≈ 3000 .

2. Membrane valve.

A so-called membrane valve consists of two molecules a permeator and a desorber (Figure 23) [54]. The permeator is divided by two polymeric gas-separation membranes, M1 and M2, between which a thin layer of the absorbent liquid is moving. The investigated gas mixture and gas-carrier are passing under the surface of sandwich. The components of the gas mixture are dissolved in the liquid absorbent and are driven out of the permeator to the desorber (membranes M3 and M4). The selective membrane valve (SMV) has one inlet for the initial gas mixture and three outlets for the product leaving the separation device. The SMV can be used to separate a three-component gas mixture: the gas insoluble in the absorbent passes above the membrane, the fast component of the gas mixture passes through the composite membrane, and the third component, dissolving well in the absorbent, is entailed by the liquid into the desorber.

There are four operating conditions of the SMV: a flowing mode without a desorber (F), a flowing mode with desorber (FD), a circulator mode without a desorber (C), and a circulator mode with a desorber (CD).

a. Mode F.

Consider gas permeability of a three-layered medium consisting of a polymeric membrane 1 (with parameters D_1 , S_1 , l_{m1} , and $A_1=d_1h_1$), a thin layer of liquid absorbent (D_ℓ , S_ℓ , l_ℓ , A_ℓ) being moved at a linear velocity v , and polymeric membrane 2 (D_{m2} , S_{m2} , l_{m2} , A_1), $H=l_{m1}+l_\ell+l_{m2}$ is the total thickness of sandwich.

If $D_1 \gg D_{m1}$ and $D_1 \gg D_{m2}$, two-dimensional task can be reduced to a one-dimension equation:

$$G_\ell l_\ell \frac{dC_\ell}{dy} = \frac{D_{m1} \left(C_{10} - C_\ell \frac{S_{m1}}{S_\ell} \right)}{l_{m1}} + \frac{D_{m2} \left(C_{2H} \frac{S_{m2}}{S_{m1}} - C_\ell \frac{S_{m2}}{S_\ell} \right)}{l_{m2}}$$

A solution of Equation 52 under boundary conditions $C_1(y=0)=C(0)$, $C_{m1}(x=0)=C_{10}=S_{m1}P_{10}$, and $C_{m2}(x=H)=C_{2H}=S_{m2}P_{1H}$ is as follows:

$$C_\ell = \frac{G_{1V} + (G_{2V} C(0) - G_{1V}) \exp\left(-\frac{G_{2V} y}{G}\right)}{G_{2V}}$$

where

$$\begin{aligned}
G &= S_{m\ell} S_{\ell} \mathcal{G} \ell_{m\ell} \ell_1 \ell_{m2} \\
G_{1V} &= S_{\ell} (P_{m1} \ell_{m2} C_{10} + P_{m2} \ell_{m1} C_{1H}) \\
G_{2V} &= S_{m1} (P_{m1} \ell_{m2} + P_{m2} \ell_{m1}) \\
P_{m1} &= D_{m1} S_{m1} P_{m2} = D_{m2} S_{m2}
\end{aligned}$$

The penetrant total flux leaving the sandwich is

$$\begin{aligned}
J_{pen} &= \frac{P_{m2} A}{S_{\ell} \ell_{m2} G_{2V}} \left[G_{1V} + G \left(\frac{G_{2V} C(0) - G_{1V}}{G_{2V}} \right) \left(1 - \exp \left(- \frac{G_{2V} h}{G} \right) \right) \right] - \\
&\quad - \frac{P_{m2} A C_{2H}}{S_{m1} \ell_{m2}}
\end{aligned}$$

If the gas concentration in the liquid at the input to the permeator is $C(0)=0$, the partial gas pressure $p_{1H}=0$ (output), $p_{10}=p_0$ (input), and $P_{m1}=P_{m2}=P$, $\ell_{m1}=\ell_{m2}=\ell$, $G_{1V}=G$, $S_{m1}=S_{m2}=S$, then

$$J_{pen} = \frac{PAp_0}{2\ell} \left\{ 1 - \frac{\mathcal{G}^* \ell S_{\ell}}{2AP} \left[1 - \exp \left(\frac{-2AP}{\mathcal{G}^* \ell S_{\ell}} \right) \right] \right\}$$

As one can see, the gas permeability through the sandwich depends on the solubility coefficient for the liquid. Under conditions of slow velocity of moving liquid ($v \rightarrow 0$), the flux $J_{3 \rightarrow AP} p_0 / 2\ell$, i.e., the flux is 0.5 times the membrane productivity, but under fast rates of moving liquid ($v \rightarrow \infty$), $J_{3 \rightarrow 0}$, i.e., the membrane valve is closed.

The separation factor for gases A and B is

$$\alpha = \frac{P^A \left(1 - \frac{1 - \exp(-2\psi^A)}{2\psi^A} \right)}{P^B \left(1 - \frac{1 - \exp(-2\psi^B)}{2\psi^B} \right)}$$

where $\psi = \frac{AP}{\mathcal{G}^* \ell S_{\ell}}$; the limits are

$$\begin{aligned}
\lim_{\mathcal{G}^* \rightarrow 0} \alpha &= \frac{P^A}{P^B} \text{ and } \lim_{\mathcal{G}^* \rightarrow \infty} \alpha = \frac{S_{\ell}^B (3 - 2\psi^A)}{S_{\ell}^A (3 - 2\psi^B)} \approx \frac{S_{\ell}^B}{S_{\ell}^A} \\
\mathcal{G}^* \rightarrow 0 \quad \mathcal{G}^* \rightarrow \infty
\end{aligned}$$

b. Mode FD

The desorber is divided by two polymeric membranes: Membrane 3 (with parameters D_{m3} , S_{m3} , l_3 and $A_2=d_2h_2$) and Membrane 4 (D_{m4} , S_{m4} , l_4 and A_2), between which is moving a thin layer of absorbent liquid (l_d is the liquid layer thickness in the desorber).

The operational peculiarities of the flowing membrane permeator that has an input flowing-membrane permeator can be illustrated by the simplest example:

$$\begin{aligned}
S_{m1} &= S_{m2} = S_{m3} = S_{m4} = S S_{2\ell} = S_{1\ell} = S_{\ell} \\
D_{m1} &= D_{m2} = D_{m3} = D_{m4} = D \\
C_{10} &= C_0 C_{2H} = C_{30} = C_{40} = 0 C(0) = 0 \\
h_1 &= h_2 = h A_1 = A_2 = A d_1 = d_2 = d \\
\ell_{m1} &= \ell_{m2} = \ell_{m3} = \ell_{m4} = \ell \ell_{\ell 1} = \ell_{\ell 2} = \ell_{\ell}
\end{aligned}$$

The gas flow from the desorber is

$$J_{des} = \frac{\mathfrak{G}^* C_0 S_\ell}{2S} \left[1 - \exp\left(-\frac{2AP}{\mathfrak{G}^* \ell S_\ell}\right) \right]^2$$

where the limits are

$$\begin{aligned} \lim_{\mathfrak{G} \rightarrow 0} J_{des} &= 0 & \lim_{\mathfrak{G} \rightarrow \infty} J_{des} &= 0 \\ \lim_{\mathfrak{G} \rightarrow 0} \alpha_{des} &= \frac{S_\ell^A}{S_\ell^B} \times \frac{S^B}{S^A} & \lim_{\mathfrak{G} \rightarrow \infty} \alpha_{des} &= \frac{D^A}{D^B} \\ \lim_{\mathfrak{G} \rightarrow 0} & & \lim_{\mathfrak{G} \rightarrow \infty} & \end{aligned}$$

Thus there are possibilities for controlling the compositions and fluxes of permeable gas mixtures through gas-membrane-liquid systems by optimizing liquid flow rates.

c. Mode CD

In the circulating SMV, a liquid absorbent is driven to the membrane desorber (MD) upon leaving the membrane permeator (MP). Passing through the MD, the liquid is degassed and is driven to the permeator input.

We shall confine ourselves to the simplest case:

$$S_{m1} = S_{m2} = S_{m3} = S_{m4} = S S_{2\ell} = S_{1\ell} = S_\ell$$

$$D_{m1} = D_{m2} = D_{m3} = D_{m4} = D$$

$$C_{10} = C_0 C_{2H} = C_{30} = C_{40} = 0 C(0) = 0$$

$$h_1 = h_2 = h A_1 = A_2 = A d_1 = d_2 = d$$

$$\ell_{m1} = \ell_{m2} = \ell_{m3} = \ell_{m4} = \ell \ell_{\ell 1} = \ell_{\ell 2} = \ell_\ell$$

The gas flux from the permeator is

$$J_{pen} = \frac{D S_\ell A C_0}{2S \ell} \left[1 - \frac{(1 - \exp(-\psi))(1 - \exp(-2\psi))}{2\psi(1 - \exp(-3\psi))} \right]$$

where the limits are

$$\begin{aligned} \lim_{\mathfrak{G} \rightarrow 0} J_3 &= \frac{D S_\ell A C_0}{2S \ell} & \text{and} & & \lim_{\mathfrak{G} \rightarrow \infty} J_{des} &= \frac{D S_\ell A C_0}{3S \ell} \\ \lim_{\mathfrak{G} \rightarrow 0} & & & & \lim_{\mathfrak{G} \rightarrow \infty} & \end{aligned}$$

In the circulation mode, the gas flow through the permeator can never be completely suppressed:

$$\begin{aligned} \lim_{\mathfrak{G} \rightarrow 0} \alpha_{perm} &= \frac{S_\ell^A}{S_\ell^B} \times \frac{S^B}{S^A} \times \frac{D^A}{D^B} = \lim_{\mathfrak{G} \rightarrow \infty} \alpha_{perm} \\ \lim_{\mathfrak{G} \rightarrow 0} & & & & \lim_{\mathfrak{G} \rightarrow \infty} & \end{aligned}$$

i.e., selectivity of the circulation permeator with a desorber is the same at both high and low speeds of liquid motion.

The gas flux from the desorber is

$$J_{des} = \frac{D S_\ell A C_0}{2S \ell \psi} \times \frac{1 - \exp(-\psi) - \exp(-2\psi) + \exp(-3\psi)}{1 - \exp(-3\psi)}$$

where the limits are

$$\lim J_{des} = 0 \lim J_{des} = 0$$

$$\lim \alpha_{des} = \left(\frac{S_\ell^A}{S_\ell^B} \right)^2 \left(\frac{S^B}{S^A} \right)^2 \lim \alpha_{des} = \frac{D^A}{D^B} x \frac{S_\ell^A}{S_\ell^B} x \frac{S^B}{S^A} = \lim \alpha_{perm}$$

$$\mathcal{G} \rightarrow 0 \quad \mathcal{G} \rightarrow \infty \quad \mathcal{G} \rightarrow 0$$

$$\mathcal{G} \rightarrow \infty$$

The proposed model has been tested by separating a three-component gas mixture CO₂-CH₄-H₂ using the SMV operating in the circulation mode with desorber. Asymmetric membranes produced from PVTMS and aqueous solutions monoethanolamine of different concentrations served as the carrier of CO₂. The initial CO₂-CH₄-H₂ gas mixture consisted of 40% CO₂, 30% CH₄, and 30% H₂, respectively. The concentrations of each separated gas obtained were more than 90% at the outlets of the membrane valve. The simplified model considered is shown to describe the experimental data adequately.

3. Facilitated transport through a flowing liquid membrane [50].

Gas separations by immobilized liquid membranes using carries that can selectively and reversibly bind certain permeate species have attracted attention because very high selectivity (due to the specificity of the reaction between carriers and permeate species) as well as high permeability (due to the facilitation effect) can be achieved [55-57].

Most of the liquid membranes used were immobilized liquid membranes, consisting of thin porous filters such as cellulose acetate impregnated with carrier solutions. These liquid membranes have the disadvantage that they are apt to degrade because the solution absorbed in the pores of the support membrane evaporates into sweep gas phases.

Another type of liquid membrane that has been used in laboratory research to obtain reproducible permeability data is a thin-layer liquid membrane, in which a membrane solution is held stationary between two microporous membranes [58]. Although the stability of this type of membrane seems to be better than that of immobilized liquid membranes in which the carrier solution is absorbed in the pores of the microporous support membranes, the mass transfer resistance through the layer of the membrane solution is large is thick and stationary.

In order to overcome these inherent problems of these two types of liquid membrane, a new type of liquid membrane for gas separation was proposed, called flowing liquid membranes [50]. Separation of ethylene from ethane by flowing liquid membrane molecules was carried out, with silver nitrate used as a carrier of ethylene. It was found that, compared with the usual immobilized liquid membrane was higher permeability and stability.

By reducing the total pressure of the receiving phase, more than 98 mol% of ethylene was obtained from an approximately equimolar mixture of ethylene and ethane.

CONCLUSION

Recovery, purification, and enrichment of gases and treatment in many processes of modern chemical technology and for ecology. The corresponding devices have considerable importance as well from the view-point of environmental protection. At the moment, the separation of gases is carried out in different apparatuses based on cryogenic, sorption, and membrane processes. Each of them has its own benefit and disadvantages. For the creation of optimized technological systems, the combined application of the different treatment methods is of interest. The next stage of the combination of different gas-separation methods is the creation of integrated systems of membrane technology (ISMT). The membrane catalysts, membrane permabsorber, membrane valve, and chemical and biochemical membrane reactors can serve as the examples.

There are several features of ISMT:

1. A complex spatial and chemical organization
2. A nonequilibrium or metastable state in the transport process
3. The non-steady-state conditions of the transport processes

The intrinsic (the original instability of systems, for example, temperature and concentration oscillations) or external (time-dependent boundary conditions such as pulsed-membrane operation, cosine, square, or triangular concentration waves, using mobile membranes, flowing liquid membranes, etc.) causes are assumed to provide the non-steady-state effects.

One might anticipate that certain advances in the field of gas separation by ISMT would result from the combined efforts of researchers in fundamental studies on the theory of unsteady-state transport of low molecular weight compound in heterogeneous media, as well as from the achievement of chemical engineers in producing the experimental apparatuses for application of time-dependent boundary conditions of the membrane reactor inlet. These results can be used as the basis for selecting the optimum conditions of operation of the integrated systems of membrane technology.

REFERENCES

1. Paul D.R., Ing. Eng. Chem. Process. Des. Dev., 1, 375, 1971

2. Beckman I.N., *Thermochim. Acta*, 190, 66, 1991
3. Beckman I.N., Shvyryaev A.A., and Balek V., in *Synthetic polymeric membranes*, Sedlazeck B. and Kohovec J., Eds., Walter de Gruyter, Berlin, 1987, 355
4. Shvyryaev A.A. and Beckman I.N., in *Diffusion phenomena in polymers*, Publ. House OICHF Academy of Sciences USSR, Chernogolovca, 1985, 44
5. Palmi G. and Olah K., *J.Membrane Sci.*, 21, 161, 1984
6. Beckman I.N., Romanovskii I.P., and Balek V., in *Synthetic polymeric membranes*, Sedlazeck B. and Kohovec J., Eds., Walter de Gruyter, Berlin, 1987, 363
7. Beckman I.N. and Balek V. in *Proc. ICOM-87*, Tokyo, 1987, 09P06
8. Beckman I.N., Gabis I.E., Kompaniets T.N., Kurdyumov A.A., and Lyasnikov V.I., In *Reviews of electronics Ser., Technology, Production, Management and equipment*, vol.1 (1084), Electronics, Moscow, 1985,1
9. Beckman I.N., Shelekin A.B. and Teplyakov V.V., *J.Membrane Sci.*, 55, 283, 1991
10. Beckman I.N. and Romanovskii I.P., *Usp.Khim.*, 57, 944, 1988
11. McNabb A. and Foster P.K., *Trans.Metall.Soc.AIME*, 337, 618, 1963
12. Beckman I.N., in the reaction of hydrogen with metals, Zakharov A.P., Ed., Nauka, Moscow, 1987, 143.
13. Dubinin M.M., *Prog. Surf. Membrane Sci.*, 9, 1, 1975
14. Koros W.J., *J.Polym. Sci.*, 18, 981, 1980
15. Cohen D.S., *J.Polym.Sci.*, 21, 2057, 1983
16. Paul D.R. and Koros W.J., *J.Polym.Sci.* 14, 675, 1976
17. Vieth W.R. and Sladek K.J., *J.Colloid. Sci.*, 27, 177, 1968
18. Petropoulos J.H., *J.Plym.Sci. A* 2(8), 1797, 1970
19. Bhatia D. and Vieth W.R. *J. Membrane Sci.*, 6, 351, 1980
20. Hurst D.G., in *CRRP-1124 Atomic energy of Canada*, Chalk River, Ontario, 1962, 1
21. Kurdyumov A.A., Gabis I.E. and Mazaev S.N., *Fiz. Metal. Metalloved.*, 12, 1754, 1988
22. Norget M.J. and Lidiard A.B., *Radiation damage in reactor materials, Diffusion of inert gases in ionic crystals*, IAEA, Vienna, 1969, 61
23. McLennan R.B. *Acta Metall.*, 27, 1655, 1969
24. Oriani R.A., *Acta Metall.*, 18, 147, 1979
25. Peak D., Corbett J.W., and Bourgoin J.C., *J.Chem.Phys.*, 65, 1206, 1976
26. Robertson W.M., *Scripta Metall.*, 15, 137, 1981
27. Barrer R.M., *J.Membrane Sci.*, 18, 25, 1984
28. Barrer R., in *Diffusion in polymers*, Crank J. and Park G.S., Eds., Academic, London, 1968, 165
29. Romanovskii I.P. and Beckman I.N., *Vestnik MGU Ser. 2 Chem.*, 28, 260, 1987
30. Ruckenstein E., Vaidyanathan A.S., and Youngquist G.R., *Chem. Eng. Sci.*, 26, 1305, 1971
31. Zolotarev P.P. and Dubinin M.M., *Dokl. Akad. Nauk USSR*, 210, 136, 1973
32. Bruggeman D.A., *Ann. Phys. (Leipzig)*, 24, 636, 1935
33. Broadbent S.R. and Hammersley J.M., *Proc. Cambridge Philos. Soc.*, 53, 629, 1957
34. Kirkpatrick S., *Rev. Mod. Phys.*, 45, 574, 1973.
35. Ottino J.M. and Shah A., *Polym. Eng. Sci.* 24, 153, 1984
36. Ievlev A.A., Teplyakov V.V., Durgarian S.G., and Nametkin N.S., *Dokl. Akad. Nauk USSR*, 264, 1421, 1982
37. Beckman I.N. *Radiokimia*, 23, 760, 1981
38. Beckman I.N. and Shvyryaev A.A., *Radiokhimiya* 24, 126, 1982
39. Buntseva I.M., in *Membranes and membrane separation*, Nicolaus Copernicus University, Torun, Poland, 1989, 81
40. Beckman I.N., *J. Radionucl. Nucl. Chem. Lett.*, 153(15), 345, 1991
41. Paterson R. and Doran P., *J.Membrane Sci.*, 27, 105, 1986
42. Barrer R.M., *J. Phys. Chem.*, 57, 351, 1953
43. Aitken A. and Barrer R.M., *Trans. Faraday Soc.*, 51, 110, 1955
44. Beckman I.N., Shelekhin A.B. and Teplyakov V.V., *Dokl. Akad. Nauk USSR*, 308, 635, 1989
45. Beckman I.N., in *Int. Symp. Membranes for gas and vapour separation*, Suzdal, USSR, 1989, 24.
46. Higuchi A. and Nakagawa T., *J.Appl.Plym. Sci.*, 37, 2181, 1989
47. Klass D.L. and Landahl C.D., U.S. patent 3,797,200, 1974
48. Klass D.L. and Landahl C.D., U.S. patent 3,818,679, 1974
49. Beckman I.N., Balek V., and Kralicek J., *Czechoslovak patent* 244,791, 1986
50. Teramoto M., Matsuyama H., Yamashiro T., and Okamoto S., *J.Membrane Sci.*, 45, 115, 1989
51. Shelekhin A.B. and Beckman I.N., in *proc. 1990 Int. Congr. Membranes and Membrane processes*, Chicago, vol.2, 1990, 1419
52. Shelekhin A.B., BECKMAN I.N., Teplyakov V.V., and Gladkov V.S., *USSR Patent SU 1637850*, 1991
53. Shelekhin A.B., Beckman., and Teplyakov V.V., *Theor. Osnov. Chem. Techn.*, 26, 570, 1992

54. Beckman I.N., Bessarabov D.G., and Teplyakov V.V., J.Ind. Eng. Chem. Res., 1993, in press.
55. Scultz J.S., Goddard J.D., and Suchde S.R., AIChE J., 20, 417, 1974
56. Scolander P.F., Science (Washington D.C.), 131, 565, 1960
57. Ward W.J. and Robb W.L., Science (Washington D.C.), 156, 1481, 1967
58. Sirkar K.K., U.S.Patent 4750918, 1988

The application of the diffusion gas probe technique for the characterization of polymeric membrane materials

New synthetic polymer, e.g. glassy polymers with microheterogeneous structure, block copolymers and polymer composite materials, containing adsorbents, catalysts, etc. have been applied recently in the technology of synthetic polymers used for preparing selective membranes.

Çàìëÿ êðóãèà - ìà êðàð àñòðáòèíÿ !

INTEGRATED MEMBRANE SYSTEMS

2.1 Membrane methods

1. Porous or non-porous (dense)
2. Active (membrane catalyst or ion-conductor) or chemical passive
3. Materials:

Inorganic membranes: Metal, alloy, ceramic, glass

Polymeric membranes: non-porous gas separation asymmetric composite membranes

4. Geometry of membrane: flat sheet or hollow fiber.

The dense polymeric membranes meet the criteria of high selectivity, but satisfying the criteria of high permeability is limited by the thickness of the membrane, which again is constrained by the mechanical strength and durability of the membrane. To meet the dual challenge of selectivity and permeability, there has been a recent thrust to support thin layers of highly selective membrane material on a porous support with high permeability. The advantages of a dense polymeric membranes are high gas permeability and selectivity and absolutely microbe non permeability. Disadvantage to this membranes are poor chemical, mechanical and radiation stability and low resistance to temperature.

As opposed to polymeric membranes, the inorganic membranes are characterized by high resistance to temperature and corrosive environments, and good mechanical stability. There is increasing interest utilising inorganic membranes to separate gas mixtures at high temperatures. One of their most promising applications is in membrane reactors where chemical conversion and product purification by separation take place in the same device. These applications are involved with chemical synthesis, but membrane reactors also have potential used in high temperature gas cleanup operations.

2.2 Permabsorbers

Recovery, purification and concentration of gases, treatment and control of the gas mixtures compositions are the key processes of modern chemical technology and ecology. At the moment the separation of gases is carried out by different methods which are cryogenic, sorption and membrane ones. Each of them has own benefits and disadvantages. For the real technological systems the combined application of the different treatment methods is of interest. The next stage of the different gas separation methods combination is the creation of integrated systems of the membrane technology.

Integrated membrane systems in gas separation: membrane-absorption systems included:

Separation modules of liquid-membrane contactor:

- 1) Membrane permabsorber;
- 2) Selective membrane valve.

Condition of operation:

- 1) Flowing;
- 2) Circulating;

Selective flowing-liquid absorbent:

- 1) Non-specific in relation to the components of gas-separation mixture;
- 2) Solubility's of the gaseous components in a liquid could differ considerably;
- 3) Liquid could react with one or several of the gas components.

At the last time it was proposed to use non-porous gas separation membranes in membrane-absorption systems combining the membrane and sorption methods. Two types of gas separating modules (*membrane permabsorber and selective membrane valve*) are suggested which are the membrane absorber and the membrane valve operating in the both flowing and circulating condition.

The main reasons for the application on non-porous polymeric membrane systems are the flexibility, selectivity, good productivity and the sterile properties of these systems.

Membrane absorber

The *membrane absorber* (Fig.7a) consists of the two cells which are absorption and desorption ones and the liquid specifically selected as an agent for extraction is circulated between them. The gas mixture is passing over the polymeric membrane in the absorption cell. The most permeable component of gas mixture diffuses selectively through non-porous polymeric membrane into the flowing liquid under it, is absorbed by this liquid and transfer to desorption module. The degassing of liquid occurs in the desorption membrane module through the non-porous polymeric membrane with obtaining of the high concentrated gaseous products. There are two operating conditions of the membrane device which are flowing one when the liquid is taken out of gas separating device, and when the liquid is continuously circulated in system.

The liquid absorbent can be non-specific in relation to the components of the gas-separation mixture. The solubility's of the gaseous components in a liquid could differ considerably. Also, a liquid could react with one or several of the gas components. The productivity and selectivity of the membrane permabsorber depend on the gas-transport properties of the polymeric membranes, on the temperature of the liquid absorbent in stripper, on the flow rate of liquid absorbents, on the concentration of a selective carrier in a liquid, etc.

We are use a hybrid process for separation of ethylene/ethane mixtures using a membrane permabsorber comprising hydrocarbon-stable composite asymmetric non-porous gas-separation flat-sheet membranes made from copolymer: polydimethylsiloxane/polyphenylsilsesquioxane with a high permeability for hydrocarbons and flowing solution of silver nitrate used as a selective absorbent for ethylene.

Membrane valve

A *membrane valve* consist of two modules: a permeator and desorber (Fig.7b). The permeator is divided by two polymeric gas-separation membranes, M1 and M2, between which a thin layer of absorbent liquid is moving. The investigated gas mixture and gas-carrier are passing under the surface of sandwich. The components of the gas mixture are dissolved in the liquid absorbent and are driven out of the permeator to the desorber (membrane M3 and M4). The selective membrane valve has one inlet for the initial gas mixture and three outlets for the product leaving the separation device. The plant can be used to separate a three-component gas mixture: the gas insoluble in the absorbent passes above the membrane, the fast component of the gas mixture passes through the composite membrane, and the third component, dissolving well in the absorbent, is entailed by the liquid into the desorber.

The proposed methods has been tested by separating a three-component gas mixture carbon dioxide-methane-hydrogen using the membrane valve operating in the circulation mode with desorber. Asymmetric membranes produced from poly(vinyltrimethyl silane) and aqueous solutions monoethanolamine of different concentrations served as the carrier of carbon dioxide.

Emission of volatile (halogenated) organic compounds (VOC) to the atmospheric are a serious problem, particularly due to large volume flows and low concentration levels. For the recovery of VOC's a new membrane based process is proposed: selective membrane absorption. selective membrane absorption is a new, very selective separation process which combines absorption and membrane technology to produce an optimized hybrid process.

Absorption is very selective process for recovering VOC's from air. With the combination of membranes and absorption, it is possible to recover VOC's at very low level ($<1 \text{ mg/m}^{-3}$) and to concentrate them in the absorption liquid. Recycling the process gas (e.g. air) is then possible. By regenerating the absorption medium, the absorbed VOC's can be recovered and reutilized.

Selectivity membrane absorption combines the advantages of these short diffusion pathways:

- compact hollow-fibre membranes with short diffusion path ways
- phase separation by the membrane
- recovery of VOC's, even at low concentrations, by high affinity absorbents

After the modelling of mass transfer in the membrane module the optimal composition of the absorption mixtures was calculated with vapour-liquid thermodynamics system options.

2.3 Permsractors

Membrane based extraction are emerging contacting technologies which have several advantages over conventional contactors, such as, high mass transfer, compactness and no fluid mixing.

We explored the possibility of perstractors in next liquid/liquid extraction processes:

- Removal of toxic organic compound from waste water
- Removal of heavy metals from industrial waste or natural water.

Perstractors with supported liquid membrane technique

The membrane extraction technique is based on selective extraction of metal or organical compounds from liquids using Supported Liquid Membrane technique (SLM-technique) and enrichment of one component using compact membrane elements, followed by component analysis in enriched pure re-extraction solution by known mode.

We was used Supported Liquid Membrane technique (SLM-technique) for monitoring of mercury and antimony in natural water sources and biological solutions with the determination limit 10^3 - 10^4 mg/l .

There is a need in convenient and simple method of mercury and antimony analysis in natural water sources and biological solutions, with the sensitivity corresponding to concentration limits for these toxic metals in water. Simple photometric, ionometric and strip methods adapted to field use often don't correspond to this sensitivity level and are under the hindering influence of many other ions. More sensitive device methods like spectroscopy of different types are too complicated for permanent use in field conditions, and often remain sensitive to excess of hindering metals.

The main features of a new method are:

1. Elaboration of the kinetic model for membrane extraction of heavy metals in cationic and anionic forms through SLM conjugated with co- and counter-current transport.
2. Achieving high extraction selectivity of the metal analysed (up to 10^2 - 10^3) due to proper choice of selective chelating agent and re-extraction phase content.
3. Concentrating of metal analysed in re-extraction solution by a factor of 10^2 - 10^4 due to "active" counter-current transport.
4. Volume of the probe analysed can be as small as 20-30 ml.

In future the method can be extended for environmental analysis of many other toxic metals, e.g. Ni, Cr, Cd, Zn, etc.

Scientific and technical description included:

1. Collection and analysis of the data on description and migration of mercury and antimony together with accompanying metals in natural water sources, biological solutions and soils.
2. Testing of SLM loaded with lipophilic metal-selective extractants selected from the classes of polyalkylarylthioureas, alkylthioethers, etc.
3. Investigation the kinetics of "active" metal transport coupled with proton or hydroxyl counter-current transport from the re-extraction phase.
4. Development of the cassette element design with thin channels for source and reextraction solutions that are separated by a porous hydrophobic support soaked with the solution of lipophilic chelating agent. The element measures not more than 6x12x2 cm; the volume of extraction solution for loading the reusable SLM in the cassette is 0.5-1 ml.
5. Field testing of the method on real natural sources, wastewaters and biological solutions. Development of procedure recommendations for using the method in monitoring and biological investigations.

Membrane extraction discs.

In Russia the continuous environmental monitoring of dissolved toxic metals using membrane extraction discs was developed.

Method is based on using of new simple units - membrane extraction discs (MED) - macrocapsules measuring a coin or a tablet, that are a micro-vessel with walls being metalselective impregnated liquid membrane. Hydrophobic pores of this membrane are soaked with hydrocarbon lipophilic chelating agent, that is selective to the metal analysed. The micro-vessel contains re-extraction solution impregnating a tablet-like porous spacer and, if necessary, an indicator that forms a colored complex with metal ions. MED being placed in a flow of analysed water selectively extracts the metal which is accumulated in the inner re-extraction solution. The analysis of metal absorbed in this solution can be carried out by traditional methods after MED opening (strontium can be determined through the complex with ethylene diamine tetraacetic acid or using atomic absorption spectroscopy). Another method is the spectrophotometry or visual estimating the intensity of complex or deposit colour directly through transparent membrane compared with standards, without destroying the MED and with the possibility of its further using (nickel determination in form red precipitated dimethylglyoxime complex).

If the process of metal ion transport is attended by the process of counter-current transport of any component from the internal re-extraction solution (e.g., hydrogen cations), this will allow to attain multiple concentrating of the metal analysed inside the MED. In this case the concentration degree can reach 10^4 .

In properly made MED the metal absorption rate is directly proportional to the metal's concentration in the external solution, i.e. the resulting value corresponds to averaged metal concentration in water source during MED's exposition time. MED's are the simplest and extremely cheap analytic units for durable quantitative accumulation of toxic metals. Using of them permits to develop a simple method of continuous environmental control of them in different water sources and wastewaters.

Authors of the work dispose of an method of hydrophobic macrocapsules' production, and of all necessary components for MED production:

- Hydrophobic membranes based on fluoropolymers and polyolefines, self-carrying and composite ones;
- Acid-resistant macroporous spacers based on polyolefines of foam, sintered and non-woven types;
- Selective lyophilic extractants for strontium and nickel extraction, of two classes: bis-(alkylcycloalkyl)-crownether and alkylene-bis-diphenylphosphine oxide with pendant aliphatic arm. Lyophilic alkylated hydroxyoximes for selective nickel extraction.

Long-term selective toxic metal (e.g. water dissolved nickel and strontium salts at concentration 10^{-2} - 10^4 mg/l) accumulation method from a wastes, potable water or natural water reservoir for its subsequent analysis was developed.

Perstractors with flowing liquids.

There is a growing need separation techniques which selectively recover metal ions from industrial process streams. The newly developed membrane-absorption or extraction process is able to recover metal-free water and a concentrated metal solution from above streams. Membrane extraction processes can be used for concentrating metal solutions from ppm-level to g/l-level with recycling of the concentrated metal solution and of the metal-free water as interesting possibility.

The permstractor was used also for separation of multicomponents liquid mixture.

The permstractor (Fig.8) consists of the three cells. The liquid mixture (L1) is passing over the polymeric membrane in the extraction cell. The most permeable components of liquid mixture diffuses selectively through porous polymeric membrane (M1) into the flowing liquid (L2) under it, is absorbed by this liquid and transfer to reextraction module. The reextraction of liquid occurs in the reextraction membrane module. Components of liquid mixture difuses selectively into the flowing liquid (L3) under it through the porous polymeric membrane (M2) with obtaining of the high concentrated products. Products cleaned with help different liquids L4 and L5 and membranes M4 and M5. There are two operating conditions of the membrane device which are flowing one when the liquid is taken out of liquid separating device, and when the liquid is continuously circulated in system.

3. MEMBRANE CHEMICAL REACTORS

The used of membranes in chemical reactors is motivated by the equilibrium shift caused by selective or preferential permeation of reaction products, leading to higher conversion in single pass. By selectively permeating one or more reaction products through the membrane wall, it is possible to achieve significant enhancement over the equilibrium conversion of the reactor feed stream. The equilibrium shift also allows attaining a given conversion at less severe conditions of temperature and pressure. As reaction and permeation proceed simultaneously, the separation of product can be accomplished in the reactor unit itself, or at least the down stream separation load is reduced. Selective or preferential permeation may prevent further reaction of a product and this may improve the yield of a desired component in a multiple reaction system. On the other hand, the ability to introduce a reactant in a controlled manner through a permeating membrane may allow the regulation of the reaction leading to better yield and selectivity and improved control. In addition, the membrane may allow hot separation of products and eliminate the need for quenching a reaction to prevent back reaction. The membrane itself may act as a catalyst or catalyst may be impregnated on the membrane. The membrane reactor may be bifunctional and two complementary reactions may take place on either side of the membrane, the product of reaction on one side acting as a reactant on the other side, while the endothermicity of one reaction is compensated by the exothermicity of the other.

In the Chemical Department of Moscow State University and in the Institute of Petrochemical Synthesis we are working in next direction:

- Construction of various new types of membrane reactors;
- Transport mechanism of fluids through active or passive membranes;
- Separation of mixed wastes;
- Steam reforming of methane;
- Water gas shift reaction;
- Dehydration of various hydrocarbons;
- Purification of tritium for thermomolecular energy installation;
- Radioactive waste management of nuclear power;
- Air and water pollutants monitoring.

There are basically two types of membranes which can be used for membrane reactors: dense (non porous) and porous. The former is called the inert membrane packed bed reactor while the latter is called inert membrane fluidized bed reactor. When the membrane itself act as a catalyst or catalyst is impregnated in the membrane and the reactants pass through the empty tube having the catalytic membrane wall, it is called a catalytic membrane reactor. When a CMR is also packed with catalysts, it is called a packed bed or fluidized bed catalytic membrane reactor. In industrial reactors, shell and tube configuration with an assembly of single tubes or multichannel monoliths may be incorporated into a large shell. The membrane reactors are usually operated in parallel or cross-flow mode, with the reactants on one side and vacuum or a sweep gas.

Let us examine the different constructions of membrane reactors. Schematic layouts for the membrane reactor systems are presented in Fig.9. The walls of reaction vessel are made from the gas selectively materials. We are suggested that in the reactor occurs a second-order reversible chemical reaction involving four gases. The each walls of reactor have different selectivity with respect to component of reaction mixture. Certain of the membrane walls are used

for the initial reaction components supplied in reaction vessel, other walls is removed of reaction products from reaction vessel). Fig.8 show membrane reactor which allows to carry out the removal of both of reaction products. It is possible to operate the system as a catalytic membrane reactor by replacing the membrane with a catalyst-impregnated membrane or a membrane which itself acts as a catalyst. The packed bed catalytic membrane reactor can be prepared by packing the catalytic membrane reactor with catalyst).

Experiments with membrane reactors included study of gas diffusion in solids with simultaneous diagnostics of membrane material.

Membrane materials: metals (Pd, Pt, Ag, Fe, Ni, Cu), alloys, materials with coats and welds, ceramics, glasses (porous or dense)

Diffusants: hydrogen isotopes (protium, deuterium, tritium), air components, inert gases (stable and radioactive)

Diffusion methods: permeability method, sorption and desorption methods, thermodesorption spectroscopic analysis, frequency probing method, autoradiography method

Methods of membrane diagnostics: 1) Gas Diffusion Probe Method. 2) Auger Electron Spectroscopy. 3) Nuclear Gamma-Ray Resonance Spectroscopy Method (Mossbauer effect).

There is increasing interest utilising inorganic membranes to separate gas mixtures at high temperatures. One of their most promising applications is in membrane reactors where chemical conversion and product purification by separation take place in the same device. These applications are involved with chemical synthesis, but membrane reactors also have potential used in high temperature gas cleanup operations.

Porous and dense ceramic membranes for the application in high temperature reaction processes and separation. Composite ceramic membranes are investigated for the application in selective gas separation membrane reactors. The type of nanostructure of those composite membranes determines the application possibility.

Dense mixed-conducting oxide membranes offer a large potential in the separating oxygen from air or for selective feeding of oxygen into chemical reactors. Oxygen is transported through the membranes in the form of anions, being charge compensated by the transport of electronic charge carriers. Promising candidates are stabilized zirconia or bismuth oxide, doped with multivalent metal ions, and perovskitetype oxides $(La,A)(Co,B)O_{3-\delta}$ ($A = Sr, Ba$; $B = Fe, Mn$). The permeability occurs above $600^{\circ}C$, reaching values that may be comparable to those exhibited by microporous membranes.

Microporous membranes based on silica or silica-composite systems transport preferably He, H_2 and CO_2 in comparison with all other gases. The permeability is relatively high (H_2 $300\text{ m}^3/\text{m}^2\cdot\text{bar}\cdot\text{day}$ at $200^{\circ}C$) and for the system H_2/C_3H_6 the separation factor is over 200 at $200^{\circ}C$. In this case the selective toplayer is very thin ($<100\text{ nm}$) and is partly present in the support.

Dense and microporous membranes can be furthermore used in high temperature reactors as passive membranes to remove selectively one of the reaction products at reaction temperature. A special case of microporous membranes are zeolite membranes. The ordered cavities and channels can be considered as micropores. Mesopores and macroporous membranes (pores $>3\text{ nm}$) are at high temperature less selective but have a high permeability. These types of materials can however be made very suitable as active membranes in high temperature reactors. The internal surface of the membranes (or membrane toplayers) are then provided with catalytically active components. With these active membranes reactions can be carried out with a feed from both sides of the membrane and process conditions can be optimized for high conversion and selectivity. A special case is air pollution control through the removal of NO_x with NH_3 .

Palladium and its alloys with ruthenium, nickel or other metals from groups VI to VIII, silver and zirconia are examples of dense membranes. Palladium-based membranes are permeable only to hydrogen while silver and zirconia are permeable only to oxygen. These membranes have high selectivity, but low permeability. Zirconia membranes are solid oxide electrolytes and their permeability depends on ionic conductivity. Examples of commercial porous inorganic membranes are ceramic membranes, silica and titania, glass and porous metals, such as stainless steel and silver. These membranes are characterized by high permeability, but low selectivity. Recently attempts are being made to combine the selectivity of the dense membranes and the permeability of porous supports using various techniques, new materials are being developed and preparation techniques devised to produce thinner membranes and/or smaller pore-sized membranes. Methods are also being developed to modify the pore structure, producing smaller pores and increasing the stability of the membrane.

The high permeability of the inorganic membranes can be combined with the good selectivity of the organic membranes. The concept of liquid-immobilized membranes can be adapted in the field of inorganic membranes with molten salts incorporated in their porous matrix.

4. MEMBRANE MICROFOTOREACTORS FOR TOTAL ORGANIC CARBON ANALYSIS

New analytical device for determination the value of Total Organic Carbons (TOC) in water solution is based on exhaustive photooxydation of water-dissolved organics in microreactors using TiO_2 semiconductive photocatalyst in a plain or tubular membrane form. In this case photochemical reaction is provided on membrane photocatalyst's surface

while UV-irradiating and at the same time removing the reaction products through the pores to the opposite membrane side. Using of membranes having a developed porous structure with open submicron pores and transmembrane permeability to liquids and gases permits to simplify the construction of a photooxidizing unit used, to make it usable repeated many times and to increase the completeness of photooxidation, that is, accuracy of the analysis. Earlier, during the preliminary research, the Russian scientists have already prepared the composite membrane photocatalysts from TiO_2 (by sol-gel method from alkoxide precursors) and have investigated them regarding their activity during the oxidative destruction of chlorinated aliphatics, phenols, aromatic acids, many phosphorus, nitrogen and sulfur containing compounds, for example, surfactants, in water solution.

It was established that in appropriate conditions (excess of oxidizing agent, Pt- and Ru-doped membranes) the end products are H_2O , CO_2 and Cl. Releasing CO_2 can be separated through gas permeable membrane (teflon, silicon, that are at authors disposal) and analysed by any known methods, like conductometric detector.

The using of membrane microphotoreactor for total organic carbon analysis with TiO_2 -based membranes permits to reach high sensitivity (determination limit corresponds some ppm of TOC in water by using conductometric detector), long-term stability and high selectivity, associated with the selectivity of gas permeable membrane.

5. MEMBRANE BIOREACTORS.

Biological water denitrification is a proven process to remediate the increasing nitrate pollution of drinking water. In anoxic conditions denitrifying bacteria are able to use nitrogen oxides as electron acceptors consequently nitrate may be sequentially reduced to molecular nitrogen. To achieve biological denitrification rates reactors with cell retention or cell immobilization must be used.

The uses of non-porous asymmetric polymeric gas-separation membranes in membrane bioreactors appears to have considerable promise. The thin dense work layer of membrane offers sterile of processes by reason of total absence of micro-organisms permeability from one compartment of reactor to another. In this case, the high aim gas membrane productivity obtain.

The membrane reactor construction is similar to integrated membrane systems construction. However, there are circulate water suspending of micro-organisms (bacteria's, algae). The equipment incorporates light source for controls of micro-organisms life.

We have made studies into membrane bioreactors with circulate suspended micro-organisms uses for next aims:

- the production of as gases as hydrogen and oxygen;
- recovery of gases to biomass;
- conversion of one gasses in another.

Examples are provided by conversion of carbon dioxide in hydrogen. Carbonic acid gas is an extreme environmental hazard, whereas hydrogen is important for energetic.

The prior analysis demonstrated that membrane bioreactors with circulate suspended micro-organisms substance hold the greatest promise for next application

- apparatus for life provision
- hydrogen energetic
- environmental protection
- production of artificial protein.

6. COMBINE EQUIPMENT

In our laboratory, new construction of combine integrated membrane systems was proposed. Equipment integrates in one module different methods of processing and separation of gas mixtures: absorption, adsorption, extraction and liquid catalyse. For regeneration of liquid carrier can be put to use desorption and reextraction processes. Equipment is dedicated to the cleaning of the liquid nuclear plant wastes from radionuclides. Its make possible remove from waste the organic volatile matter, two radioactive metals and two gasses. Integrated system have one input and six output for remove the cleansed streams.

In summary it may be said that in Russia carried out to investigations to the prospects for use different type membrane reactor in chemical industry, biotechnology and environment. The emphasis is on the evolution of the new energetic- and resource save, safe and little waste production.