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Potential of unsteady state membrane gas separation: From pulses to harmonic function

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Membranes become the key component of modern separation technologies and allow exploring new opportunities and creating new molecular selective processes for purification, concentration and separation of liquids and gases. Particularly the development of new highly effective processes of gas separation with application of existing materials and membranes take specific place. In present time special attention devotes to purification of gas and liquid waste streams from ecologically harmful and toxic substances such as greenhouse gases, VOCs and others. From the fundamental point of view the development on new highly effective processes of gas separation demands the investigation of mass transfer in the unsteady (kinetic) area of gas diffusion through a membrane. This approach allows in some cases to obtain much higher selectivity of separation (using the same membrane materials) compared to traditional process where steady state conditions are applied. First studies of membrane separation processes under unsteady state conditions (Paul, 1971; Hwang & Kammermeyer, 1975; Beckman, 1993) have demonstrated both opportunities and problems of such approach. It was shown that effective separation in unsteady membrane processes is possible if residence times of mixture components significantly differ from each other that is the rare situation in traditional polymeric materials but well known for liquid membranes with chemical absorbents (Shalygin et al., 2006). It should be noted that the functioning of live organisms is related with controllable mass transfer through cell membranes which “operate” in particular rhythms. The development of highly effective unsteady membrane separation processes is far from systematic understanding and practical evaluation. Therefore the evolution of investigations in this area will allow accumulating new knowledge about unsteady gas separation processes which can be prototypes of new pulse membrane separation technologies.

Theoretical description of unsteady mass transfer of gases in membranes is presented in this work. Examples of gas mixture separation are considered for three cases of gas concentration variation on membrane: step function, pulse function and harmonic function. Unsteady gas flow rates and unsteady separation factors are calculated for all cases. Amplitude-frequency, phase-frequency and amplitude-phase characteristics as well as Lissajous figures are calculated for harmonic functions. The comparison of mixture separation efficiency under steady and unsteady mass transfer conditions is carried out. Calculations were performed for oxygen-nitrogen and oxygen- nitrogen-xenon gas mixtures separation by membranes based on polyvinyltrimethylsilane (PVTMS) and for CO_2 transfer in liquid membrane with chemical absorbent of CO_2.

In the frames of “classical” diffusion mechanism (that is the diffusion obedient to Fick’s law and the solubility – to Henry’s law) the unsteady distribution of concentration of diffusing gas $C(x,t)$ across the flat membrane with thickness H, is determined by the 2nd Fick’s law. As to step function variation of gas concentration in upstream it is shown that the non steady-state selectivity factor (α_{us}) depends on diffusion time: the highest value of selectivity can be achieved at short times. In the case of pulse permeation method we deduced the equations describing the response function of gas flux with duration Δt in upstream. The calculation of binary mixtures separation nitrogen-xenon was done with using of experimental data for PVTMS films and demonstrates that peaks are well resolved.

Method of the concentration wave is based on study of wave deformation during penetration through a membrane. The variation of gas flux at the downstream is mathematically described. Obtained dependencies of amplitude and phase variation on frequency are used for the characterization of membrane. The existing of five degrees of freedom (steady-state condition

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relatively of which the harmonic function takes place; time of the steady-state achieving; change of the amplitude and phase characteristics after transfer through membrane and their dependences on the frequency) allows controlling the diffusion of gas and consequently the separation process. Concentration waves decay strongly as a rule; however they possess all properties of waves, in particularly, interference and diffraction. During harmonic function the quasi-stationary gas flux value is determined by membrane permeance; the amplitude of the transmitted wave depends on permeability (i.e., on diffusivity and solubility coefficients), thickness of membrane and frequency. However, the ratio between the amplitude of the oscillations in upstream and downstream does not depend on the permeability coefficient. The phase shift depends on the diffusivity coefficient. The separation of ternary gas mixture (oxygen-nitrogen-xenon) is possible under the concentration wave regime as well. The results of mathematical modeling of permeation of the concentration wave (of nitrogen, oxygen or xenon) were obtained for PVTMS film. Following values of parameters were used for calculations: thickness of film H= 0.01 cm; area A_S=10 cm^2; reference frequency: ω_0= 0.01 s^{-1} (range of frequency 0-0.04 s^{-1}); time interval: t=0-4000 s; transport parameters for O_2,N_2 and Xe. The selectivity factor fluctuates on periodical (but not sinusoidal) low: the fluctuations are substantial for gas mixtures enriched by Xe and lower for ones with lower content of Xe.

As it follows from results of mathematical modeling the application of unsteady mass transfer regimes allows effectively control the selectivity of gas mixture separation by membrane. Particularly, the application of pulse and harmonic oscillations of gas concentration permits to adjust separation process by variation of frequency causing variation of amplitude and phase of the concentration waves passing through a membrane and therefore variation of productivity and selectivity of separation. This technique can provide extremely high separation factors at initial times but unfortunately at low productivity. For O_2/N_2 gas mixture concentration wave method is low effective but for Xe/N_2 and Xe/O_2 good separation can be obtained. The study of unsteady mass transfer is important for development of gas sensors with membrane coating since they have low selectivity and therefore respond to all components of gas mixture. Suggested mathematical apparatus allows to solve these tasks and to formulate requirements to the system “membrane-gas mixture” for realization of unsteady highly effective gas separation processes. The development of mathematical apparatus of selective unsteady transfer of gas mixtures through membranes is necessary for development of phenomenological description of dynamics of mass transfer of O_2, N_2 and CO_2 in breathing apparatus of humans and animals for understanding of functioning of live organisms.

Keywords: Unsteady state permeability, mathematics of diffusion, concentration waves