

NOMENCLATURE	I
ABSTRACT	V
KURZREFERAT	VI
CHAPTER 1: INTRODUCTION.....	1
1.1 Literature review.....	1
1.1.1 Preparation of porous glass membranes	2
1.1.2 Transport investigation of gases through porous glass membranes	3
1.1.3 Potential application of porous glass membranes	5
1.2 Research objective and outline.....	7
1.3 References	9
CHAPTER 2: GAS DIFFUSION THROUGH POROUS MEDIA	14
2.1 Fundamentals of diffusion.....	15
2.2 Diffusion regimes: From mesopore to micropore diffusion.....	16
2.2.1 Continuum diffusion (Molecular diffusion)	17
2.2.2 Knudsen diffusion	20
2.2.3 Viscous flow	20
2.2.4 Configurational diffusion	22
2.2.5 Surface diffusion	23
2.3 Mass balances considering parallel transport mechanisms	26
2.4 Models for description of gas and surface transport through porous media.....	27
2.4.1 Standard models for description of combined gas transport	27
2.4.2 Maxwell-Stefan approach for description of surface transport.....	30
2.5 Numerical method	31
2.6 An overview of experimental measurement techniques	32

2.7 Chapter conclusions.....	36
2.8 References	36

CHAPTER 3: SELECTED POROUS GLASS MEMBRANES 40

3.1 Preparation of membrane materials.....	41
3.1.1 Vycor membrane with mean pore diameter of 4 nm	41
3.1.2 CPG membranes in meso- and microporous range with mean pore diameters from 1.4 to 4.2 nm.	43
3.1.2.1 <i>Preparation of mesoporous membranes with mean pore diameters: 2.3 nm (M1), 3.1 nm (M2) and 4.2 nm (M3)</i>	45
3.1.2.2 <i>Preparation of microporous membranes with mean pore diameters: 1.4 nm (M4) and 1.5 nm (M5)</i>	45
3.1.3 Surface modification of CPG membrane M1	46
3.2 Characterization of CPG membranes	46
3.2.1 Low temperature nitrogen adsorption.....	46
3.2.2 Positronium annihilation lifetime spectroscopy.....	48
3.2.3 Scanning electron microscopy	49
3.2.4 Thermogravimetry	50
3.2.5 Inverse gas chromatography.....	51
3.3 Chapter conclusions.....	52
3.4 References	53

CHAPTER 4: GAS DIFFUSION THROUGH VYCOR MEMBRANE: MEASUREMENTS AND MODELING..... 55

4.1 Experimental set-up for transient diffusion measurements. Application of Wicke-Kallenbach technique.....	56
4.2 Determination of single gas and binary mixture adsorption isotherms	59
4.2.1. Single gas adsorption.....	59
4.2.2 Binary mixture adsorption.....	60
4.3 Determination of the diffusion coefficients from single transient experiments with inert and adsorbable gases	66
4.3.1 Mathematical modeling of single transient experiments	67
4.3.2 Transient diffusion with inert gases.....	68
4.3.3 Transient diffusion with adsorbable gases	70
4.4 Competitive diffusion	72
4.4.1 Mathematical modeling of counter-diffusion experiments.....	72
4.4.2 Counter-diffusion of two inert gases.....	73

4.4.3 Counter-diffusion of one inert and one adsorbable gas. Influence of site blocking	75
4.4.4 Counter-diffusion of two adsorbable gases. Influence of gas composition and site blocking.....	77
4.4.4.1 Selective permeation of examined gas mixtures C_3H_8/CO_2	81
4.5 Chapter conclusions.....	84
4.6 References	85

CHAPTER 5: GAS DIFFUSION THROUGH CPG MESOPOROUS MEMBRANES: EFFECT OF PORE DIAMETER AND SURFACE PROPERTIES.....87

5.1 Experimental procedure	88
5.1.1 Experimental set-up for diffusion measurements	88
5.1.2 Experimental set-up for adsorption equilibrium measurements.....	90
5.2 Mathematical modeling of single gas diffusion and counter-diffusion experiments	92
5.2.1 Single gas diffusion experiment.....	92
5.2.2 Counter-diffusion experiment.....	93
5.3 Single gas diffusion	94
5.3.1 Evaluation of adsorption isotherms	94
5.3.2 Evaluation of permeability	98
5.3.3 Comparison between ideal selectivities of modified and unmodified membranes	107
5.4 Competitive diffusion	107
5.4.1 Evaluation of the binary mixture adsorption isotherms	108
5.4.2 General trends of counter-diffusion experiments using W-K cell.....	113
5.4.3 Simulations of the pressure responses for different Maxwell-Stefan constitutive equations	116
5.4.4 Comparison between suggested prediction models and measured pressure responses for different pairs of gases (membrane M1)	122
5.4.4.1 Limitations of the W-K cell for counter-diffusion measurements.....	123
5.4.5 Partial fluxes vs. single gas fluxes and corresponding selectivities.....	127
5.4.5.1 Gas pair $He-N_2$	127
5.4.5.2 Gas pair CO_2-N_2	128
5.4.5.3 Gas pair $CO_2-C_3H_8$	129
5.5 Chapter conclusions.....	133
5.6 References	134

**CHAPTER 6: GAS DIFFUSION THROUGH CPG MICROPOROUS MEMBRANES:
TRANSITION BETWEEN KNUDSEN AND CONFIGURATIONAL
DIFFUSION..... 136**

6.1 Single gas diffusion	137
6.1.1 Evaluation of adsorption isotherms	137
6.1.2 Evaluation of permeability and ideal selectivity	139
6.1.3 Reproducibility and sensitivity in preparing the microstructure.....	147
6.1.3.1 Evaluation of permeability and selectivity of membrane M5	148
6.2 Competitive diffusion	152
6.2.1 Evaluation of binary mixture adsorption isotherms.....	152
6.2.2 General trends of counter-diffusion experiments and comparison with model predictions	155
6.2.2.1 Counter-diffusion of He and N ₂	156
6.2.2.2 Counter-diffusion of CO ₂ and N ₂	158
6.2.2.3 Counter-diffusion of CO ₂ and C ₃ H ₈	160
6.2.3 Partial fluxes vs. single gas fluxes and corresponding selectivities.....	162
6.2.3.1 Gas pair He-N ₂	162
6.2.3.2 Gas pair CO ₂ -N ₂	163
6.2.3.3 Gas pair CO ₂ -C ₃ H ₈	164
6.3 Chapter conclusions.....	165
6.4 References	166

CHAPTER 7: CONCLUSIONS AND OUTLOOK..... 168

7.1 The results: An overview	169
7.1.1 Single gas diffusion	169
7.1.2 Competitive diffusion	171
7.1.3 Membrane performances	173
7.2 Answers to the questions posed in introduction	175
7.3 Further aspects and outlook	177

APPENDICES..... 178

Appendix A: Expressions of surface diffusion fluxes for binary system.....	179
Appendix B: Scanning electron micrographs of membrane M2 at different length scales.....	181
Appendix C: Gas adsorption equilibrium measurements on different investigated membranes.....	185
Appendix C1: Row data for single and binary adsorption equilibria.....	185

Appendix C2: Correlation of binary competitive isotherms of $\text{CO}_2\text{:C}_3\text{H}_8$ mixtures	193
Appendix D: Estimation of errors of permeability data	195
Appendix E: Reproducibility problem for counter-diffusion of two adsorbable gases through meso- and microporous CPG membranes	198
Appendix F: Summary of the time lag permeation technique for determination of diffusion coefficients.....	201
Appendix G: Gas diffusion through membrane M5.....	204
Appendix G1: Single gas diffusion	204
Appendix G2: Competitive diffusion	208