ADSORPTION EQUILIBRIA
AND MASS TRANSPORT
CHARACTERISTICS OF POROUS SOLIDS

Weiruo Sun

Department of Chemical Engineering
Faculty of Engineering, University of Porto
Porto, Portugal

February 1993
This work is dedicated to all my teachers who fostered and educated me.
PREFACE

Adsorption phenomena have been recognized for a long time. The early applications of adsorption were concentrated on the purification processes of fluid mixtures. Owing to the high selectivity of the adsorbent to the impurity, very high purity of the desired products can be achieved by the adsorption purification technique. Compared with other purification methods, the adsorption processes have the advantages of equipment and operation simplicity and good purification effects. While as a separation technique for bulk fluid mixtures, adsorption is still young. The key issues for the application of adsorption to purification and separation are the behavior of the adsorption equilibrium and mass transport rate inside the adsorbents. Because of the complexity of the solid adsorptive surface structure and of the limited knowledge about the interaction between adsorbate molecules and surface atoms, the entire prediction of the adsorption equilibrium characteristics is difficult for most adsorption systems. One of the most widely applied and successfully predicted systems is the adsorption of gases in zeolite molecular sieves. Due to the regular crystal microscopic structure of the zeolites their adsorption surface properties are potential candidates to be quantitatively analyzed. The intracrystalline diffusion processes of gases in zeolites are an important rate controlling step for some zeolite catalyzed reactions; the reactants must efficiently diffuse into the active sites of the zeolite and the products must efficiently diffuse out of the catalyst. Slow intracrystalline diffusion rate will result in low apparent reaction rates. The improvement of the intracrystalline diffusion process will greatly increase the whole process rate. In adsorption applications, the physical adsorption rate is enough fast to be considered as an instantaneous process and when other mass transport resistances are small the intracrystalline diffusion process becomes the main rate controlling step. The differences on intracrystalline diffusion rates for different components in the same zeolite can be used to the dynamic separation of a mixture composed by these different components. The magnitude of the intracrystalline diffusion rate is a critical factor on process development and design of adsorption processes.

Other important topics on processes involving porous media are the mass transport rates in macropores and external fluid phase. A lot of catalysts and adsorbents are made up of small microparticles in which the catalytic active sites and adsorption surface exist. Industrial processes require that catalysts and adsorbents have some desired shape, dimension and physical strength. Such requirements result in the existence of macropore diffusion resistances. The bulk phase operating conditions will influence the external mass transport resistances. In some limiting situations the macropore diffusion and/or external mass transport rates will be dominant over other resistances. Because of the complexity of the macropore network structure, its quantitative description is impractical. Overall effective diffusivities characterizing the mass transport rate in the macropores will be very helpful in practical process development and design. These effective diffusivities can be extracted from experimental rate data by means of theoretical mass transport model analysis.

This thesis is arranged as follows: The first chapter includes a short description of the fundamental theories of pure component adsorption thermodynamics, molecular kinetics, mass transport processes inside porous media, quantum calculations of molecular partition functions of the adsorbed phase and ordinary experimental techniques for the determination of adsorption equilibrium and mass transport rate parameters of gases in porous media. The second chapter deals with the theoretical prediction of adsorption thermodynamic functions, adsorption isotherms and adsorption heats of gases in the zeolite A series. Beginning with the quantitative description of the interaction potential between the adsorbate molecules and the zeolite surface atoms, the molecular partition
functions of the adsorbed phases can be obtained by solving the Schrödinger steady state equation with the calculated interaction potential field. All adsorption thermodynamic functions, isotherms and heats can be related to the corresponding molecular partition functions of bulk and adsorbed phases. The assumption of negligible interaction potentials between adsorbate molecules implies that the methodology is only valid for the low loading case. The good agreement of predicted results with published experimental data confirms that the theory is reasonable. The intracrystalline diffusion of gases in the zeolite A series is discussed in the third chapter. Based on the relative size of the kinetic diameter of diffusing molecules and of the zeolite window, diffusion is classified in two types: the unblocked window diffusion and the blocked window diffusion. The main characteristics of the former are that the diffusing molecule is smaller than the free diameter of the window and the interaction potential is minimum at the window center. The diffusing molecule can temporally move in the window and the diffusion resistance is composed by the resistances to the diffusion from the cavity to window and to the diffusion from the window intermediate state to the cavity. This diffusion is an activated process and when at the intermediate state, the molecule must overcome the energy barrier between the window and the cavity. The main characteristics of the second mechanism are that there is a strong repulsion in the window and there are only very few chances that a diffusing molecule can cross the window, so diffusion is a strongly activated process and the corresponding activation energy is much larger than that of the former case. The fourth chapter is concentrated on the discussion of the experimental techniques, single pellet diffusion cell, shallow bed diffusion cell and single pellet string fixed bed, and the corresponding mathematical models. Direct time domain matching of theoretical values to the experimental data is preferred to extract the effective diffusivities. The last chapter analyzes the relative importance of the various mass transport resistances and gives some criteria for neglecting one of them in single pellet diffusion cell, shallow bed diffusion cell and single string pellet fixed bed experimental techniques. The adsorption equilibria and mass transport parameters for argon, nitrogen and oxygen in different solids are obtained by simulating the experimental results. The comparison of results obtained using different experimental techniques confirms that both experimental techniques and the corresponding models are reliable.

I would like to take this opportunity to thank my supervisor, Prof. Carlos A.V. Costa, for his careful guidance, Prof. Alfrido E. Rodrigues, Prof. José Miguel Loureiro, Prof. Mário Rui Costa and Prof. José Carlos Lopes for their helpful guidance and aid, all my colleagues for their help, Centro de Informática Prof. Correia de Araújo and Dr. L. M. Ribeiro for the computer utilization. Fundação Oriente is highly acknowledged for granting me a scholarship (scholarship number IC/ic D.S.E.C.F./ 000516 ). Without these helps I could not have finished my degree work. I sincerely thank them for their kind help.

Weiruo Sun

February 10, 1993
RESUMO

Neste trabalho foi desenvolvida uma metodologia para a previsão do equilíbrio de adsorção bem como de difusividades intracrystalinas a taxa de recobrimento zero, para gases permanentes em zeólitos da série A. O equilíbrio de adsorção bem como as funções termodinâmicas podem ser relacionadas com as funções partição molecular e do sistema para o gas e para a fase adsorvida por meio da termodinâmica estatística. O potencial de interacção entre a molécula adsorvida e os átomos da parede da cavidade foi simulado adicionando todos os potenciais de interacção binários. Esta função potencial foi seguidamente substituída na equação de Schrödinger em estado estacionário que descreve os estados de movimento do adsorvato. A resolução numérica deste problema de Sturm-Liouville dá um número infinito de valores próprios e as correspondentes funções próprias. A função partição pode ser calculada a partir dos valores próprios. A difusão de pequenas moléculas gasosas em zeólitos A pode efetuar-se por dois mecanismos. No caso do zeólito SA o adsorvato pode formar um estado intermediário na janela quando difunde de uma cavidade para outra e uma vez neste estado intermediário tem que vencer uma barreira energética para passar para a próxima cavidade ou voltar à anterior. Os vários tempos por passo e probabilidades podem ser calculados usando as funções partição da cavidade e da janela e portanto as difusividades podem ser obtidas usando a fórmula de Einstein. A difusão destes gases no zeólito 4A é um processo tipicamente activado e sômente quando o adsorvato tem energia cinética suficiente, pode atravessar a janela bloqueada. A probabilidade da molécula possuir energia cinética maior do que um dado valor pode ser calculada usando a distribuição de Boltzmann que pode ser obtida resolvendo a equação de Schrödinger em estado estacionário podendo pois a difusividade ser obtida a partir daquela distribuição. O método quasi-clássico para cálculo da distribuição de energia cinética causa grandes erros na zona de elevadas energias. Os resultados previstos para o argon, azoto e oxigénio no 4A e no 5A estão de acordo com dados publicados. Nestes modelos, sômente as propriedades físicas e químicas das moléculas de adsorvato e dos átomos de adsorvente foram usadas e dada a inexistência de parâmetros ajustáveis, os modelos são verdadeiramente predictivos e espera-se que possam vir a ser aplicados a outros sistemas de adsorção.

Os parâmetros de transporte de massa em sólidos porosos mono e bidispersos foram determinados usando a célula de difusão com uma única pelete, a célula de difusão em camada fina e o leito fixo com cordão de peletes. Foram desenvolvidos modelos matemáticos para cada um destes métodos experimentais. As várias resistências à transferência de massa foram examinadas usando modelos e análise de momentos e é dado um conjunto de critérios para comparação da importância relativa das referidas resistências. A análise teórica das várias contribuições para o escoamento convectivo mostrou que a lei de Darcy pode ser usada no nosso sistema experimental. Usando ajuste em tempo real obtiveram-se os vários parâmetros de transporte de massa.

Os resultados simulados explicam bem os obtidos experimentalmente. O comportamento dinâmico simulado e experimental dos três sistemas de medida mostrou que as técnicas experimentais e os modelos são fiáveis.
ABSTRACT

A methodology for predicting the adsorption equilibria and intracrystalline zero coverage diffusivities of permanent gases in zeolite A series was developed. The adsorption equilibria and thermodynamic functions can be related to the molecular and system partition functions of the gas and adsorbed phases by means of statistical thermodynamics. The interaction potential between adsorbate molecule and cavity wall atoms was simulated by adding all pairwise potentials. This potential function was then substituted into the steady state Schrödinger equation that describes the adsorbate molecular motion states. The numerical solution of this Sturm - Liouville problem gives an infinite set of eigenvalues and the corresponding eigenfunctions. The partition function can be calculated from the eigenvalues. The diffusion of small molecular gases in zeolite A series has two mechanisms. For 5A zeolite the adsorbate can form an intermediate state at the window when it diffuses from one cavity to another and once at this intermediate state must overcome an energy barrier so that it goes to next cavity or returns to original one. The various step times and probabilities can be calculated using the cavity and window partition functions and thus the diffusivities can be obtained by Einstein formula. Whereas the diffusion of gases in 4A zeolite is a typical activated process and only when the adsorbate has enough kinetic energy it can cross the blocked window. The probability that a molecule has kinetic energy greater than a given value can be calculated by the Bolizmann distribution that can be obtained by solving the steady state Schrödinger equation so that the diffusivity can be evaluated from this distribution. The quasiclassical way to calculate the kinetic energy distribution for high energy values will cause big errors. The predicted results for argon, nitrogen and oxygen in 4A and 5A agree well with the published data. In these models, only the physical and chemical properties of adsorbate molecules and adsorbent atoms were used and no any adjustable parameter exists, so it is a truly predictive model and it is expected that it can be applied to other adsorption systems.

The mass transport parameters in monodispersed and bidispersed porous solids were determined by single pellet diffusion cell, shallow bed diffusion cell and single string pellet fixed bed. The models corresponding to these experimental processes were developed. The various mass transport resistances were examined using the models and moment analysis and a set of criteria for comparing their relative importance is given. Theoretical analysis for the various convective flow contributions shown that the Darcy law can be used in our experimental system. Using the time domain fitting technique the various mass transport parameters were obtained. The model simulated results explain well the experimental results. Both simulated and experimental dynamic behavior for these three measurement systems shown that the experimental techniques and models are reliable.
RESUMÉ

Ce travail a mis en œuvre une méthodologie pour la prévision soit de l'équilibre d'adsorption, soit des diffusivités intracrystallines à taux de recouvrement zéro, pour des gaz permanents en zéolites de la série A. L'équilibre d'adsorption, ainsi que les fonctions thermodynamiques, peuvent être mises en rapport avec les fonctions de partition moléculaire et du système pour le gaz et pour la phase adsorbée d'après la thermodynamique statistique. Le potentiel d'interaction entre la molécule adsorbée et les atomes de la paroi de la cavité a été simulé en rajoutant tous les potentiels d'interaction binaires. Cette fonction potentielle est introduite dans l'équation de Schrödinger en état stationnaire, qui décrit les états de mouvement des molécules adsorbées. La résolution numérique de ce problème de Sturm - Liouville donne un nombre infini pour les valeurs propres et pour les fonctions propres associées. La fonction de partition peut être calculée à partir de ces valeurs propres. La diffusion des petites molécules gazeuses en zéolites A peut avoir lieu selon deux mécanismes. Dans le cas du zéolite 5A, l'adsorbé peut former un état intermédiaire dans la fenêtre lorsqu'il diffuse d'une cavité à l'autre et, une fois dans cet état intermédiaire, il lui faut vaincre une barrière énergétique pour passer à la prochaine cavité ou retourner à la précédente. Les temps par pas et leurs probabilités peuvent être calculés en partant des fonctions de partition de la cavité et de la fenêtre et ensuite les diffusivités peuvent être obtenues d'après la formule d'Einstein. La diffusion des gaz dans le zéolite 4A est un procédé typiquement activé et seulement lorsqu'une molécule adsorbée a une énergie cinétique suffisante est-elle capable de traverser la fenêtre bloquée. La probabilité de trouver une molécule avec une énergie cinétique plus grande qu'une certaine valeur peut être calculée d'après la distribution de Boltzmann, obtenue par la résolution de l'équation de Schrödinger en état stationnaire, et la diffusivité peut être obtenue à l'aide de cette distribution. La méthode quasi-classique pour le calcul de la distribution de l'énergie cinétique donne des erreurs grossières dans la zone des hautes énergies. Les résultats prévus pour l'argon, l'azote et l'oxygène dans les zéolites 4A et 5A sont en accord avec les données de la littérature. Dans ces modèles, seulement les propriétés physiques et chimiques des molécules de soluté et des atomes de l'adsorbant sont utilisées et comme il n'y a pas de paramètres ajustables, les modèles sont vraiment prédictifs et on espère qu'ils puissent être appliqués à d'autres systèmes d'adsorption.

Les paramètres de transport de matière en solides poreux mono et bidispersés ont été déterminés avec la cellule de diffusion mono - grain, la cellule de diffusion à couche mince et le lit de garnissage. Les résistances au transfert de matière ont été analysées avec les modèles et l'analyse des moments et un ensemble de critères est fourni pour la comparaison de l'importance relative de ces résistances.

L'analyse théorique des plusieurs contributions à l'écoulement convectif a montré que la loi de Darcy peut être utilisée dans notre système expérimental. Les paramètres de transport de matière ont été obtenus d'après un ajustement en temps réel. Les résultats simulés expliquent bien ceux obtenus dans les expériences. Le comportement dynamique simulé et expérimental des trois systèmes de mesures a montré que les techniques expérimentales et les modèles associés sont fiables.
摘要

本文发展了一套预测永久气体在A型分子筛上吸附平衡和晶内扩散系数的理论。统计热力学提供了从吸附相配分函数计算吸附平衡常数和热力学函数的方法。通过迭代计算吸附质分子和所有吸附剂表面原子的相互作用势能，可以计算出吸附质分子在吸附相中任一空间位置的势函数。从薛定谔方程的本征能谱和相应的本征解可计算出吸附质分子在吸附相的平均势能和配分函数。势分布函数和配分函数的计算结果表明永久气体分子在5A分子筛上的扩散由以下三步构成：1. 从笼子到8元环窗口；2. 在窗口上形成一个短暂的中间态；3. 从中间态分子扩散到下一个笼子或回到原笼子。第一步是能量降低过程，而中间态分子扩散到笼子则是活化过程。所有这三步过程的跃迁几率或停留时间可由配分函数求出。而永久气体在4A分子筛上的扩散是一个典型的活化过程，存在于窗口的一个可交换阳离子阻挡了吸附质分子的扩散通道。只有当吸附质分子具有足够的动能撞击窗口使阳离子偏移窗口平衡位置时，吸附质分子才能完成一步扩散。布尔兹曼分布函数揭示了吸附相中吸附质分子的动能分布，由此可计算出一个吸附质分子穿越窗口的机率，扩散系数可由机率求出。计算结果表明用经典力学和量子力学求出的动能分布函数具有数量级的差异，尤其在较高的能量区域，而活化扩散恰恰涵盖这一区域。本文提出的模型可以在无需任何吸附实验数据的前提下计算出吸附平衡常数和热力学函数，且易于推广到其它吸附质和沸石系统。

本文应用了三种实验技术（单颗粒扩散池、浅层床扩散池和单粒串固定床）测定气体在多孔固体内的传质系数。
开发了相应上述实验方法的三套数学模型，它们可用于从实验数据计算传输参数和模拟实验响应。本文还详细地讨论了各项传输阻力在不同实验条件下的相对重要性并提出了一套分析和判断相对重要性的规则。实验和模拟结果同时表明使用的实验技术和模型是可靠的、有效的。
SUMMARY

The theoretical study, process development and design of adsorption separation and gas-solid heterogeneous catalytic reactions fundamentally involve two aspects: one is the adsorption equilibrium of gases on the surface of porous solids and another is the mass transport rate of gases inside the solids. Zeolites are widely used adsorbents and catalyst supports. Due to its regular microscopic crystal structure, it is possible to have shape-selective catalysis and molecular sieve separations. Zeolite A series are the most widely used adsorbents in gas separation and purification. Important applications are the production of pure nitrogen and oxygen from air by pressure swing adsorption. The fundamentals of the separation operation are the differences on adsorption equilibria and mass transport rates of individual components of air in zeolites A. In order to improve the operating efficiency and develop new adsorbents and processes it is indispensable to develop a theoretical methodology for the prediction of adsorption equilibria and intracrystalline diffusivities of gases in zeolites.

The adsorption equilibria and thermodynamic functions can be related to the molecular and system partition functions of the gas and adsorbed phases by means of statistical thermodynamics. At low coverage the interaction potential among adsorbate molecules can be neglected and the potential field between adsorbate molecule and cavity wall atoms was simulated by adding all pairwise potentials. The results for nonpolar adsorbate Ar, weak quadruple adsorbate O₂ and strong quadruple adsorbate N₂ in zeolites A shown that the interaction potential field acting on the adsorbate molecule inside cavity is close to a spherically symmetrical potential field in the interesting spatial region. This potential function was then substituted into the steady state Schrödinger equation that describes the adsorbate molecular motion states that can be reduced to a set of second order ordinary differential equations with Sturm-Liouville form by a variable separation technique. The numerical solution of this Sturm-Liouville problem gives an infinite set of eigenvalues and the corresponding eigenfunctions. The partition function describing the number of microscopic states can be calculated from the eigenvalues. Furthermore, the average total potential and kinetic energies and the average position of an adsorbate molecule inside a cavity can be evaluated at given macroscopic system conditions such as temperature and pressure. In this model, only the physical and chemical properties of adsorbate molecules and adsorbent atoms were used and no any adjustable parameter exists, so it is a truly predictive model and it is expected that it can be applied to other adsorption systems. The principal disadvantage of this methodology is associated with the form of the potential field function that can prevent the solution of the Schrödinger equation. We applied this methodology to the adsorption of Ar, O₂ or N₂ in zeolites A. The potential field was calculated assuming that the nonnegligible interactions were of the repulsion-dispersion, induction and field quadrupole types. It is worthwhile to mention that some of the parameters used in these calculations are affected by uncertainty that reflects on the quality of the potential field prediction. All predicted results of isosteric heats agree well with the experimental ones and the adsorption Henry constants are fairly in agreement with the published experimental results. The comparison of the calculation of the molecular partition functions by the classical and quantum approaches shows that the classical approach is only valid at moderate temperatures and for large cavities.

The diffusion of small molecular gases, such as, Ar, O₂ and N₂ in the crystals of 5A zeolite at low coverage can be considered as the case where a molecule under thermal motion inside a cavity has a few chances to escape and to form a temporary state at the window plane. This adsorbate molecule at the window intermediate state can diffuse into next cavity, or return to the original one. The probability of both possibilities should be
equal at very low occupation. The whole diffusional process of an adsorbate molecule from a cavity to another cavity undergoes three steps: the molecule diffuses to the window, temporary moves at the window plane and then diffuses to the next cavity or returns to the original one. Calculated results shown that the stability of a molecule located at the window plane is lower than inside the cavity. The self diffusivity of the adsorbate molecule from cavity to window can be calculated by considering the probability of an adsorbate molecule striking the window. The self diffusivity of an adsorbate molecule from window to cavity over an energy barrier can be calculated using the molecular kinetic energy distribution considering that only these molecules that have kinetic energy greater than the energy barrier can cross it. The transient state theory is unable to explain such diffusional processes. The gas diffusion process over blocked windows is a strong activated process. The adsorbate molecules will be interacted by a strong repulsion potential. Only when the molecule has enough translational kinetic energy to strike the window it can cross the window otherwise it will be bounded to the original cavity. The translational kinetic energy distribution of an adsorbate molecule inside the cavity of zeolite A can be evaluated by the microscopic state eigenenergies which are obtained by solving the steady state Schrödinger equation. The calculation of the translational kinetic energy distribution by the classical approach can introduce great errors. The error may be more than one order of magnitude in the higher energy area that is interesting since the activated diffusion processes involve this part of the distribution. In this methodology, the calculations of the interaction potential and of the intracrystalline diffusivities are independent of any adsorption kinetic experimental data and thus the models are truly predictive. In these models the zeolite structure and the adsorbate molecular characteristics are included and thus they should be able to translate to other systems in which the zeolites have similar cavity and window structures. The most similar system may be the diffusion of gases in X and Y zeolites. This methodology is also ready to be used in other zeolite systems by adjusting the calculation of the interaction potential. The predicted diffusivities and activation energies for permanent gases in 5A and 4A zeolites are of the same order of magnitude as published experimental results. Due to the quick diffusion of small molecules like helium, argon, oxygen and nitrogen in the relatively large unblocked eight membered ring, the usual macroscopic experimental results suffer the same limits.

The determination of the mass transport rate of gases in porous solids is still heavily dependent on the experimental measurements. Due to the complexity of the pore network including macropores and non-regular micropores and the lack of experimental information, theoretical prediction of such pore structures is very rough. In the analysis and optimization of the operating conditions of processes involving mass transport between gas and porous solids some black box parameters are used to describe the mass transport rate and dynamic characteristics. Diffusion cell and chromatographic methods are widely used techniques to determine the mass transport rate of gases in porous solids. According to the experimental conditions a set of dynamic equations to describe the dynamic behavior can be developed. The solutions of these equations give the theoretical responses. The mass transport parameters existing in these equations can be determined by fitting the theoretical responses to the experimental ones. Traditionally, diffusion cell is used in the determination of the monodisperse or bidisperse mass transport parameters of single pellets. In this work the successful determination of adsorption equilibria and macropore and micropore effective diffusivities of gases in a diffusion cell packed with small particles broadens the application of the diffusion cell in the measurement of mass transport parameter field. The response of the chromatographic column includes the effects of the gas flow patterns in the bulk phase and thus the explanation of the regression results is more complicated. The use of the single pellet string column can reduce the effects of the flow patterns using high velocity. The regression of mass transport rate parameters is dependent on the sensitivity of the responses to the parameters to be regressed. Good precision can be achieved only in systems that have
high sensitivity. The experimental methods used in this work belong to the macroscopic technique that is inapplicable to determine the micropore diffusivities of small molecular gases in relative large micropores due to the small micropore diffusional resistance compared to the macropore diffusional resistance. Both experimental and calculated results that include argon, nitrogen and oxygen in single large alumina pellets, zeolites 4A and 5A and alumina small pellets at different temperatures show that the experimental techniques and the models for these processes are reasonable.
CONTENTS

Chapter I Thermodynamics and Mass Transport in Adsorption

1 Adsorbents and Pores 2
2 Adsorption Equilibrium and Isotherms of Pure Components 5
   2.1 Adsorption Thermodynamics 6
   2.2 Approaches to Isotherm Representations 9
3 Calculation of Partition Functions 20
   3.1 Calculation of Molecular Partition Functions
       by Classical Mechanics 20
   3.2 Calculation of Molecular Partition Functions
       by Quantum Mechanics 24
4 Mass Transfer Processes of Gases in Porous solids 36
   4.1 Molecular Diffusion 40
   4.2 Knudsen Diffusion 41
   4.3 Convection inside the Pores 42
   4.4 Surface Diffusion 43
   4.5 Combination of Various Diffusional and Flow Mechanisms 44
   4.6 The Influence of Pore Geometry 46
   4.7 Macropore Diffusion Theories 47
   4.8 Micropore Diffusion Theories 48
5 Experimental Techniques for Mass Transfer Parameter Determination 50
   5.1 Nuclear Magnetic Resonance Methods (NMR) 52
   5.2 Macroscopic Experimental Techniques 53
   5.3 Comparison among Different Methods 58
6 Mass Transport Model Solutions and Data Fitting 59
   6.1 Fitting in the Laplace Domain 60
   6.2 Moment Fitting 61
   6.3 Laplace Domain Solutions and Time Domain Fitting 62
   6.4 Solving by Orthogonal Collocation 64
   6.5 Relationship between Pulse and Step Inputs 65
References 66

Chapter II Theoretical Prediction of Permanent Gases Adsorption

Equilibria in Zeolite A Series 75

1 Crystal Structure of 4A and 5A Zeolites 78
2 Calculation of the Potential Energy of a Molecule inside a Cavity 80
3 Evaluation of Adsorbed Phase Partition Function by Quantum Mechanics 85
4 Theoretical Prediction of Adsorption Isotherms, Adsorption Heats
   and Adsorption Thermodynamic Functions 88
   4.1 Calculation of the Potential Field 88
   4.2 Molecular Partition Function inside the Cavity 102
   4.3 Energy Terms 104
   4.4 Adsorption Thermodynamic Functions 105
   4.5 Adsorption Isotherms 106
5 Comparison of the Results Calculated by Classical and Quantum Mechanics 108
6 Conclusions 110
   Appendix: Procedure for the Calculation of the Interaction Potential 111
   References 113

Chapter III Intracrystalline Diffusion and Diffusivities 116

1 Theoretical Evaluation of Diffusivities 118
   1.1 Small Molecules Diffusion in Relatively Large Pores 120
   1.2 Activated Diffusion 125
Chapter IV Experimental Determination of Mass Transport Parameters and Models

1 Diffusion Cell Apparatus and Models
   1.1 Apparatus Description
   1.2 Experimental Procedure
   1.3 Mass Transfer Model with Macropore Diffusion and Convection for a Single Pellet Diffusion Cell
   1.4 Convective Flux

2 Shallow Bed Apparatus and Models
   2.1 Evaluation of Linear Adsorption Equilibrium Constants
   2.2 Mass Transport Equations in a Shallow Bed
   2.3 Numerical Solution Techniques

3 Fixed-Bed Apparatus and Models
   3.1 Apparatus Design and Experimental Procedure
   3.2 Mass Transport Model

Chapter V Results and Discussion of Mass Transport Parameters

1 Diffusion Cell Packed with a Single Pellet
   1.1 Pore Structure Properties of Pellets
   1.2 Effective Diffusivities and Simulation of the Response Values
   1.3 Convective Flow Coefficients

2 Shallow Bed Diffusion Cell
   2.1 Effective Diffusivity Determination
   2.2 Optimization of Cell Dimensions and Operating Conditions

3 Single Pellet String Fixed Bed

4 Conclusions

References

Chapter VI Conclusion and Future Ideas

Nomenclature
I. THERMODYNAMICS AND MASS TRANSPORT IN ADSORPTION

Gas adsorption technology is being largely used as a separation and purification unit operation in the chemical and petrochemical industries. The successful development of new adsorbents, such as zeolites and carbon molecular sieves, and of new technologies, such as pressure swing adsorption [Guerin de Montgureuil and Domine, 1957 and Skarstrom, 1960] and simulated moving bed [Broughton et al, 1970], has promoted the growth on the use of the adsorption technologies in large scale plants. A number of research results on adsorption equilibria, adsorption thermodynamic functions and mass transfer theories have been published. New theoretical research achievements supply the tools for developing new adsorption processes and improving operation efficiency.

Due to the discontinuity of the solid structure on the surface, the physical and chemical interaction forces among the atoms of the solid become asymmetric. The atoms on the surface have a tendency to catch the fluid molecules to balance the unbalanced forces acting on the surface when the surface is exposed to the fluid. The term adsorption refers to the physical and chemical phenomena in which the fluid molecules will be attracted and caught by physical and chemical bond forces resulting from such surface unbalanced forces. The adsorption causes an increase of fluid concentration on the surface of the solid. The interaction forces between adsorbing atoms and adsorbate molecules are dependent on the kind of atom and molecule, on the surface and solid structures and on the environmental conditions (for example temperature). Differences on interaction forces between different adsorbate molecules result in an adsorption selective effect. Based on the nature of the forces between the adsorbate molecules and the adsorbent surface, adsorption can be classified as physical or chemical adsorption. When the interaction forces are strong enough to change the structural configuration of adsorbate molecules and form a new chemical bond between adsorbate molecules and surface atoms, the adsorption is chemical adsorption. The chemical adsorption involves electron transfer between adsorbate and surface atoms and has the characteristics of a chemical reaction whereas the interaction forces in physical adsorption are van der Waals and Coulombic (or electrostatic) forces which are much weaker than the chemical bonding forces. A rough qualitative comparison between chemical and physical adsorption can be given based on the following macroscopic and microscopic characteristics: in chemical adsorption a greater heat effect is present (adsorption heat usually is greater than 15 kcal/mol thus at the same level as chemical reaction), adsorption rate is strongly temperature dependent, adsorption has strong selectivity and always exists monolayer adsorption. While physical adsorption heats are about 2 - 3 times the vaporization heats for gas/vapor adsorption [White, 1990]. The approaches to study chemical adsorption are similar to these of chemical reaction. Almost all adsorption separation processes utilize physical adsorption rather than chemical adsorption [Ruthven, 1984] and this work is mainly focused on handling gas adsorption systems, so only the characteristics of physical adsorption will be discussed.

One of the thermodynamic characteristics of gas phase physical adsorption is that exothermicity occurs and it automatically takes place, that is, the enthalpy change ΔH and the Gibbs free energy change ΔG of the adsorption process at constant pressure are always negative. ΔG < 0 because the large amount of adsorbent surface area results in high surface energy and the adsorbent has the potential ability to catch the adsorbate to minimize the system energy and to reach the most stable state. Exothermicity can be explained because the adsorbate molecules have much more restricted motion in the
adsorbed phase under the interaction forces of the adsorbent surface rather than in gas phase. The molecule in adsorbed phase usually undergoes a two-dimensional or localized three-dimensional motion and the degrees of freedom or spaces for translational motion are reduced. Even the rotation motion of an adsorbate molecule in some adsorbed states will be restricted. Such changes result in the decrease of the degree of disorder and so the entropy decreases ($\Delta S < 0$). The adsorption heat, $\Delta H$, can be expressed as $\Delta H = \Delta G + T\Delta S$ that requires a negative $\Delta H$ value, that is, adsorption is exothermic.

Adsorbents which are used as adsorption and diffusion media must have a great amount of specific surface area to provide large adsorption capacity. For most of the industrial adsorbents, it is usually greater than 100 m$^2$/g. The creation of abundant specific surface area in a limited volume inevitably gives rise to a large number of pores. On the basis of their size, pores can be divided into micropores ($\text{pore diameter} \leq 20$ Angstrom), mesopores or transient pores ($\text{pore diameter from 20 to 500}$ Angstrom) and macropores ($\text{pore diameter} > 500$ Angstrom) [Suzuki, 1990]. The effective pores on separation and purification are only the micropores. The other two merely play the role of a network of mass transfer paths. Adsorbents are characterized by the surface properties such as specific area, polarity and pore size distribution.

1 ADSORBENTS AND PORES

An eligible industrial adsorbent requires adequate adsorptive capacity or specific surface area that restricts the choice of adsorbents. The important physical and chemical characteristics of an adsorbent include pore volume, pore size distribution and polarizability of the adsorption surface. The pore volume can be characterized by the helium filling volume. Helium is usually considered as a non-adsorbable gas and can penetrate into all adsorption pores due to its small molecular dimension. The pore size distribution can be estimated by the mercury porosimetry technique for pore dimensions greater than 100 Å and from the desorption (or adsorption) curves of nitrogen for the pore dimensions in the range of 10 - 250 Å [Yang, 1987]. For still smaller pores the pore dimension can be calculated by adsorption of trial molecules with different dimensions. The pore volume can be calculated by using the Gurvitsch rule which assumes the pores are filled with liquid [Yang, 1987]. For zeolitic adsorbents the intracrystalline volumes can be theoretically evaluated from the structure properties. The surface of an adsorbent can be estimated by correlating nitrogen adsorption isotherms at liquid nitrogen temperature to BET adsorption isotherm equation [Ruthven, 1984]. The surface interaction properties of an adsorbent can be examined by analyzing the adsorption heats. polar surfaces will prefer to adsorb polar adsorbates and the corresponding adsorption heats are ordinarily greater than those of nonpolar adsorbates.

The possibility and efficiency of separations and purifications by adsorption are principally related to the steric, equilibrium and kinetic properties of the system adsorbent/ components to be separated. The steric selectivity results from the molecular sieving effect of adsorbate in some zeolites and molecular sieve carbons. Depending on the dimension and shape of individual components in a mixture, only small and properly shaped molecules can diffuse into the micropores of the adsorbent and be adsorbed, whereas other molecules are virtually excluded. Based on the adsorption equilibrium differences of individual components in a mixture to be separated, the concentration inside the adsorbent of the more favorably adsorbable component increases and the bulk phase concentration of the less favorably adsorbable component increases. As long as there are enough equilibrium stages between adsorbent and bulk phase, the complete
separation of various components is theoretically possible. The kinetic separation is achieved by the differences in diffusion rates of different adsorbate molecules in an adsorbent. In the case of kinetic selectivity, the choice of operating conditions becomes very critical. Specially, when the influences of kinetic and equilibrium selectivities are in opposite directions, the separation efficiency is very sensitive to the operating conditions.

The adsorbents ordinarily used in industry for gas separation and purification include silica gel, activated alumina, activated carbon and zeolites. According to the pore structure and pore size distribution, there is a fundamental difference between zeolitic adsorbents and others. The micropore size of a zeolitic adsorbent is controlled by the crystal structure and there is substantially no distribution of pore sizes. This property leads to a real molecular sieve effect. By contrast, there are pore size distributions about the mean pore size for other adsorbents and the width of pore size distributions and the mean pore size can be adjusted by the manufacturing process. Some adsorbents have larger pores, macropores, in addition to micropores in which the adsorption occurs, which result from the agglomeration of fine powders into pellets or originate from the texture of the raw materials. The size of macropores can be several micrometers. The macropores work as diffusional paths for adsorbate molecules when traveling from outside the granule to the micropores in fine powders and crystals. Adsorbents containing macropores and micropores are often said to have bidisperse pore structures.

Silica gel is one of the synthetic amorphous silicas. It is a rigid, continuous network of spherical particles of colloidal silica. The reaction of a sodium silicate solution with sulfuric or hydrochloric acid produces a concentrated dispersion of finely divided particles of SiO₂ (silica hydrosol). Silica gel is prepared by the silica hydrosol polymerization. After washed, dried and activated, the commercial silica gel particles are obtained. Silica gel adsorptive pores are formed by partial dehydration of polymeric colloidal silicic acid. The silicic acid liberated polymerizes and condenses in the aqueous solution to form chains and nets of linked SiO₄ tetrahedra which aggregate to form approximately spherical particles of 20 - 200 Å diameter. When dried the particle agglomeration to form a microporous structure, the pore size is determined largely by the size of the original microparticle. The adsorptive surface of silica gel is polar and so it prefers to adsorb polar adsorbates. The primary use of silica gel is as a desiccant due to its great adsorptive capacity at low temperature and moderate water vapor pressure [Ruthven, 1984]. The relatively small adsorption heat and weak surface adsorption forces for water compared to zeolites result in an easy regeneration and low regeneration temperatures. The low regeneration temperature means that a cheap heat source like saturated water vapor can be utilized and thus the regeneration operation is economic.

Aluminum oxides have several crystal forms. The activated alumina commercially used as adsorbent and catalyst support is γ alumina. Activated alumina is directly obtained from bauxite (Al₂O₃·3H₂O) or from the monohydrate by dehydration and recrystallization at high temperature. It has strong selectivity for polar adsorbates. The typical specific surface area is around 150 - 500 m²/g and the pore radius is in the range of 15 - 60 Å depending on the preparation process [Yang, 1987]. Owing to its high stability to temperature and easy regeneration by burning, it is used as a desiccant for drying organic streams containing toxic components and as a catalyst support. As adsorbent it has been widely replaced by zeolites. Both acidic and basic characteristics of the activated alumina surface and its good temperature stability make it to become one of the most widely used support for catalysts.

Activated carbon is obtained from carbonaceous materials that have some initial pores such as wood, peat, coals, petroleum coke, coconut shell and fruit nuts. The raw materials are carbonized at temperature around 400 - 500 °C to eliminate the volatile materials existing in the initial pores, and then partial gasified at 800 - 1000 °C to develop
the porosity and surface by the presence of some mild oxidizing gases. Activated carbon micropores where adsorption occurs are usually considered as in the form of two-dimensional spaces between two graphite-like walls. The adsorption surface is the surface of these two-dimensional walls and the spaces between them are the micropores. The surface properties of activated carbon are important in determining its capacity and activity for adsorption of specific organic substances and depend on the raw material used and on the activation process. Originally, activated carbon adsorbents were nonpolar and prefer to adsorb nonpolar adsorbates, but the oxide groups on the surface which arise from either the raw materials or chemical action during the activation and storage cause the surface to have small polarity. The size of micropores is determined during pyrolyzation and activation steps. By using proper source materials and special control of conditions such as temperature and time, a variety of activated carbons, called molecular sieve carbons, which have very narrow pore size distribution in the region of molecular dimensions can be produced. The mean pore size can be adjusted according to the requirement of the molecules to be sieved. There are two forms of activated carbon in commercial use, powder and granular. The granular activated carbon can be prepared either in the form of crushed granular raw materials or in the pelletized form obtained by agglomeration of pulverized powders using binders such as coal or petroleum pitch [Suzuki, 1990]. The applications of ordinary activated carbon include recovery and removal of organic components from water streams and color removal [Smisek and Cerny, 1970]. The molecular sieve carbon is used in the separation of air by PSA [Ruthven et al, 1986] and in the purification of dyes [Kasaoka et al, 1989].

Since the report of the first successful synthesis of zeolite A in 1956 appeared [Broussard and Shoemaker, 1960], zeolite adsorbents and catalysts have been widely used in separation, purification and catalysis. Zeolithic adsorbents are aluminosilicate crystals. The different arrangements of the most basic element, AlO$_2$ or SiO$_2$ form different crystal units, cells and channel structures through which the adsorbate molecule diffuses and is adsorbed. The different arrangements of the different fundamental units or cells in space and different ratios of Si/Al result in different types of zeolites. Because of the negative electrostatic charges coming from AlO$_2$ on crystal framework and the cations which balance these negative charges, there are strong local electrostatic fields and electrostatic field gradients which interact with the adsorbate molecular dipoles and higher electrostatic moments and result in good selectivity for polar molecules.

The diffusional channels in zeolites are composed of framework oxygen atoms in the form of AlO$_2$ or SiO$_2$. Their dimension is determined by the positions and size of the framework oxygen atoms and is uniform over all crystals. None of the amorphous micropore carbons, alumina oxides and silica gels has such regular micropore characteristics. The channel dimensions of non-blocked crystals are solely determined by the crystal lattice and therefore qualitatively molecular sieving properties on zeolites are possible. The channel free dimensions can be profoundly modified by ion exchange. The charge of exchangeable cations will change the number of cations to balance the framework negative charges. The cation properties will affect the local electrostatic field and electrostatic field gradient distribution which will change the adsorption characteristics of zeolites. Specially, when the positions of the exchangeable ions are located at the diffusion channels, the existence of exchangeable ions will dramatically change the free dimensions of the diffusional path. The larger the exchangeable ions are, more obvious such blocking effect is. Therefore the zeolite adsorption and diffusional characteristics can be improved by selecting suitable exchangeable ions. A more detailed discussion of crystal structure of zeolites A and the effect of ion exchange on the diffusional path dimension will be held in Chapter II.
In practice, zeolite crystals are synthesized in the typical size of 1 - 10 μm and then pellets into suitable dimensions, porosity and strength. During the pelletization the free spaces between the crystals form the macropores with size of the same order of magnitude as crystal size [Draj et al., 1985]. Due to the clear distinction between macropores and micropores in the pellet, such pore structure offers two distinct diffusional resistances to mass transfer. The micropore diffusion existing inside the crystal depends on the adsorbate and crystal structure as well as crystal size. Due to the necessity of a small resistance to mass transfer, the crystal size should be also small. But a small crystal size will cause the reduction of the diameter of the intercrystalline macropores and so increase the macro pore diffusional resistance. The difference in macropore diffusional rates between different adsorbates is essentially determined by the molecular mass of the adsorbates and thus the resistance is normally hopeless to the separation of adsorbate mixtures. The macropore resistance may be reduced by reducing the pellet size, but this reduction is limited by pressure drop. On the other hand, the differences in micropore diffusion between adsorbates can improve the separation of mixtures. In the condition of keeping the difference, the absolute resistance is also desirable to be minimum. The optimal choice of crystal size should consider the balance of intercrystalline and intracrystalline diffusional resistances.

The adsorption ability of a gas molecule on a given adsorbent depends on the size of the interaction forces between the gas molecule and the surface of solid which are affected by temperature and adsorbate concentration. A suitable choice of adsorbent enables the separation and purification of gas mixtures.

2 ADSORPTION EQUILIBRIA AND ISOTHERMS OF PURE COMPONENTS

A great amount of insight on adsorption equilibrium has been achieved through long term systematic studies. The nature of adsorption was gradually revealed by researchers. The approach to study adsorption equilibrium is in general the same as the one used for other phase equilibria. Both classical and statistical thermodynamics are the methodologies. Taking into account the speciality of the adsorbent surface as an inert medium to support the adsorbed phase, there are two different views to understand and express the adsorption equilibrium. Naturally the two methods are entirely consistent from the standpoint of thermodynamic principles. In the view of adsorption solution theory, the adsorbed phase (including the adsorbent surface and adsorbate) is considered as a virtual solution, and thus all thermodynamic laws and inductive relationships between state functions can be directly borrowed. Alternatively, the Gibbs two dimensional theory deals with the adsorbed phase as a two-dimensional system. The adsorbed molecules are recognized as a distinct phase, while the thermodynamic and geometric properties of adsorbents are independent of environmental conditions and the function of adsorbent is only to create an adsorptive interaction force field. Compared to the fluid three-dimensional system, a series of corresponding thermodynamic relationships in adsorptive system are discussed. The various methods of approach differ in their choice of the characteristic thermodynamic functions.

Considerable attention has been paid to correlate the adsorption behavior with the adsorbate molecular properties and adsorbent structural information. For the special case of gases and zeolites whose crystalline structure and cation distribution are almost regular and well known, a priori calculation of equilibrium constants and thermodynamic functions is potentially possible. A large number of published papers have successfully predicted the adsorption characteristics by calculating adsorbate physical and chemical
properties, such as electric moments, dipole, quadruple and polarizability and adsorbent surface electrostatic field [ Kingston and Madeed, 1959, Barrer and Cram, 1971, Sargent and Whitford, 1971, Ruthven, 1984, Nowak et al, 1987, Razmous and Hall, 1991, Karavias and Myers, 1991 and Baksh and Yang, 1991]. No matter what means are used to study adsorption equilibrium, the results must satisfy the thermodynamic laws.

Another objective to study adsorption thermodynamics is to reveal the relation between various adsorption heats. The heat effect of adsorption is an essential parameter for the design of industrial processes. Because the adsorption heat is not a thermodynamic state function, only at some special conditions it can be linked to some state function changes. In the following part, the fundamental adsorption thermodynamic relationships will be discussed.

2.1 Adsorption Thermodynamics

In the classical thermodynamic description of the adsorption state functions, the microscopic properties of the system are ignored and only the macroscopic relationships are invoked. The purpose of classical thermodynamic studies is to express some useful state functions, which are usually not measurable, as a function of other measurable state functions. By combination of the first and second thermodynamic laws, the following discussion is focused on the topic of the relationships among state variables or functions, temperature T, volume V, pressure P (or concentration C), molar internal energy U, molar enthalpy H, molar entropy S, molar Helmholtz free energy F, molar Gibbs free energy G and chemical potential \( \mu \). This systematic discussion of the adsorption thermodynamics was first finished by Everett [Everett, 1950 I, II and III and Everett and Stone, 1958].

For a pure component adsorption system with state variables, volume \( V_a \), chemical potential \( \mu_a \) and number of moles \( n_a \) for the adsorbate and \( V_a, \mu_a \) and \( n_a \) for the adsorbent, the basic differential equation combining the first and second laws of thermodynamics is

\[
dU = TdS - PdV + \mu_a dn_a + \mu_s dn_s \quad (1.1)
\]

The corresponding integrated form is

\[
U = TS - PV + \mu_a n_a + \mu_s n_s \quad (1.2)
\]

If we look at the adsorbent without adsorbate, there is a similar differential equation:

\[
dU_{os} = TdS_{os} - PdV_{os} + \mu_{os} dn_s \quad (1.3)
\]

where subscript \( os \) represents the properties of the adsorbent without adsorbate. By subtracting (1.3) from (1.1), we have:
\[ dU_a = TdS_a - PdV_a - \zeta dn_a + \mu d\mu_a \quad (1.4) \]

where \( U_a = U - U_{os} \), \( V_a = V - V_{os} \), \( S_a = S - S_{os} \) and \( \zeta = (\mu_a - \mu_{os}) \). As for the relationships in the gas phase, the fundamental thermodynamic equations representing the combined first and second laws can be written in four equivalent ways in terms \( U, H, F \) and \( G \). For the adsorbed phase, we have:

\[ dH_a = TdS_a + V_adP - \zeta dn_a + \mu d\mu_a \quad (1.5) \]
\[ dF_a = -S_adT - PdV_a - \zeta dn_a + \mu d\mu_a \quad (1.6) \]
\[ dG_a = -S_adT + V_adP - \zeta dn_a + \mu d\mu_a \quad (1.7) \]

where \( H_a = H - H_{os}, F_a = F - F_{os} \) and \( G_a = G - G_{os} \). The meaning of the variable \( \zeta \) can be showed by further considering:

\[ \zeta = (\mu_a - \mu_{os}) = \left( \frac{\partial U_a}{\partial n_a} \right)_{S_a,V_a} - \left( \frac{\partial U}{\partial n} \right)_{S,V} = \left( \frac{\partial U_a}{\partial n} \right)_{S_a,V_a} \quad (1.8) \]

\( \zeta \) represents the change of internal energy per unit of adsorbent owing to the spreading of adsorbate over the surface or through the pore. For the two dimensional surface, the surface area \( A \) is directly proportional to \( n_a \) and the proportionality coefficient is \( \pi \) while for the three dimensional pore, the pore volume \( V \) is proportional to \( n_a \) and the proportional coefficient is \( \Pi \). That is:

\[ \zeta d n_a = \pi dA = \Pi dV \quad (1.9) \]

It is obvious that the proportionality coefficients, \( \pi \) and \( \Pi \), can be written as:

\[ \pi = -\left( \frac{\partial U_a}{\partial A} \right)_{S_a,V_a,n_a} \]
\[ \Pi = -\left( \frac{\partial U_a}{\partial V} \right)_{S_a,V_a,n_a} \quad (1.10) \]

There is a special name for the proportionality coefficients \( \pi \) or \( \Pi \), that are called spreading pressure and represent the difference in surface tension between a clear surface and a surface covered with adsorbate. The term \( \zeta d n_a \) in equations (1.4) to (1.7) can be replaced by either \( \pi dA \) or \( \Pi dV \) depending on the understanding of the adsorbed phase. From equations (1.4) to (1.7), the variable \( \zeta \) can be further defined similarly to the chemical potential in three thermodynamic systems.
\[
\begin{align*}
\zeta &= -\left(\frac{\partial U_a}{\partial n_a}\right)_{S_a, V_s, n_s} = -\left(\frac{\partial H_a}{\partial n_a}\right)_{S_a, P, n_s} = -\left(\frac{\partial F_a}{\partial n_a}\right)_{T, V_s, n_s} = -\left(\frac{\partial G_a}{\partial n_a}\right)_{T, P, n_s} \quad (1.11) \\
\mu_a &= \left(\frac{\partial U_a}{\partial n_a}\right)_{S_a, V_s, n_s} = \left(\frac{\partial H_a}{\partial n_a}\right)_{S_a, P, n_s} = \left(\frac{\partial F_a}{\partial n_a}\right)_{T, V_s, n_s} = \left(\frac{\partial G_a}{\partial n_a}\right)_{T, P, n_s} \quad (1.12)
\end{align*}
\]

In the above equations, there are three subscripts to show the conditions, which means that to define an extensive thermodynamic property in a pure component system it is required one more variable than in normal three dimensional thermodynamic systems. The additional variable is the total surface area or quantity of adsorbent over which the \( n_a \) moles of adsorbate are distributed.

The adsorption heat \( q_a \) has no exact meaning unless the conditions under which adsorption takes place are very carefully specified. In some special processes it can be linked to different state function changes. If the heat evolved (at constant temperature) during the adsorption of \( n \) moles on a surface initially clean, under certain specified conditions is \( Q \), then the corresponding differential heat \( q \) is defined by \( \partial Q/\partial n \).

The heat liberated at constant volume has been called the differential heat \( q_{\text{diff}} \) which is usually measured in a calorimeter with the conditions of constant gas volume \( V_a \), adsorbed phase volume \( V_s \) and adsorbent surface area \( A \) and is equal to \( \text{[White, 1990]} \):

\[ q_{\text{diff}} = U_a - U_a' = \Delta U \quad (1.13) \]

The isosteric heat of adsorption is defined at constant gas pressure \( P \), adsorbed phase volume \( V_s \) and adsorbent surface area \( A \) and is given by:

\[ q_{\text{st}} = H_a - H_a' = \Delta H \quad (1.14) \]

where \( U_a' \) and \( H_a' \) are partial molar quantities defined by:

\[ U_a' = \left(\frac{\partial U_a}{\partial n_a}\right)_{T, V_s, A} \quad H_a' = \left(\frac{\partial H_a}{\partial n_a}\right)_{T, P, A} \quad (1.15) \]

The adsorption heats can be related to the variation of equilibrium gas pressure \( P \) of adsorbed phase with temperature \( T \) by a set of equations of the Clausius - Clapeyron Type \( \text{[Ruthven, 1984]} \):

\[ \left(\frac{\partial \ln(n_a)}{\partial T}\right)_{V_s, A} = -\frac{\Delta U}{RT^2} \quad (1.16) \]

\[ \left(\frac{\partial \ln(P)}{\partial T}\right)_{P, A} = -\frac{\Delta H}{RT^2} \quad (1.17) \]
where \( n_a \) is the number of moles in a constant volume \( V_a \) of gas phase and \( R \) is the ideal gas constant. So \( q_{at} \) can be calculated from the adsorption equilibrium data by equation (1.17). There is a relationship to link \( q_{diff} \) and \( q_{at} \) [Everett, 1950 I]:

\[
q_{diff} - q_{at} = PV_a - PV_s + T \Gamma \left( \frac{\partial V_s}{\partial T} \right)_{T,P} \left( \frac{\partial P}{\partial T} \right)_{V_s,T} = RT
\]

where \( \Gamma \) is the adsorbed amount per unit surface area defined as \( \Gamma = n_a / A \). The volume of adsorbed phase is normally negligible compared to the volume of gas and so the first two terms are equal to RT. The value of the derivative of adsorbed phase volume relative \( T \) is usually negligible [Everett, 1950 I]. When the adsorption sites are energetically homogeneous and there is no interaction between adsorbed molecules, the adsorption heat should be independent of the amount adsorbed.

The objective of the discussion of thermodynamic functions in adsorption was to stress that the mathematical forms of various adsorption isotherm equations can be derived on the basis of different tools and to relate the adsorptive heats each other. In the following section, some simple adsorption isotherms of pure components are derived using three tools: classical thermodynamics, kinetic theory and statistical mechanics.

\[2.2 \text{ Approaches to Isotherm Representations}\]

When an adsorbent is exposed to the adsorbate, adsorption occurs and after a sufficiently long time, the adsorbent and surrounding adsorbate reach equilibrium. At the equilibrium state, the adsorbed amount and composition are determined by the properties of the adsorbate and adsorbent and by the environmental conditions. The results of studies on adsorption equilibrium for single components have been reviewed by a lot of researchers [Ross and Olivier, 1964, Barrer, 1978 and Ruthven, 1984]. The term "isotherm" means the equation which relates the adsorbed amount to the bulk phase concentration at a given temperature. From the previous discussion, we know that it is required three independent state variables to identify the state of a pure component adsorption system. In the following discussion, the condition of constant surface of adsorbent is implicit. Langmuir, BET and Freundlish equations are most widely used for single component adsorption systems of gases at moderate pressure. Originally, the parameters in Langmuir and BET equations have identical physical meanings. The adsorption layer concept is not accepted for zeolite adsorbents. The equation parameters can be obtained by fitting the experimental isotherms. Although statistical thermodynamics gave new physical explanations for these equation parameters, the their values are still obtained from experimental data. Dubinin proposed an adsorption mechanism which can predict adsorption equilibria over a sufficiently wide range of temperatures for a gas / adsorbent system by using one or two experimental isotherms at different temperatures [Dubinin and Astakhov, 1971]. But this model violates the physical requirement that the adsorption equation reduces to Henry law when concentration tends to zero [Ruthven, 1984]. The adsorption isotherm equations usually contain two or three parameters. The use of more empirical parameters usually enables a better equation fit to the experimental data. The parameters of empirical equations have no physical meaning, so the extrapolation of calculated values beyond the range of experimental data in which the parameters were determined is unreliable.
A. Classical Thermodynamic Approaches

Although the previous thermodynamic functions provide the fundamental relation between spreading pressure in two or three dimension systems and adsorbed amount, neither spreading $\pi$ (I) nor the $\zeta$ can be experimentally determined directly. In practice we try to convert these relationships to some quantities whose values can be experimentally accessed. The most convenient variable for experimental determination is the gas pressure at the equilibrium state. In a pure component gas phase the concentration is determined by temperature and pressure. Similarly, in a pure component adsorbed phase system the concentration is determined by temperature and spreading pressure because the condition of constant surface area of adsorbent is implicit. For the gas system a state equation relates pressure, temperature and concentration. For adsorbed phase, there is also a state equation to characterize the spreading pressure, temperature and adsorbed phase surface area or volume. Using the state equation, some simple and classical isotherm equations can be derived. Table 1.1 presents part of the results published by Everett [Everett, 1950 II].

B. Kinetic approach

The process of adsorption of a molecule on the surface of an adsorbent is considered as a reaction mechanism. The adsorption equilibrium is regarded as similar to equilibrium between reactants and products in a reversible chemical reaction. From the molecular kinetic point of view the adsorbate molecules in gas phase randomly strike the surface of the adsorbent. Because there is an energy barrier between the free molecules in gas phase and adsorbed molecules, only these molecules which have kinetic energy greater than the barrier can overcome that energy barrier and be adsorbed by the surface. Other molecules whose kinetic energy is less than the barrier fail to go through and rebound to the gas phase. After adsorbed the molecules have potential ability to escape the action of the interaction forces of the adsorbent surface and return to gas phase as long as their kinetic energy is greater than the adsorptive energy barrier plus the released adsorption heat. These energies are schematically showed in Figure 1.1. At the equilibrium state, the number of adsorbing and desorbing molecules is equal. According to the principles of molecular kinetics [Hirschfelder et al, 1954], the number of molecules that strike a surface per unit area during a unit time can be expressed by:

$$\zeta^* = \frac{1}{4} \nu (8kT/\pi M)^{1/2}$$  \hspace{1cm} (1.19)

where $\nu$ is the gas number density (molecules/cm$^3$), $k$ is the Boltzmann constant and $M$ is the molecular mass (g). This equation represents the maximum rate of adsorption if every encounter with the surface leads to the adsorbed state. The energy required for adsorption is just the activation energy, $E_{ad}$, and molecules having kinetic energy less than $E$ will not be adsorbed. The fraction $P(T,E_{ad})$ of molecules showing kinetic energy greater than or equal to energy, $E_{ad}$, is given by the Boltzmann energy distribution equation [Hirschfelder et al, 1954].
Table 1.1 Adsorption isotherms from classical thermodynamics [Everett, 1950 II]

<table>
<thead>
<tr>
<th></th>
<th>Equations of State</th>
<th>Adsorptive Isotherms</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \pi = RT \Gamma )</td>
<td>( p = K \Gamma )</td>
</tr>
<tr>
<td>2</td>
<td>( \pi = mRT \Gamma )</td>
<td>( p = K \Gamma ^n )</td>
</tr>
<tr>
<td>3</td>
<td>( \pi = \frac{RT \Gamma}{1 - b \Gamma} )</td>
<td>( p = \frac{K \Gamma}{1 - b \Gamma} \exp \left( \frac{b \Gamma}{1 - b \Gamma} \right) )</td>
</tr>
<tr>
<td>4</td>
<td>( \pi = \frac{RT \Gamma}{1 - b \Gamma} + a \Gamma^2 )</td>
<td>( p = \frac{K \Gamma}{1 - b \Gamma} \exp \left( \frac{b \Gamma}{1 - b \Gamma} \right) + \frac{2a\Gamma}{RT} )</td>
</tr>
<tr>
<td>5</td>
<td>( \pi = RT \Gamma (1 + \alpha \Gamma + \beta \Gamma^2 + \gamma \Gamma^3 + ...) )</td>
<td>( \ln \frac{p}{\Gamma} = K + 2\alpha \Gamma + \frac{3}{2} \beta \Gamma^2 - \frac{4}{3} \gamma \Gamma^3 + \ldots )</td>
</tr>
<tr>
<td>6</td>
<td>( \pi = RT \Gamma_0 \ln \left( \frac{1 - \Gamma}{\Gamma_0} \right) )</td>
<td>( p = \frac{K \Gamma_0 / \Gamma}{1 - \Gamma / \Gamma_0} = \frac{K \theta}{1 - \theta} )</td>
</tr>
</tbody>
</table>

1. Henry's law, \( K \) is a constant
2. Freundlich isotherm, \( m \) and \( K \) are constants
3. Volmer's isotherm, \( b \) and \( K \) are constants
4. Magnus' isotherm, \( a, b \) and \( K \) are constants
5. Virial isotherm, \( K, \alpha, \beta \) and \( \gamma \) are constants
6. Langmuir isotherm, \( K \) is a constant

\( p \) is the partial pressure of adsorbate in gas phase and \( \Gamma_0 \) is the adsorbed amount at monolayer coverage.

\[
\mathcal{P}(T,E) = \exp\left( -E_{ad}/kT \right) \tag{1.20}
\]

Only those sites which are unoccupied will accept an incoming species, the fraction of sites uncovered will be denoted by \( f(\theta) \), while the fraction of sites which are covered is \( g(\theta) \). The rate, \( \mathcal{z} \) of collisions with the surface resulting in adsorption is then given by:

\[
\mathcal{z} = \mathcal{z}' f(\theta) \exp\left( -E_{ad}/kT \right) = \frac{1}{4} \nu (8kT/\pi M)^{1/2} f(\theta) \exp\left( -E_{ad}/kT \right) \tag{1.21}
\]
Equation (1.21) gives the absolute rate of adsorption, molecules/time per unit surface area based on the collision theory of gases with a plane interface. The rate is linear in the adsorbate partial pressure and it shows an exponential temperature dependence multiplied by $T^{1/2}$. The desorption rates are assumed to have the same form by the law of microreversibility [White, 1990]:

$$ q'' = k_{des} g(\theta) \exp\left(-\frac{E_{des}}{RT}\right) $$  \hspace{1cm} (1.22) $$

where $k_{des}$ is the desorption constant and $E_{des}$ is the energy difference of adsorbate between adsorbed and bulk phases. At equilibrium, the rates of adsorption and desorption must be equal, which results in

$$ \frac{g(\theta)}{f(\theta)} = \frac{p}{k (2\pi M kT)^{1/2}} \exp\left(\frac{E_{ads} - E_{ad}/kT}{kT}\right) $$  \hspace{1cm} (1.23) $\frac{g(\theta)}{f(\theta)} = \frac{p}{k (2\pi M kT)^{1/2}} \exp\left(\frac{E_{ads} - E_{ad}/kT}{kT}\right)$

In equation (1.23) $E_{ads} - E_{ad}$ is the differential adsorption heat. The functions, $f(\theta)$ and $g(\theta)$ describe the stoichiometry of the adsorptive event. If one adsorptive site can be occupied only by one adsorbate molecule, $f(\theta) = 1 - \theta$ and $g(\theta) = \theta$ and if we let $K = \frac{\exp\left(\frac{E_{ads} - E_{ad}}{kT}\right)}{k (2\pi M kT)^{1/2}}$, the equation (1.23) becomes of the same form as Langmuir isotherm in Table 1.1. Situations for other stoichiometries are showed in Table 1.2 [White, 1990].
Table 1.2 Adsorption stoichiometries [White, 1990]

<table>
<thead>
<tr>
<th>adsorption type</th>
<th>f(θ)</th>
<th>g(θ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>one adsorbate (associative)</td>
<td>(1 - θ)</td>
<td>θ</td>
</tr>
<tr>
<td>one adsorbate (dissociative)</td>
<td>(1 - θ)^2</td>
<td>θ^2</td>
</tr>
<tr>
<td>two adsorbates (competitive adsorption)</td>
<td>(1 - θ_i - θ_j)</td>
<td>θ_i or θ_j</td>
</tr>
<tr>
<td>two adsorbates (non-competitive)</td>
<td>(1 - θ_i) and (1 - θ_j)</td>
<td>θ_i or θ_j</td>
</tr>
</tbody>
</table>

C. Statistical Mechanics

The above discussion on the expressions for adsorption isotherms is based on the classical macroscopic thermodynamic and kinetic theories. The classical macroscopic adsorption thermodynamics deals with macroscopic systems only. From the basic thermodynamic laws, it establishes the relationships among the observed macroscopic properties of a system. Because only macroscopic properties are involved in derivations, it is recognized that it can not explain why an adsorption system has the properties it does. The explanation of the microscopic nature of adsorption phenomena can be derived via statistical mechanics which applies the results of quantum and classical mechanics to the evaluation of the properties of a macroscopic system from the properties of its constituent particles. Statistical thermodynamics provides the bridge between the microscopic and macroscopic systems. The adsorptive phenomena happen at the molecular level and the statistical thermodynamics can deal with the microscopic systems at that. So it is expected that statistical thermodynamics can be used as a tool to link the microscopic molecular motion states to the observable macroscopic properties.

Statistical thermodynamics provides a useful alternative to the correlation and prediction of adsorption equilibria. In statistical thermodynamics, the equilibrium properties of a system are deduced by considering the statistical behavior of a large number of loosely coupled identical subsystems (ensemble). This approach has been successfully applied to the correlation of single-component isotherms and to the prediction of multicomponent equilibrium data from pure component isotherms [Brüuer et al, 1971 and Ruthven, 1984]. In statistical models, the parameters have generally defined physical significance and so this approach provides a reliable basis for interpolation and extrapolation from limited experimental data.
Basically, there are two approaches of statistical thermodynamics to link the characteristics of microscopic states and macroscopic properties. One is to find out the most probable microscopic, detailed state of a system, then calculate the gross, macroscopic properties of interest for this state and finally identify the experimentally observable properties with these most probable values. Another is to find out the probability of each microscopic state, construct a weighted average with these probabilities and then identify the experimental observable properties with the averages. For many real systems, the probability distribution functions are almost always sharply peaked in one region, so the most probable values are close to the average values [Kilpatrick, 1967].

For a closed system with total number of particles $N$ and total energy $U$ composed of $\nu_i$ particles associated with energy level $\varepsilon_i$, the following equations can be written:

\[ N = \sum_i \nu_i \quad (1.24) \]

\[ U = \sum_i \varepsilon_i \nu_i \quad (1.25) \]

The number of ways $\omega$, of distributing $N$ particles among the different energy levels with degeneracy $g_i$, which means that there are $g_i$ possible different arrangements at a given energy level and satisfying the above equations can be expressed as [Fried et al, 1977]

\[ \omega = N! \prod_i \left( \frac{g_i^{\nu_i}}{\nu_i!} \right) \quad (1.26) \]

The number of ways, $\omega_i$, of differently distributing $N$ particles among all possible quantum states and keeping the same total energy is not equally probable. The Maxwell-Boltzmann distribution $\Phi$ of finding a certain number of particles at the energy level $i$ can be derived from the above equations. The final form is [Atkins, 1986]:

\[ \Phi = \frac{\nu_i}{N} = \frac{g_i \exp(-\varepsilon_i/kT)}{\sum_i g_i \exp(-\varepsilon_i/kT)} \quad (1.27) \]

Equation (1.27) shows the basic relation between the number of particles $\nu_i$, associated with energy level $i$ and energy $\varepsilon_i$. The summation over all possible microscopic states in the above equation appears so frequently in statistical thermodynamics that it has been given a special name, the molecular partition function, $\phi$. 

14
\[ \varphi = \sum_i g_i \exp( -\varepsilon_i / kT ) \]  \hspace{1cm} (1.28)

Although in the derivation of \( \varphi \) we used \( N \) particles, equation (1.28) is independent of the number of particles \( N \) and \( \nu_\gamma \). When \( N \) tends to infinity equation (1.27) becomes the density function of the energy distribution. The energy distributions for each molecule and system should be the same and thus the quantity \( \varphi \), is also related to the total number of possible states for one molecule.

A moving molecule has different energy distributions. At the same energy level there are different arrangements \( g_i \). The energy level probability distribution \( \hat{P}(\varepsilon) \) can be also expressed by equation (1.27)

\[ \hat{P}(\varepsilon) = \frac{g_i \exp( -\varepsilon_i / kT )}{\sum_i g_i \exp( -\varepsilon_i / kT )} \]  \hspace{1cm} (1.29)

and the corresponding cumulative probability \( \mathcal{P}(\varepsilon > \varepsilon_b) \) of a molecule having energy greater than a given value \( \varepsilon_b \) is:

\[ \mathcal{P}(\varepsilon > \varepsilon_b) = \frac{\sum_{i_b} \sum_{i_b}^\infty g_i \exp( -\varepsilon_i / kT )}{\sum_0^\infty g_i \exp( -\varepsilon_i / kT )} \]  \hspace{1cm} (1.30)

where \( i_b \) is the quantum number corresponding the energy level \( \varepsilon_b \). When we consider the translational motion of a molecule and follow the classical manipulation of the kinetic energy distribution, the summation can be replaced by an integration and equation (1.30) reduces to equation (1.20). The detailed illustration will be discussed later.

The population ratio of two adjacent microscopic energy states is

\[ \frac{n_{i+1} / g_{i+1}}{n_i / g_i} = \exp( -\frac{\varepsilon_{i+1} - \varepsilon_i}{kT} ) \]  \hspace{1cm} (1.31)

When \( \varepsilon_{i+1} > \varepsilon_i \), the above ratio is always less than 1, meaning that the higher the energy of the state, the less it is populated.

From the requirements of probability functions, \( \mathcal{P} \) must be strictly nonnegative and the total probability over all possible quantum states must be 1.
\[ \sum_{i} \phi(x) = 1 \quad \text{or} \quad \int \phi(x) \, dx = 1 \quad (1.32) \]

An average value of the observable variable, \( x \) can be calculated:

\[ \overline{x} = \sum_{i} x \phi(x) \quad \text{or} \quad \overline{x} = \int x \phi(x) \, dx \quad (1.33) \]

and the average of any function of \( x \), \( f(x) \), as:

\[ \overline{f(x)} = \sum_{i} f(x) \phi(x) \quad \text{or} \quad \overline{f(x)} = \int f(x) \phi(x) \, dx \quad (1.34) \]

So the average energy of a particle is:

\[ \overline{\varepsilon} = \frac{\sum_{i} \varepsilon_i \, g_i \, \exp(-\varepsilon_i/kT)}{\sum_{i} g_i \, \exp(-\varepsilon_i/kT)} \quad (1.35) \]

The importance of the molecular partition function is because all thermodynamic state functions can be expressed by means of it. Since thermodynamic state functions are usually expressed in a molar basis rather than a molecular basis, the molar partition function may be a more convenient expression. The relationship between them is discussed below.

In the case of an ideal gas, each independent molecule is free to move through the whole system, and an interchange of coordinates between molecules does not create a new quantum state. Therefore the molecules of an ideal gas lose their distinguishability. Consequently, quantum states in the gaseous phase that differ merely by the interchange of two molecules are indistinguishable and should be counted only once. So the molar partition function, \( Q \), is equal to [Atkins, 1986]

\[ Q = \frac{N_o^N}{N_o!} \quad (1.36) \]

where \( N_o \) is the Avogadro's constant. The molar internal energy \( U_a \), is [Atkins, 1986]:
\[ U_a = \sum_i \varepsilon_i \eta_i = \frac{N_o \sum \varepsilon_i g_i \exp\left(-\varepsilon_i/kT\right)}{\sum_i g_i \exp\left(-\varepsilon_i/kT\right)} = kT^2 \left( \frac{\partial \ln \Omega}{\partial T} \right)_{V_a,N} \] (1.37)

where the subscript means that the derivative is at constant volume, \( V_a \), and at constant number of molecules. The molar entropy, \( S_a \), is

\[ S_a = U_a/T + k \ln \Omega \] (1.38)

The other thermodynamic state functions such as molar enthalpy \( H \), Helmholtz free energy \( F \), Gibbs free energy \( G \) and the chemical potential \( \mu \) can be derived:

\[ H_a = U_a + RT = kT^2 \left( \frac{\partial \ln \Omega}{\partial T} \right)_{V_a,N} + RT \] (1.39)

\[ F_a = -kT \ln \Omega \] (1.40)

\[ G_a = -kT \ln \frac{\Omega}{N_o} + RT \] (1.41)

\[ \mu_a = -kT \ln \frac{\Omega}{N_o} \] (1.42)

An ideal gas molecule possesses translational, rotational, vibration, nuclear and electronic motion degrees of freedom. Its total internal energy can be decomposed into the corresponding terms.

\[ \varepsilon_{\text{total}} = \varepsilon_{\text{tr}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}} + \varepsilon_{\text{nu}} + \varepsilon_{\text{ele}} = \varepsilon_{\text{tr}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{int}} \] (1.43)

Except the translational and rotation energies, all others belong to the internal motion states of the molecule. The total molecular partition function can be expressed as:

\[ \Omega_{\text{total}} = \Omega_{\text{tr}} \Omega_{\text{rot}} \Omega_{\text{vib}} \Omega_{\text{nu}} \Omega_{\text{ele}} = \Omega_{\text{tr}} \Omega_{\text{rot}} \Omega_{\text{int}} \] (1.44)

The translational partition function of an ideal gas molecule can be obtained by solving Schrödinger equation for a free moving particle in a three dimensional space [Atkins, 1986].
\[ \varphi_{nu} = V \left( \frac{2\pi MKT}{\hbar^2} \right)^{3/2} \tag{1.45} \]

where \( M \) is the mass of the molecule, \( V \) is the volume of the system and \( \hbar \) is the Planck constant.

Let us consider an adsorptive site on a homogenous adsorbent surface that is distinguishable, independent and where no more than one adsorbate molecule can exist. There is no any interaction between adsorbate molecules at different adsorption sites. The number of ways in which \( N \) indistinguishable adsorbate molecules can be located among \( \mathcal{M} \) equivalent but distinguishable adsorption sites is \[ \frac{\mathcal{M}!}{N!(\mathcal{M} - N)!} \] \cite{Fried1977}.

The corresponding molar partition function is

\[ \varrho = \frac{\mathcal{M}!}{N!(\mathcal{M} - N)!} \varphi^N \tag{1.46} \]

Using Stirling’s approximation formula to replace the expressions of \( \ln N! \), \( \ln \mathcal{M}! \) and \( \ln (\mathcal{M} - N)! \), equation (1.46) can be rewritten into

\[ \ln \varrho = \mathcal{M} \ln \mathcal{M} - N \ln N - (\mathcal{M} - N) \ln (\mathcal{M} - N) + N \ln \varphi \tag{1.47} \]

Similar to gas phase, the thermodynamic state functions of adsorbed phase can be expressed as \cite{Ruthven1984}:

\[ U_{ad} = N_o \bar{e}_{ad} = N_o \bar{e}_{ad} + N_o \bar{U} \tag{1.48} \]

\[ H_{ad} = U_{ad} \tag{1.49} \]

\[ S_{ad} = \frac{U_{ad}}{T} + k \ln \varrho_{ad} \tag{1.50} \]

\[ F_{ad} = -kT \ln \varrho_{ad} \tag{1.51} \]

\[ G_{ad} = -kT \ln \varrho_{ad} + N_o \bar{U} \tag{1.52} \]
\[ \mu_{ad} = -kT \ln \left\{ \frac{(\mathcal{N} - N) \varphi_{ad}}{N} \right\} \quad (1.53) \]

where \( \overline{U} \) is the average molecular potential energy of adsorbate over all possible energy levels and quantum states. The differential adsorption heat \( q_{\text{diff}} \) is defined as the heat flow with the conditions of constant volume of gas and adsorbed phase, constant adsorbent surface area, and constant temperature and can be measured in a calorimeter. \( q_{\text{diff}} \) is the difference between translational internal energy of gas and adsorbed phases:

\[ q_{\text{diff}} = N_o(\overline{e}_{\text{ad}} - \overline{e}_a) \quad (1.54) \]

At equilibrium, the chemical potential of the adsorbate in bulk phase \( \mu_{ab} \) and in adsorbed phase \( \mu_{ad} \) must be equal. Consequently

\[ -kT \ln \left\{ \frac{\varphi_{ad}}{N} \right\} = -kT \ln \left\{ \frac{(\mathcal{N} - N) \varphi_{ad}}{N} \right\} \quad (1.55) \]

In physical adsorption the interaction forces between adsorbate molecules and adsorbent atoms are much weaker than the chemical bonding forces, so the state of adsorbate molecules is negligibly affected by the adsorbent interaction forces and so the \( \varphi_{\text{ele}} \) and \( \varphi_{\text{nu}} \) can be considered as invariant between adsorbed and gas phases. For some special adsorbate molecules such as the inert gases, the vibration and rotation energies of the molecule are zero and thus the corresponding molecular partition functions are equal to 1. The only energy and partition function contributions arise from the translational motion.

The coverage is defined as \( N/\mathcal{N} \) and substituting equation (1.45) into (1.55), it yields

\[ \frac{\theta}{1 - \theta} = \frac{\Phi^3 \varphi_{ad}}{kT(2\pi M kT)^{3/2}} \quad (1.56) \]

For other permanent gases such as oxygen and nitrogen, when the adsorbent micropores are relatively large the molecules in adsorbed phase can have a localized three-dimensional motion and we can still assume the condition of approximately constant vibration and rotation energies between adsorbed and gas phases and so equation (1.56) can be used. If we let \( \kappa = \frac{h^3 \varphi_{ad}}{kT(2\pi M kT)^{3/2}} \), equation (1.56) is equivalent to the Langmuir isotherm expression. In the range of low coverage, \( \theta \ll 1 \) equation (1.56) reduces to the Henry isotherm. The \( q_{\text{st}} \) can be obtained from adsorption isotherms at different temperatures \([\text{Ruthven, 1984}]\). As long as the molecular partition functions in adsorbed phase are available, all these state functions can be evaluated.
3 CALCULATION OF PARTITION FUNCTIONS

From the previous discussion, we know that all adsorption thermodynamics including adsorption isotherms, adsorption thermodynamic functions and adsorption heat can be directly related to the molecular and system partition functions. The concept of partition function results from the microscopic view of molecular states and it is equal to the summation of the number of all possible microscopic states. It is a quantity related to microscopic properties and from it the macroscopic observable quantities can be obtained. So the partition function plays a bridge role in linking the microscopic nature and macroscopic observations. The original definition of molecular partition function $\varphi$ as the denominator of the Boltzmann distribution function is

$$\varphi = \sum_i g_i \exp\left(-\frac{\varepsilon_i}{kT}\right)$$ (1.28)

The definitions of the system partition functions are different depending on the choice of the system type.

Based on using classical Newtonian or quantum mechanics, the calculation of the molecular partition functions can be classified into the corresponding types. In the classical method, the kinetic energy of a molecule is considered as a continuous distribution, that is the molecule can have any kinetic energy. The Newton motion laws can be used to describe the molecular translational motion. This is nearly true when the temperature is not too low (higher than 200 K for most gases at moderate pressures). In quantum mechanics, the wave function of a particle or the microscopic system described by a set of quantum numbers exactly specifies the state of the microscopic system. Different combinations of quantum numbers result in different quantum states that can lead to the same energy. The quantum states having the same energy may be grouped together into an energy level. The number of quantum states belonging to the same energy level is the degeneracy or statistical weight, $g$ of that level. The basic postulate of statistical thermodynamics is that all quantum states are equally probable. But the energy levels are not equally probable owing to the different degeneracies of each level [Atkins, 1986]. Anyway the classical method is an approximation to quantum mechanics. When temperature decreases and pressure increases the quantum effects become more important. When the internal motions of the molecule such as rotation and vibration are involved, only the quantum mechanics approach is valid because the energy levels of the internal motion states are more often quantized than the translational motion. In the following section these two ways are discussed.

3.1 Calculation of Molecular Partition Functions by Classical Mechanics

When we focus our interest in molecular translational motion, we can approximately consider the molecule as a mass point. To specify the position of a single point three coordinates, $x$, $y$ and $z$ (in a Cartesian coordinate system) need to be given. Analogously, the momentum of this moving point may be described by a point in a three-dimensional momentum coordinate system. The combination of location and momentum coordinates form a six-dimensional coordinate system to identify a moving particle. The total translational energy of a moving molecule can be expressed using Newton law
\[ \varepsilon = \frac{1}{2M} \left[ p_x^2 + p_y^2 + p_z^2 \right] + U(x,y,z) \quad (1.57) \]

where \( \frac{1}{2M} \left[ p_x^2 + p_y^2 + p_z^2 \right] \) is the translational kinetic energy of the molecule that is dependent on the molecular momentum and independent of the position. While the molecular potential energy is only dependent on the position. In the classical approach the translational energy distribution is postulated to be a continuous function, that is, \( \varepsilon \) can take any values. Substituting equation (1.57) into equation (1.28) yields

\[ \psi = \sum_i g_i \exp \left[ -\frac{\left( p_x^2 + p_y^2 + p_z^2 \right)/2M + U(x,y,z)}{kT} \right] \quad (1.58) \]

In order to transform the summation in equation (1.58) into integration, we need to obtain the relationship among degeneracy, momentum and position. According to the Heisenberg uncertainty principle in the six-dimensional momentum and position coordinate system, the minimum distinguishable elemental volume is \( h^3 \) (\( \Delta p_x \, dx \geq h \), \( \Delta p_y \, dy \geq h \) and \( \Delta p_z \, dz \geq h \)). That is, at any given energy level, when the elemental volume is less than or equal to \( h^3 \) there is only one state and thus the degeneracy becomes unit. For any elemental volume (\( \Delta p_x \Delta p_y \Delta p_z \Delta x \Delta y \Delta z \)) greater than this minimum distinguishable volume the possible degeneracy is equal to \( [\text{Hu et al. 1979}] \)

\[ g = \frac{\Delta p_x \Delta p_y \Delta p_z \Delta x \Delta y \Delta z}{h^3} \quad (1.59) \]

Combining equations (1.58) and (1.59) into (1.28) and changing the summation into integration yields

\[ \psi = \frac{1}{h^3} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \exp\left( -\frac{\left( p_x^2 + p_y^2 + p_z^2 \right)/2M + U(x,y,z)}{kT} \right) \, dp_x \, dp_y \, dp_z \, dx \, dy \, dz \quad (1.60) \]

Because the momentum is independent of position this equation can be separated into two parts, one including the kinetic energy and another the potential field:
\[ \psi = \frac{1}{\hbar^3} \int_{-\infty}^{+\infty} \exp\left(-\frac{p_x^2 + p_y^2 + p_z^2}{2\text{MkT}}\right) d\rho_x d\rho_y d\rho_z \int_{0}^{v} \exp\left(-\frac{U(x,y,z)}{kT}\right) dx dy dz \] (1.61)

The kinetic energy part can be analytically integrated and is equal to \((\sqrt{2\pi\text{MkT}})^3\) and so the molecular partition function in a potential field is given by

\[ \psi = \left(\sqrt{2\pi\text{MkT}}\right)^3 \frac{1}{\hbar^3} \int_{0}^{v} \exp\left(-\frac{U(x,y,z)}{kT}\right) dx dy dz \] (1.62)

When the potential field is equal to zero everywhere, that is, the ideal gas situation, the integration in equation (1.62) is equal to the volume of the system and the equation directly reduces to the translational molecular partition function of an ideal gas.

It should be mentioned that the fundamental assumption in deducing this equation is that the kinetic energy distribution is a continuous function, so the summation can be replaced by an integration. The quantum mechanics calculation shows that the space between two adjacent translational energy levels is small in the low energy region but it increases when energy increases and thus this approximation is only valid for the low energy region. Similar to equation (1.37) the total internal energy of a molecule in a potential field can be represented by

\[ U_a = kN_o T^2 \left(\frac{\partial \ln \psi}{\partial T}\right)_V \] (1.63)

Substituting equation (1.62) into (1.63) we have

\[ U_a = \frac{3kN_o T}{2} + \frac{3N_o}{2} \int_{0}^{v} \exp\left(-\frac{U(x,y,z)}{kT}\right) dx dy dz \] (1.64)

The average quantities depending on the spatial position can be calculated by equations (1.32) to (1.35). The average position of a molecule, \(<xyz>\), is
\[ v \]

\[
\langle xyz \rangle = \frac{\int_{0}^{v} \exp\left(-\frac{U(x,y,z)}{kT}\right) \, dx \, dy \, dz}{\int_{0}^{v} \exp\left(-\frac{U(x,y,z)}{kT}\right) \, dx \, dy \, dz}
\]

(1.65)

The average potential energy is

\[
\bar{U} = \frac{\int_{0}^{v} U(x,y,z) \exp\left(-\frac{U(x,y,z)}{kT}\right) \, dx \, dy \, dz}{\int_{0}^{v} \exp\left(-\frac{U(x,y,z)}{kT}\right) \, dx \, dy \, dz}
\]

(1.66)

The comparison between equation (1.64) and (1.66) shows that the average kinetic energy of a molecule moving in a potential field is equal to that moving in a zero potential field. The kinetic energy is only dependent on the motion degrees of freedom.

One important function to calculate the intracrystalline diffusivity is the kinetic energy distribution. When the Boltzmann energy distribution equation (1.27) is suitable, the kinetic energy distribution can be simply deducted as follows.

Substituting equation (1.57) into equation (1.30) and using integration to replace the summation yields:

\[
P(\varepsilon > \varepsilon_0) = \frac{\int_{\varepsilon_0}^{+\infty} \int \exp\left(-\frac{[(p_x^2 + p_y^2 + p_z^2)/2M + \bar{U}(x,y,z)]}{kT}\right) \, dp_x \, dp_y \, dp_z \, dx \, dy \, dz}{\int_{0}^{+\infty} \int \exp\left(-\frac{[(p_x^2 + p_y^2 + p_z^2)/2M + \bar{U}(x,y,z)]}{kT}\right) \, dp_x \, dp_y \, dp_z \, dx \, dy \, dz}
\]

23
\[
\int_{-\infty}^{+\infty} \exp\left( - \frac{\mathbf{p}_x^2 + \mathbf{p}_y^2 + \mathbf{p}_z^2}{2\text{MT}} \right) d\mathbf{p}_x d\mathbf{p}_y d\mathbf{p}_z \int_{-\infty}^{+\infty} \exp\left( - \frac{V(x,y,z)}{kT} \right) dx dy dz
\]

\[
= \frac{1}{(\sqrt{2\pi\text{MT}})^3} \int_{-\infty}^{+\infty} \exp\left( - \frac{V(x,y,z)}{kT} \right) dx dy dz \tag{1.67}
\]

Because the kinetic energy distribution is independent of the spatial position and potential energy we can write

\[
\mathcal{P}(\varepsilon > \varepsilon_b) = \frac{1}{(\sqrt{2\pi\text{MT}})^3} \int_{-\infty}^{+\infty} \exp\left( - \frac{\mathbf{p}_x^2 + \mathbf{p}_y^2 + \mathbf{p}_z^2}{2\text{MT}} \right) d\mathbf{p}_x d\mathbf{p}_y d\mathbf{p}_z
\]

\[
= \exp\left( - \varepsilon_b/kT \right) \tag{1.68}
\]

In this development we again used the integration instead of summation; this is only valid when the spacing between the kinetic energy levels is small and thus kinetic energy can be considered as a continuous function. When the kinetic energy increases, the corresponding level spacing also increases. When a molecule crosses the window of a zeolite with a cation blockage, the molecule will interact with a strong repulsion potential; only if the molecule has enough kinetic energy and strike the blocked window, the position of the cation can deviate and increase the free dimension of the diffusion channel. In this case we are specially interested in the kinetic energy distribution at very high kinetic energy values. In this case the validity of using equation (1.68) is questionable.

### 3.2 Calculation of Molecular Partition Functions by Quantum Mechanics

The description of the translational motion of a molecule at moderate temperature and pressure by classical mechanics is reasonable and valid. When the environmental conditions change, the region of the validity of classical mechanics varies too. In classical mechanics, only the particle properties are considered. There are two types of quantum effects which result from the wave nature of the molecules: spin and wave effects. A useful criterion to neglect wave properties is the de Broglie wave length. The so-called de Broglie wave length \( \lambda \) is defined as [Atkins, 1986]

\[
\lambda = \frac{\hbar}{p} \tag{1.69}
\]

where \( p \) is the momentum of the moving molecule. When the de Broglie wave length associated with the molecule is of the order of magnitude of the average distance between the molecules in the gas, the classical statistical thermodynamics (Boltzmann statistics) is incomplete. Taking into account the symmetry effects, the restricted Fermi - Dirac or
Bose - Einstein statistics should be applied. The symmetry effects are important only at high density and very low temperatures (several Kelvin). When the de Broglie wavelength associated with the molecule is of the order of magnitude of the molecular diameter, one of the wave motion characteristics, the diffraction effect becomes important. This quantum effect will affect the transport properties of a molecule crossing an energy barrier. Experimental measurements shown that at room temperature, the diffraction effects are measurable in helium and hydrogen but unimportant for heavier gases and at lower temperature the quantum deviations associated with these effects are quite appreciable for helium and hydrogen and of some importance for the heavier gases [Hirschfelder et al., 1954].

Similar to the classical Newton motion equations describing the trajectories of particles, the Schrödinger equation describes the wave trajectories of microscopic particles. For a microscopic particle with mass M and energy ε, the time-independent motion equation in a three-dimensional space is [Fried et al., 1977]:

\[
\frac{-\hbar^2}{2M} \nabla^2 \Psi + V \Psi = \varepsilon \Psi \quad (1.70)
\]

Where Ψ is the equation solution and stands for the wave mechanics function of the moving particle, V is the potential energy acting on the particle and Ψ (ħ - cross or h bar) is a convenient modification of Planck's constant (ħ = h/2π). The time-independence of equation (1.70) means that all variables and physical quantities are independent of time.

The interpretation of the wavefunction Ψ is similar to the wave theory of light in which the square of the amplitude of an electromagnetic wave is considered as the intensity. The Born's explanation [Atkins, 1986] of the Ψ shows that the square of the wavefunction (for the complex Ψ, replaced by ΨΨ* where Ψ* is the complex conjugate of Ψ) is proportional to the probability of finding the particle at each spatial point and that ΨΨ* is a probability density function. To turn this explanation reasonable, some requirements on Ψ or ΨΨ* must be met. As a probability density function ΨΨ*, Ψ is at least everywhere bounded and the total probability of finding the particle in a closed system must be equal to unity, that is

\[
\int \Psi \Psi^* \, dV = 1 \quad (1.71)
\]

Because the Schrödinger equation is a second order differential equation, it must satisfy some mathematical requirements. The wavefunction Ψ must be meaningful in the interesting region, that is, it must be continuous and must have continuous first order derivative. Physical meaning implies that, ΨΨ* being a probability density, Ψ must be a single-valued function. It is well known from the theory of partial differential equations that the Schrödinger equation (1.70) has no solution that satisfies both equations (1.70) and (1.71) unless the energy ε takes only some special discrete values. The special
energy values by which the solution can satisfy both equations are the energy eigenvalues and the corresponding solutions are the eigenfunctions.

In order to understand the physical and mathematical meaning of the eigenfunctions, energy eigenvalues and eigenvalue distribution over all possible energy values (energy spectrum) we take the one-dimensional translational motion of a molecule in a potential field \( V(x) \)

\[
-\frac{\hbar^2}{2M} \frac{d^2\Psi}{dx^2} + [V(x) - \epsilon] \Psi = 0 \tag{1.72}
\]

The boundary conditions for this equation are \( x \rightarrow \pm \infty, \Psi \rightarrow 0 \). This is a second order ordinary differential equation and when \( \{V(x) - \epsilon\} = 0 \), the curvature \( \frac{d^2\Psi}{dx^2} = 0 \) and the solution in this case is \( \Psi = C_1 x + C_2 \) (\( C_1 \) and \( C_2 \) are any integral constants). This solution gives \( \Psi \rightarrow \pm \infty \) when \( x \rightarrow \pm \infty \) that violates the condition of \( \Psi \) being bounded. Otherwise we needed \( C_1 = 0 \) and the solution is reduced to the classical approach (\( \Psi = \text{constant} \)). So \( \epsilon \neq V(x) \) wherever. When \( V(x) > \epsilon \) (or \( V(x) < \epsilon \)) in the whole interval, \( \Psi \) monotonically increases (decreases) and the condition of \( \Psi \) being finite is violated. The choice of \( \epsilon \) should give a \( \frac{d^2\Psi}{dx^2} \) that changes sign at least twice. If we define the wavelength, \( \lambda(x) \), as the distance between two points where \( \{V(x) - \epsilon\} \) changes sign, from equation (1.72) we can obtain the relationship \[ \text{[ ter Haar, 1969]} \]

\[
\lambda(x) = \frac{\hbar}{\sqrt{2M(\epsilon - V(x))}} \tag{1.73}
\]

By using the classical relation, \( \epsilon = \frac{p^2}{2M} + V \) equation (1.73) reduces to equation (1.69). This relationship shows that the greater the difference between the total energy and the potential energy, the shorter the wavelength of the wavefunction. A stationary particle with zero kinetic energy has infinite wavelength, that is the wavefunction \( \Psi \) is a constant everywhere. An explanation for the relationship between the kinetic energy and the wavefunction sharpness can be shown by equations (1.72) and (1.73). When there is a large kinetic energy at some region, the wavelength \( \lambda(x) \) corresponding to this region is short, \( \frac{d^2\Psi}{dx^2} \) quickly changes sign and thus the wavefunction \( \Psi \) is sharply curved; when the wavefunction \( \Psi \) is not sharply curved (its wavelength is long), the kinetic energy is low.

The simplest case for equation (1.72) is the motion of a molecule when the potential function is equal to zero in a one-dimensional container. The solution is \[ \text{[ Atkins, 1986]} \]
\[
\Psi = \sqrt{\frac{2}{L}} \sin \left( \frac{n \pi x}{L} \right)
\]

and the eigen energy spectrum is

\[
\varepsilon_n = \frac{n^2 \hbar^2}{8ML^2}
\]

\[n = 1, 2, 3, \ldots\]

(1.75)

Because \(n\) cannot be zero the lowest energy that a molecule may have when it is in a one-dimensional container is not zero (as would be allowed by classical mechanics). The physical explanation of this lowest irreremovable energy is that the uncertainty principle requires a molecule to have kinetic energy if it is confined to a finite region. This is because the molecule location is not completely definite and thus its momentum cannot be precisely zero. The difference between two neighboring energy levels is

\[
\Delta \varepsilon = \varepsilon_{n+1} - \varepsilon_n = \frac{(2n + 1) \hbar^2}{8ML^2}
\]

(1.76)

which decreases as the length of the container increases. When \(L\) is close to the molecule size and \(n\) is a large number, the quantum effects can not be neglected.

One important quantum phenomenon of a moving molecule that results from its wave nature is the quantum leak. In classical mechanics, when a moving particle meets an energy barrier whose energy value is greater than the translational kinetic energy of the particle, the particle will be completely reflected and no any possibility for the particle to cross such barrier. The wave nature of a moving particle implies that when a wave meets a finite energy barrier it will decompose into two parts, one is a reflected wave and another is the diffracted part. The ratio of the two parts is dependent on the dimension of the energy barrier. This characteristic may affect the molecular transport properties inside zeolite crystals and so we should pay more attention to illustrate this phenomenon. For simplification we use the case in which a molecule moves in a one-dimensional field with potential distribution \(U(x) = 0\) inside the region \((-L < x < L)\) and \(U(x) = U_o\) out of that region \((x \leq -L \text{ and } x \geq L)\). The Schrödinger equation (1.70) becomes

\[
-\frac{\hbar^2}{2M} \frac{d^2 \Psi}{dx^2} + (U - \varepsilon) \Psi = 0
\]

(1.77)

with the boundary conditions,

\[x \longrightarrow \pm \infty, \quad \Psi \longrightarrow 0\]

(1.78)
According to the previous analysis, there are regions where $\frac{d^2\psi}{dx^2}$ changes twice its sign based on the second-order differential equation theory. At region I, $x \in (-\infty, 0]$, $\varepsilon < \mathcal{U}_o$, at region II, $x \in (0, L)$ and $\mathcal{U} = 0$ and at region III, $x \in (L, +\infty)$ and again $\varepsilon < \mathcal{U}_o$. In regions I and III the kinetic energy becomes $< 0$ and the classical mechanics theory rejects the existence of these regions.

In region I the solution is $\Psi_I = C_1 \exp\left[\sqrt{2M(\mathcal{U}_o - \varepsilon)/\hbar^2} x\right]$ and in region III is $\Psi_{III} = C_2 \exp\left[-\sqrt{2M(\mathcal{U}_o - \varepsilon)/\hbar^2} x\right]$. The problem is symmetric with respect to the substitution $x \longrightarrow -x$, and thus we should expect that the solutions are either invariant under this substitution, or are transformed into the same solution, but with a minus sign. That is, the constant $C_1 = \pm C_2$.

The solutions in the region II are

$$\Psi_{II}^{(e)} = C_3 \cos\left[\sqrt{2M\varepsilon/\hbar^2} x\right] \quad \text{for } C_1 = C_2 \quad (1.79)$$

$$\Psi_{II}^{(o)} = C_4 \sin\left[\sqrt{2M\varepsilon/\hbar^2} x\right] \quad \text{for } C_1 = -C_2 \quad (1.80)$$

where the superscripts indicate even $\Psi_{II}^{(e)}(x) = \Psi_{II}^{(e)}(-x)$ or odd ( $\Psi_{II}^{(o)}(x) = -\Psi_{II}^{(o)}(-x)$ ) parity. The continuity requirements of the wavefunction and of its first-order derivative lead to the calculations of the energy eigenvalues through the transcendental equations:

$$\sqrt{2M\varepsilon/\hbar^2} \cdot L = n\pi - 2\arcsin\left[\sqrt{\varepsilon/\mathcal{U}_o}\right] \quad (1.81)$$

The solutions of equation (1.81) give the eigen energy spectrum. When $n = 1, 3, 5, \ldots$, we have even symmetry and when $n = 2, 4, 6, \ldots$, we have odd symmetry. The wavefunctions out of region II (in the $\mathcal{U}_o$ potential region) exponentially decay. When the energy eigenvalue $\varepsilon$ increases, the corresponding region II extends. In the limiting situation, when $\mathcal{U}_o \longrightarrow +\infty$, this case reduces to the motion of a free particle in a one-dimensional container and the solution reduces to equations (1.74) and (1.75). We are interested in a case where the potential energy of the molecule is finite out of region II and the potential acting region is also very limited, that is, a potential energy barrier that is thin and where potential energy falls to zero after a short distance. From the previous solutions of equations (1.74) and (1.75), we know that the wavefunctions will exponentially decay in the $\mathcal{U}_o$ potential region. When the potential field disappears, the wavefunctions stop to decay and begin to oscillate like in the case of a particle inside a one-dimensional container. This shows that a moving particle with insufficient energy to escape will always be reflected by the barrier in classical mechanics, whereas the quantum mechanics treatment predicts a certain probability of diffraction.
$\mathcal{P}$ that a particle with mass $M$ and energy $\epsilon$ penetrates a potential energy barrier of height $\mathcal{U}$ (with $\mathcal{U} > \epsilon$) and thickness $L$ is [Atkins, 1986]

$$\mathcal{P} = \frac{1}{1 + G} \quad (1.82)$$

where

$$G = \left[ \frac{\exp(L/\mathcal{D}) - \exp(-L/\mathcal{D})}{4 \, t \, (1 - t)} \right]^2 \quad (1.83)$$

where $\mathcal{D} = \hbar/\sqrt{2M(\mathcal{U} - \epsilon)}$ and $t = \epsilon/\mathcal{U}$. When the barrier is high and thick, so that $L/\mathcal{D} \gg 1$, the first exponential dominates the second and then $G \gg 1$. Finally $\mathcal{P}$ is approximately equal to

$$\mathcal{P} = 4 \, t \, (1 - t) \exp(-2L/\mathcal{D}) \quad (1.84)$$

The probability $\mathcal{P}$ depends exponentially on the square root of the mass of the particle and on the thickness of the barrier.

As an illustration, we try to compare the importance of considering the wave nature in the calculation of the diffusion of a helium molecule through a square energy barrier using classical mechanics, that is, only considering the particle effects and quantum mechanics. The mass $M$ of a helium molecule is $6.64 \times 10^{-24}$ gram. If the height, $\mathcal{U}$, and the thickness, $L$, of the potential energy barrier are $1.5 \times 10^{-13}$ ergs and $2 \times 10^{-8}$ cm respectively, the helium molecular energy, $\epsilon$, is $4.14 \times 10^{-14}$ ergs (the average translation kinetic energy $\frac{3}{2} kT$ with $T = 183.15$ K). The $\mathcal{D}$ and $\sigma$ values are equal to $8.78 \times 10^{-10}$ cm and 0.276, respectively. The $\mathcal{P}(\epsilon<\mathcal{U})$ for wave mechanics under the condition that the molecule energy is less than the energy barrier is equal to $1.64 \times 10^{-20}$ (equation (1.82)). The total probability that a molecule with the Boltzmann energy distribution crosses the energy barrier is equal to $\mathcal{P}(\epsilon<\mathcal{U})$ plus the probability, $\mathcal{P}(\epsilon>\mathcal{U})$, that the molecule has energy greater than the energy barrier. If the probability, $\mathcal{P}(\epsilon>\mathcal{U})$, of a molecule having energy greater than the energy barrier $\mathcal{U}$ can be calculated by the Boltzmann energy distribution equation (1.28), the total probability, $\mathcal{P}_{\text{total}}$, of the helium molecule crossing an energy barrier by quantum mechanics is $\mathcal{P}_{\text{total}} = 1.64 \times 10^{-20} + \exp(-V/kT) = 1.64 \times 10^{-20} + 0.0026 = 0.0026$. This typical example shows that the wave natural contribution in the case of a light gaseous molecule crossing an energy barrier with several angstrom width can be safely neglected. The heavier the molecule is, the smaller the contribution will be. This contribution is very sensitive to the energy.
barrier width and when the width is equal to 0.3 angstrom, the contribution of the wave nature mechanism is about 3%. But when the width reduces to 0.2 angstrom, the contribution of the wave mechanism exceeds the contribution of the term $\exp(-\sqrt{U/kT})$.

The width of the diffusion energy barriers of an adsorbate molecule passing through the blocked window of 4Å zeolite is roughly close to the cation dimension ($\approx 2Å$) so the wave mechanism contribution is negligible.

Only in very few systems equation (1.70) may have analytical solutions and the corresponding energy eigenvalue spectrum. The numerical techniques are useful tools to solve the Schrödinger equation. Taking into account the specificity of the interaction potential distribution of an adsorbate molecule inside the cavity or at the window of zeolite A that can be approximately considered as being spherical symmetric. The corresponding Schrödinger equations can be simplified to one-dimensional ordinary differential equations by separation of variables. In the following section, these two special cases will be discussed.

A. Evaluation of the Translational Energy Levels inside the Cavity of Zeolite A

The Schrödinger equation of a moving molecule in a spherical symmetrical interaction potential field $U(r)$, in spherical coordinates has the form [ ter Haar, 1969 ]

$$-\frac{\hbar^2}{2M} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \Psi}{\partial r} \right) + \frac{1}{r \sin \eta} \frac{\partial}{\partial \eta} \left( \sin \eta \frac{\partial \Psi}{\partial \eta} \right) + \frac{1}{r^2 \sin^2 \eta} \frac{\partial^2 \Psi}{\partial \xi^2} \right] + U(r) \Psi = \varepsilon \Psi \quad (1.85)$$

where $\eta, \xi$, and $r$ are the coordinate variables and $\varepsilon$ is the translational energy of a molecule. By using the method of separation of variables the function $\Psi$ in above equation can be separated into the product of three functions depending each one on one independent variable

$$\Psi = \frac{\mathcal{R}(r)}{r} \mathcal{Y}_\eta(\eta) \mathcal{Y}_\xi(\xi) \quad (1.86)$$

Substituting equation (1.86) into (1.85) we have the following equation for the function $\mathcal{Y}_\xi(\xi)$

$$\frac{d^2 \mathcal{Y}_\xi(\xi)}{d\xi^2} = -m^2 \mathcal{Y}_\xi(\xi) \quad (1.87)$$

The choice of the constant $m$ must satisfy the implicit physical condition of $\mathcal{Y}_\xi(\xi)$ being a periodic function. Under this condition, the solution of equation (1.87) is
\[ \psi_n^m(\xi) = e^{i m \xi} \quad m = 0, \pm 1, \pm 2, \ldots \quad (1.88) \]

where \( i \) is the imaginary unit. Similarly, function \( \psi_n^m(\eta) \) must satisfy the following equation

\[ \frac{1}{\sin \theta} \frac{d}{d\eta} \left( \sin \theta \frac{d \psi_n^m(\eta)}{d\eta} \right) - \frac{m^2 \psi_n^m(\eta)}{\sin^2 \eta} + \ell (\ell + 1) \psi_n^m(\eta) = 0 \quad \ell \geq l_{ml} \quad (1.89) \]

where the constant \( \ell (\ell + 1) \) is chosen in order to guarantee physical acceptable solutions and \( \ell \) must be an integer \( \geq l_{ml} \). The solution of \( \psi_n^m(\eta) \) is then:

\[ \psi_n^m(\eta) = A(\sin \eta)^m \frac{d^{\ell-m}(\sin \eta)^{2\ell}}{(d \cos \eta)^{2m}} \quad \ell \geq l_{ml} \quad (1.90) \]

where \( A \) is a normalization constant.

Finally there is an equation for the function \( \mathcal{R}(r) \):

\[ -\frac{\hbar^2}{2M} \frac{d^2 \mathcal{R}}{dr^2} + \left[ \psi_n^m(r) + \frac{\hbar^2}{2M} \frac{\ell (\ell + 1)}{r^2} \right] \mathcal{R} = \varepsilon \mathcal{R} \quad (1.91) \]

Equation (1.91) is singular at the points \( r = 0 \) and \( r = r_w \), where \( r_w \) is the radius of the spherical shell, that is, the potential or the term \( \frac{\ell (\ell + 1)}{r^2} \) tends to infinity. The requirement of physical meaning for the wave function \( \Psi \) implies that at point \( r = 0 \), \( \Psi \) must be finite or \( \frac{d\psi}{dr} \bigg|_{r=0} = 0 \) which results in \( \frac{d\mathcal{R}}{dr} \bigg|_{r=0} = 0 \) or \( r \mathcal{R} \bigg|_{r=0} = 0 \).

The condition \( \mathcal{R} \big|_{r=0} = 0 \) includes \( \frac{d\mathcal{R}}{dr} \bigg|_{r=0} = 0 \). At the cavity wall \( r = r_w \), \( \Psi = 0 \) and \( \mathcal{R} = 0 \). So equation (1.91) has the following two boundary conditions:

\[ r = 0, \mathcal{R} = 0 \quad ; \quad r = r_w, \mathcal{R} = 0 \quad (1.92) \]

Equations (1.91) and (1.92) are a Sturm - Liouville eigenvalue problem [Kreyszig, 1988]. Equation (1.91) depends on a quantum number \( \ell \) and the eigen energy \( \varepsilon \) also varies with \( \ell \). The values of \( \ell \) must satisfy equation (1.89) and the independence of \( \varepsilon \) on quantum
number m implies that e is at least \((2\ell + 1)\) fold degenerate, as for each value of \(\ell\) there are \(2\ell + 1\) possible values of \(m\) \((m = 0, \pm 1, \pm 2, \ldots, \pm \ell)\).

The physical meaning requires that the wave function, \(\Psi(r)^*\Psi(r)\) is proportional to the probability of finding the molecule at each point in space. If \(\Psi\) is a solution of equation (1.86), then the same is valid for \(C\Psi\) where \(C\) is any constant \([\text{Atkins, 1986}]\). This means that we can find a factor such that the proportionality of the \(\Psi^*\Psi\) to probability becomes unity. This constant can be chosen by considering that the total probability of finding a molecule inside a closed volume must be equal to 1. The normalization of \(\Psi\) results in a normalization of \(R\) when \(\Psi_n(\eta)\Psi_\xi(\xi)\) is normalized

\[
\int \Psi_n(\eta)\Psi_\xi(\xi)\sin\eta\,d\eta\,d\xi = 1
\]

\[
\int R^*(r) R(r)\,dr = 1 \quad (1.93)
\]

The three dimensional Schrödinger equation has been reduced to a one - dimensional equation with the usual normalization condition. In equation (1.91) a modified potential

\[
\mathcal{U}(r) + \frac{\hbar^2}{2M} \ell (\ell + 1) \frac{1}{r^2}
\]

replaces the original potential function \(\mathcal{U}(r)\).

Prior to solve the eigen value problem, some important characteristics can be deduced from the Sturm - Liouville theory. For a given quantum number \(\ell\), there are infinite sets of eigenvalues and corresponding eigenfunctions and the eigenvalues monotonically increase with the increase of the eigenvalue index; different eigenfunctions are orthogonal and when the index of eigenvalues increases one, the corresponding eigenfunction undergoes a sign change. The later two properties can help to check the correctness of the solutions.

Depending on the potential distribution form, only in a very few cases of simple potential functions equation (1.91) can be analytically solved. When the potential function only has singular points with order less than or equal two, the power series expansion method can be used to solve the equation and corresponding boundary conditions \([\text{Kreyszig, 1988}]\) but complicated recurrence relations for the calculation of the eigenvalues and eigenfunctions will appear. The worse cases are when the power series solution numerically fails to converge because the power series solutions will usually produce great oscillations before convergence. Specially solutions close to the singular points are very unsteady. Big oscillations imply that the calculation results loss precision and computer overflows. In the case of potential functions being given by a set of discrete values, the numerical technique is the better choice for directly calculating eigenvalues and the corresponding eigenfunctions.

The public domain software SLEDGE \([\text{Pness and Fulton, 1991}]\) is specially designed for dealing with the Sturm - Liouville problem. The inputs to SLEDGE software package are the coefficient functions of the Sturm - Liouville equation, boundary condition types (regular or singular) and the error limits for eigenvalues and eigenfunctions. From the output of SLEDGE both eigenvalues and eigenfunctions can be obtained. There is an
In order to examine the stability and accuracy of the numerical results on eigenvalues and eigenfunctions obtained from SLEDGE, we selected the motion of an ideal gas molecule in a one-dimensional free potential container for which there are simple analytical solutions. The eigenvalue spectrum and corresponding eigenfunctions are 
\[ \varepsilon_n = n^2 \hbar^2 / 8Ml^2 \] and 
\[ \sqrt{\frac{2}{l}} \sin \left( \frac{n\pi x}{l} \right) \] respectively. Comparing the results shows that the differences between analytical and direct numerical solutions are within the error limits that were set for the input of SLEDGE. Obtaining an accurate eigenvalue by SLEDGE is much easier than to obtain an accurate eigenfunction. Our calculation practice shown that high precision for eigenvalues was easily achieved but for eigenfunctions was relatively difficult. Our main interest is to obtain the eigenvalues so that the accurate kinetic energy distribution can be achieved.

The average coordinate and potential energy of an adsorbate molecule at a given quantum state \( \ell \) associated with energy state \( i \) can be evaluated by means of the wave function \( \mathcal{R}(r) \):

\[ \bar{r}_i = \int \mathcal{R}^*(r) \mathcal{R}(r) \, r \, dr \]  
(1.94)

\[ \bar{U}_i = \int \mathcal{R}^*(r) \mathcal{R}(r) \, U \, dr \]  
(1.95)

\[ \bar{\kappa}_i = \varepsilon_i - \bar{U}_i \]  
(1.96)

The total average coordinate \( \bar{r} \), average potential energy \( \bar{U} \), total average energy \( \bar{\varepsilon} \) and average kinetic energy \( \bar{\kappa} \) of an adsorbate molecule over all quantum numbers \( \ell \) and possible energy states can be obtained using the partition function of the adsorbed phase:

\[ \bar{r} = \frac{\sum_{i=0}^{\infty} r_i g_i \exp(-\varepsilon_i/kT)}{\mathcal{V}r} \]  
(1.97)

\[ \bar{U} = \frac{\sum_{i=0}^{\infty} U_i \exp(-\varepsilon_i/kT)}{\mathcal{V}r} \]  
(1.98)

\[ \bar{\varepsilon} = \frac{\sum_{i=0}^{\infty} \varepsilon_i \exp(-\varepsilon_i/kT)}{\mathcal{V}r} \]  
(1.99)
\[ \overline{\mathbf{E}} = \overline{\mathbf{e}} - \overline{\mathbf{U}} \]  

(1.100)

B. Evaluation of the Translational Energy Levels at the Window of Zeolite A

The interaction potential field of an adsorbate molecule at the window of the 8 membered ring can be approximately considered as radially symmetrical. Similarly the motion of a molecule at the window can be described by the stationary state Schrödinger equation, which has the form in polar coordinates

\[
- \frac{\hbar^2}{2M} \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \Psi}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 \Psi}{\partial \xi^2} \right] + U(r) \Psi = \varepsilon \Psi
\]  

(1.101)

Where \( \xi \) and \( r \) are the coordinate variables and \( \varepsilon \) is the translational energy of a molecule at the window plane. By using the method of separation of variables the function \( \Psi \) in the above equation can be separated into the product of two functions depending each one on one independent variable:

\[
\Psi = R(r) \ U_\xi(\xi)
\]  

(1.102)

The solution of \( U_\xi(\xi) \) is the same as for equation (1.88).

The equation for function \( R(r) \) is:

\[
- \frac{\hbar^2}{2M} \frac{d}{dr} \left( r \frac{dR}{dr} \right) + \left[ rU(r) + \frac{\hbar^2 m^2}{2M} \frac{1}{r^2} \right] R = \varepsilon r R
\]  

(1.103)

At point \( r = 0 \), \( \Psi \) must be finite or \( \frac{d\Psi}{dr} \bigg|_{r=0} = 0 \) and \( \frac{dR}{dr} \bigg|_{r=0} = 0 \). At the window wall \( r = r_w \), \( \Psi = 0 \) and \( R = 0 \). So equation (1.103) has following two boundary conditions:

\[
r = 0, \ \frac{dR}{dr} = 0; \quad r = r_w, \ R = 0
\]  

(1.104)

The equations (1.103) and (1.104) constitute a Sturm-Liouville eigenvalue problem [Kreyszig, 1988]. Equation (1.103) depends on a quantum number \( m \) and the eigen energy \( \varepsilon \) also varies with \( m \). Because \( m^2 \geq 0 \), the effect of quantum number \( m \) on the molecular
motion at the window plane is similar to the existence of an additional repulsion interaction potential. When m is small, the value of term \( \frac{K^2 m^2}{2M r} \) is small compared to the term \( rU'(r) \). But the term \( \frac{K^2 m^2}{2M r} \) becomes dominant with the increase of quantum number m and the original potential becomes negligible.

From the definition of the partition function, only the negative eigenvalues make significant contributions to the translational partition function, \( \varphi_{\lambda r} \), whose value quickly decreases when \( \varepsilon_i \) increases. At large values of the quantum number m ( \( rU'(r) + \frac{K^2 m^2}{2M r} > 0 \) ), all eigenvalues are positive and the contributions of them to \( \varphi_{\lambda r} \) are small, so these microscopic states with positive eigen energies can be neglected. The values of quantum number m must satisfy equation (1.88) and there is no any degeneracy ( \( g_i = 1 \) ) of microscopic states at the same energy level at the window plane.

The normalization of \( \Psi \) results in the a normalization of \( R \) when \( U_\xi(\xi) \) is normalized

\[
\int R^*(r)R(r) \, dr = 1
\]

(1.105)

If we let \( \Psi(r) = R \cdot r^{1/2} \), the equation (1.105) becomes:

\[
\int \Psi^*(r)\Psi(r) \, dr = 1
\]

(1.106)

In this equation \( \Psi^*(r)\Psi(r) \) becomes the probability distribution function of finding a molecule in a given position r, so the average of variables and functions can be evaluated in the same way as already shown (see equations (1.94) to (1.100).

The potential tends to infinity when r is close to the wall and so both the points r = 0 and \( r = r_w \) in equations (1.103) and (1.104) are singular.

The average properties of adsorbate molecule inside the cavities of 4A and 5A zeolites can be calculated in this way. The dimension of the cavities of 4A and 5A zeolites is relatively large compared to the dimension of adsorbate molecules and thus the vibration and rotation motion of the adsorbate molecules can be considered as the same as for a free molecule.
4. MASS TRANSFER PROCESSES OF GASES IN POROUS SOLIDS

In practical operation, maximum capacity of the adsorbent can not be fully utilized because there are mass transfer resistances. Mass transfer resistances can greatly affect the adsorbent choice. Mass transport rates in the bulk phase and within the pores including micropores and macropores play an important role in catalytic and non catalytic gas solid reactions involving particles and pellets. A lot of industrially important gas solid reactions occur in the transition regime of intraparticle diffusion and reaction, that is, under reaction conditions where both intrinsic kinetics and intraparticle diffusion are important. The mass transfer rate inside porous solids may become an important limitation of the overall efficiency [Satterfield, 1970, Smith, 1970, Weisz, 1973, Turner, 1974 and Szekely et al, 1976]. When the mass transport process becomes the rate limiting step it must be well known in order to understand the kinetic and dynamic behavior of the system in quantitative terms.

For other gas solid operations such as adsorption separations and purifications, the physical adsorption rate usually is highly fast and can be neglected when compared with the mass transport rate of adsorbate molecules within the pores of the adsorbents. The choice of operating conditions heavily depends on the kinetics of the mass transport processes. The separation of air to produce pure nitrogen by PSA technique on 4A zeolite does use the difference on mass transport rates of oxygen and nitrogen molecules in intracrystalline pores [Shin and Knaebel, 1987].

A lot of good reviews on mass transport processes in porous solids can be found [Barrer, 1951 and 1963, Carman, 1956, Bird et al, 1960, Jackson, 1970, Satterfield, 1970, Youngquist, 1970, Dullien, 1975, Mason and Malinauskas, 1983, Ruthven, 1984, Kärger and Ruthven, 1992]. The structure of ordinary porous solids based on the pore size distributions can be divided in two types: monodisperse and bidisperse. Alumina, activated carbon and silica gel belong to first kind with continuous pore size distribution function of pore dimensions from several to thousand Angstroms. The second type of porous solids includes zeolites and carbon molecular sieves where pore size distributions have two steep peaks, one located in the vicinity of microparticle dimensions and another in the range of intramicroparticle pore dimensions. In the first kind of porous solids, the molecules in the bulk phase permeate the gas solid interface into the pellet pore by a molecular diffusional mechanism and then move towards the center of the pellet by different diffusional mechanisms such as molecular. Knudsen and surface diffusion which depend on pore structure and environmental conditions, until the concentration in the pore becomes uniform. Whereas in the second type there is a series mechanism in the diffusion of molecules towards the center of the microparticle.

The mechanisms of molecular motion in the intraparticle and interparticle pores are different due to the pore size. The dimension of intramicroparticle pores is of the same order of magnitude as molecules.

Although there are a number of published papers that tried to predict the mass transfer rate inside porous particles, the presently available means are still unsatisfactory. Because of the complexity of the pore structure including pore shape and pore size distribution, it is impractical to expect the use of a general model to predict the intraparticle mass transport rate covering a wide range of porous media. The real pore structures were approximately represented by introducing reasonable assumptions based on experimentally determined pore structures such as pore size distribution, porosity, specific area, etc. Based on these assumptions, there are many models, for example capillary cylindrical pores, spherical
and cubic geometry stacked pores, cylindrical neck with spherical cavity pore, and varying diameter pores [Payatakes et al, 1973, Dullien, 1975, Iorio et al, 1976, Gavala and Kim, 1981, Ballal and Zygourakis, 1985, Sahimi et al, 1983, Huizenga and Smith, 1986, Burganos and Sotirchos, 1989, Melkote and Jenson, 1989, Lane, 1991, Petropoulos et al, 1991 and Reyes and Iglesia, 1991] to explain the diffusional behavior of molecules in pores. Due to the differences on porous media structure a diffusional mechanism under some special assumptions may only describe a few systems. In addition, the environmental conditions such as temperature and pressure will also change the mass transport mechanism.

The mass transfer parameters inside pellets are usually obtained by fitting the experimental transient curves of mass flux into or through the porous solid to the appropriate theoretical models which are usually the analytical or numerical solution of Fick’s diffusional equations under given boundary conditions. The interpretation of measurements of the most important parameters such as diffusivities, greatly depends on the definitions, the boundary conditions of the diffusional equations and the approximation methods used for the real pore network of the porous solid. So these values are only related to each specific case. Models for diffusion and flow within porous media rarely allow for a reliable prediction of transport resistances and firm agreement only comes through experimental determination. Their determination is usually dependent on the mass transfer models that are used to simulate the experimental process.

In order to describe diffusion quantitatively, there is clearly a demand for general, reliable and reproducible experimental methods and models for the evaluation of effective diffusivities and convection coefficients within pores. One purpose of this work is to develop the experimental methods and corresponding mathematical models which can meet the requirements of process design and theoretical research involving diffusion within porous media.

Diffusion can be described by a mechanistic approach in which the consideration of molecular movement is important or by a continuum approach such as Fick’s first law, where no consideration is given to the actual mechanism by which molecule transfer occurs. The nature of gas diffusion is the molecular random movement and the diffusional phenomena can be described by means of the molecular kinetic theory. From a statistical point of view, there is an average macroscopic characteristic of the microscopic molecular random movement. In chemical engineering field, we are mainly interested in average macroscopic properties of mass transfer which are most readily apparent by a phenomenological description of the process and so we prefer to choose the continuum approach to describe the molecular diffusional phenomena.

The first quantitative study of gas diffusion was carried out by Fick [Fick, 1855] who found that the diffusing mass flux in a binary mixture is proportional to the concentration gradient which causes the diffusion, called diffusional driving force, and formulated the relationship now known as Fick’s first diffusion law:

\[ J = -D \frac{dc}{dz} \]  \hspace{1cm} (1.107)

where \( J \) is the diffusional mass flux with the dimensions in mass or moles per unit area and per unit time and the concentration expressed in mass or moles per unit volume. The above equation provides a convenient mathematical representation and illustrates that mass transfer is due to the concentration gradient. The equation implies that the diffusivity is independent of the concentration gradient. But it usually depends on
concentration and only when the system is thermodynamically ideal it is a constant. Recent studies revealed that the real driving force for diffusional mass transfer is the chemical potential gradient [Ruthven, 1984]. When the systems studied are ideal and the activity of components can be substituted by concentration, the chemical potential gradient equals the concentration gradient. In practice, when the system temperature is not too low and the pressure is not too high, the general gas behavior is close to the ideal gas. In order to keep the simplicity, we still use the concentration gradient instead of the chemical potential gradient.

The Fick’s first diffusion law expresses the statistical fact of the proportionality of the net displacement rate (net flux) to the difference between the existing population densities (concentrations) of mobile species across a volume element. The proportionality coefficient is the diffusivity which can be related to mobility parameters of the stepwise statistical events, such as an average jump distance L and an average kinetic velocity v. For a three dimensional medium, it yields [Garcia and Weisz, 1990]:

\[ D = \frac{1}{3} \mathcal{P} L v \]  \hspace{1cm} (1.108)

where \( \mathcal{P} \) is the probability of a successful propagative jump (usually assumed to be 1/2).

Equation (1.107) is convenient to use in steady state systems in which the concentration gradient and diffusional mass flux are only function of the spatial position. When the systems studied are not in steady state, it is more convenient to eliminate the dependent variable \( J \) and to use other measurable variables related to concentration variables. The Fick's first law is inadequate for the solution of most diffusion problems, because the concentrations are usually unknown. The fundamental equation for the mathematical treatment of diffusion processes is the diffusion equation known as Fick’s second law. Let us consider that the diffusional component mass flux at a plane \( z \) with unit area is \( J \) and the corresponding quantity at plane \( z + dz \) with unit area is \( J + dJ \). The mass accumulates due to the diffusion in the volume element of unit section area and thickness \( dz \) and gives rise to an increase of the amount of diffusing component within this volume element. The amount accumulated in this element \( \frac{\partial c}{\partial t} dz \) should be equal to the mass difference between input and output of this element. From this mass balance the following equation, named Fick’s second diffusion law, is obtained:

\[ \frac{\partial c}{\partial t} = \frac{\partial}{\partial z}(D \frac{\partial c}{\partial z}) \]  \hspace{1cm} (1.109)

Equation (1.109) is the Fick’s second equation which expresses the mass balance for a volume element by equating the difference between the incoming and outcoming flux of molecules and it is specially important in the interpretation of experimental work on unsteady state systems. To obtain the values of the diffusivity \( D \) from such experimental results it is necessary to solve equation (1.109) subjected to boundary conditions for the particular experimental arrangement. Equation (1.109) contains the inherent assumption that all molecules contribute equally to the process of stochastic displacement and that the molecules that at any time participate in the statistical process driven by the gradient of mobile species are identical to the total molecules which represent the accumulation.
When the molecules in the mobile state at any one time exist only internally with a concentration \( c_m \) and the accumulation is dependent on the total concentration including both mobile and immobilized species, the Fick's diffusion equations should be expressed as \cite{Garcia and Weisz, 1990}

\[
J = -D \frac{\partial c_m}{\partial z} \quad (1.107a)
\]

\[
\frac{\partial c_{\text{total}}}{\partial t} = \frac{\partial}{\partial z} (D \frac{\partial c_m}{\partial z}) \quad (1.109a)
\]

The solution of equation (1.109a) is impractical unless the functional relationship between the species concentration \( c_m \) and \( c_{\text{total}} \) is known. If local mobility and immobility are subject to kinetic transitions, no simple solution will be meaningful \cite{Garcia and Weisz, 1990}. The equilibrium relationships may give such information. For linear isotherms, the relationships between \( c_{\text{total}} \) and \( c_m \) at the boundary of a porous solid can be expressed by:

\[
c_{\text{total}} = Kc_o \quad ; \quad c_m = mc_o \quad (1.110)
\]

where \( K \) is the Henry adsorption equilibrium constant and \( m \) is the equilibrium ratio of the concentration of species in the mobile state within porous solid to that external to the boundary, \( c_o \). If we define a variable \( \phi(z) \) as the fractional depletion of concentration from the boundary with \( \phi = 1 \) at \( z = 0 \), equation (1.109a) can be rewritten as

\[
\frac{\partial \phi}{\partial t} = \frac{\partial}{\partial z} \left( \frac{m}{K} D \frac{\partial \phi}{\partial z} \right) \quad (1.109b)
\]

In diffusivity determinations based on the calculation of non steady state experimental responses, equation (1.109b) should be used instead of equation (1.109). We define the non - steady state diffusivity \( D_{ns} \) that differs from the intrinsic stochastic diffusivity \( D \), as

\[
D_{ns} = \frac{m}{K} D \quad (1.111)
\]

The whole mass transfer process of a gas molecule from the gas to the adsorbed phases in a porous solid with a bidisperse structure pore network in a flow system includes five distinct mechanisms of transport:

* Molecular diffusion: the adsorbate molecules in bulk phase come to the external film or to the pellet surface by molecular diffusion. When the diameter of macropore is large in comparison to the mean free path of the gas molecules, the mechanism of diffusion is also considered as molecular diffusion;
* Film diffusion: the adsorbate molecules on external surface of film permeate through the film and arrive to the surface of the pellets;

* Knudsen diffusion: the adsorbate molecules on external surface of pellets diffuse towards the pellet center via the macropores. The Knudsen diffusion occurs when pores are small in comparison to the mean free path of the gas molecules.

* Surface diffusion: the adsorbate molecules on external surface of pellets diffuse towards the pellet center via the macropore surface by the mechanism of surface diffusion. The surface diffusion results from molecules adsorbed on the surface of the pore that are subsequently transported from one site to another in the direction of decreasing concentration;

* Micropore diffusion: the adsorbate molecules in the macropore network diffuse towards the center of the microparticles.

* Convective flow: when there is a pressure difference between the inlet and the outlet along the bulk phase flow direction or when the adsorption and mass transfer rates are very quick there is a pressure difference between the pellet surface and the center region, then convective flow occurs.

The effective mass transfer parameter is thus a complex quantity which often includes contributions from more than one mechanism. Depending on the mass transfer systems including the adsorbate molecules, the pore network structure and the environmental conditions such as temperature, pressure and bulk phase flow rate, some of the above contributions, may be important. When there is no bulk phase flow, the film diffusion does not exist. Increasing the flow rate will reduce the film diffusion contribution to the total mass transfer resistance. The diffusion in porous media may occur by several different mechanisms depending on the pore size, structure, gas concentration and other conditions. In very fine pores, namely micropores such as the intracrystalline pores of zeolites and intraparticle micropores of molecular sieve carbons, the diffusing molecules never escape from the force field of the solid surface and transport occurs by an activated process involving jumps between adsorption sites (Kärger and Ruthven, 1992). While diffusion in larger pores, namely macropores such as the intercrystalline pores of zeolites and transport pores of molecular sieve carbons, the effect of the interaction potential field between the diffusing molecules and pore surface is weak and the diffusion can be considered as the motion of molecules inside a stiff and irregular shape pore. In the following section, some mass transfer theories for these steps are discussed.

4.1 Molecular Diffusion

When the pore diameter is much larger than the molecular mean free path or the mass transfer occurs in gas bulk phase resulting from a concentration difference, the diffusional process can be described by the molecular diffusion mechanism. Molecular diffusion results from molecular collisions. Randomly moving molecules collide with others and on collision, exchange such properties as energy and momentum and change their moving directions. The influence of the pore wall is minor and the diffusion occurs essentially by the same mechanism as in the bulk phase. The pore diffusivity for a straight cylindrical pore is then identical with the molecular diffusion. The derivation of an expression for the self-diffusivity of an ideal gas can be achieved by considering the relation between the mean free path $\lambda$ between molecular collisions and the theory of molecular velocity distribution (Kärger and Ruthven, 1992). The self-diffusivity $D_m$ is then (Present, 1958):
\[ D_m = \frac{3}{8\sigma^3} \left( \frac{kT}{p} \right) \sqrt{\frac{kT}{M\pi}} \] (1.112)

where \( \sigma \) is the molecular diameter, \( p \) is the pressure and \( M \) is the molecular weight. Equation (1.112) gives a good estimate of the self-diffusivities. There are some empirical and half empirical equations to estimate the molecular self-diffusivities of gases [Lee and Thodos, 1988]. For a binary mixture with different molecular weights, the dependency of \( D_m \) on \( M \) results in wrong conclusions in which the mutual diffusivities will strongly vary with the composition when the difference between the two molecular weights is large. In fact the binary diffusivities are nearly independent of the proportions of the two components in a wide range for most systems [Kärger and Ruthven, 1992].

For a binary mixture system composed of components A and B, when there is a concentration gradient, the microscopic random molecular movement results in a macroscopic net mass flux for A and B with direction opposite to the concentration gradient. The net mass flux for each component can be expressed by equation (1.107). Based on the molecular kinetic theory, there are a lot of semi-empirical correlations to predict the molecular diffusivities. Typically the Chapman-Enskog equation is well known for a binary mixture [Bird et al, 1960]:

\[ D_m = 0.0018583 \frac{T^{3/2} \left( 1/M_A + 1/M_B \right)^{1/2}}{P\sigma_{AB}^{2} \Omega_{AB}} \] (1.113)

where \( D_m \) is the binary molecular diffusivity (cm\(^2\)/s), \( T \) is the absolute temperature (K), \( M_A \) and \( M_B \) are molecular weights, \( P \) is the total pressure (atm), \( \sigma_{AB} \) is the kinetic molecular diameter of the Lennard-Jones potential energy function (Å) and \( \Omega_{AB} \) is the collision function. The molecular diffusivity is a function of temperature and pressure of the system.

### 4.2 Knudsen Diffusion

The original studies on Knudsen diffusion were limited to small holes in very thin plates and considerable detailed results were obtained [Knudsen, 1950]. The fundamental assumption of the Knudsen diffusion mechanism is that the molecules collide more often with the pore walls than with other molecules during the diffusive molecular passage through the pore. Upon collision, the molecules are instantly adsorbed on the surface and then are desorbed in a diffusive manner. As a result of the frequent collisions with the pore wall, the transport of the molecule is obstructed and molecules of different species move entirely independent of each other. The flux of molecules of any species through any pore is equal to the number of molecules of that species passing into the entrance of the pore per unit area per unit time multiplied by the probability that a molecule that enters the pore will eventually get all the way through and not bounce back to the entrance and out. This probability depends only on the geometry of the pore and on the law of reflection for molecules hitting the pore inner walls.

The Knudsen diffusivity \( D_K \) can be defined by means of the diffusional equation:
\[ J_K = -D_K \nabla C \quad (1.114) \]

where \( J_K \) is the flux and \( \nabla C \) is the gradient of concentration. \( D_K \) for a cylindrical pore can be predicted from the kinetic theory by relating the diameter of the pore and the mean free path of the gas by the expression [Smith, 1970]:

\[ D_K = 9700 \tau_p \sqrt{\frac{T}{M}} \quad (1.115) \]

Where \( \tau_p \) is the pore radius, \( T \) is the absolute temperature and \( M \) is the molecular weight. Knudsen diffusivity depends on temperature and pore size and is almost independent of pressure since the mechanism does not depend on the intermolecular collisions. The inverse square root dependence on molecular weight is the same as in the case of molecular self-diffusion.

4.3 Convection inside the Pores

When there is a pressure gradient in the pore, the diffusing gas acts as a continuum fluid driven by the pressure gradient and a continuous flow is produced. The computation of convective flow for gases is treated as in the case of liquids through the Poiseuille's law [Mason and Malinauskas, 1983]. For a gas not being accelerated, the net force on any element of it must be zero; the viscous - drag force just balances the force due to the pressure difference across the element. The result in terms of convective flux, \( J_{\text{conv}} \), can be expressed as:

\[ J_{\text{conv}} = - (\tau_B \omega / \nu) \nabla P \quad (1.116) \]

where \( n \) is the total number density, \( B_0 \) is the convective flow coefficient which is a characteristic constant of the pore geometry having units of cm², \( \nu \) is the coefficient of viscosity of the gas in g/cm-sec and \( \nabla P \) is the pressure gradient. The value of \( B_0 \) for a long, straight, circular capillary of radius, \( r \), is \( r^2/8 \) [Mason and Malinauskas, 1983]. For a porous media or a bed of packed particles it is usually much easier to determine \( B_0 \) than to calculate it from geometrical considerations. In such cases equation (1.116) works as an empirical result known as Darcy's equation.

For mixtures, because the coefficient of viscosity \( \nu \) is independent of gas pressure at constant temperature [Cowling, 1950], the convective flux of component \( i \) is proportional to its mole fraction \( x_i \) in mixture, since the flow is nonseparative [Mason and Malinauskas, 1983]

\[ J_{\text{conv},i} = x_i J_{\text{conv}} \quad (1.117) \]
4.4 Surface Diffusion

All above transport mechanisms involve the transport through the fluid phase in the central region of the pore. If there is significant adsorption on the pore wall, there is the possibility of an additional flux due to diffusion in the adsorbed phase. When adsorbed molecules are mobile on the surface of the adsorbent pores, there is a migration flow of adsorbate along the pore surface. The mechanism of surface diffusion is still not very clear and the rates of diffusion by this way can not be predicted well. There are a couple of theories to try to describe quantitatively surface diffusion.

Fluid phase diffusion expressed by Fick’s law has been used to deal with surface diffusion with a concentration dependent surface diffusivity [Chen and Yang, 1991 and Kapoor and Yang, 1991] and a hydrodynamic model in which surface diffusion can be explained as a flow at the outer layer of a condensed phase (adsorbed phase) [Everett and Stone, 1958].

Another one is the activated energy model in which surface diffusion is considered as an activated process depending on surface and molecular characteristics [Smith and Metzner, 1964]. When a molecule in gas phase strikes the pore wall and is adsorbed, there are two possibilities: desorption into the gas (Knudsen diffusion) or movement to an adjacent active site on the pore wall (surface diffusion). If desorption occurs, the molecule can continue its journey in the void space of the pore or be readorsbed by again striking the wall. This model is based on the kinetic study of the hopping movement of adsorbed molecules along a solid surface. For a single component system under thermodynamic equilibrium described by the adsorption isotherm, the adsorbed molecules migrate along the adsorbent surface by means of small hops. In order to hop a molecule need an activation energy to move from an adsorbed state to another. The average concentration gradient in the adsorbed phase resulting from the hops in random directions yields a net flux opposite to the concentration gradient direction. The relative contribution of surface diffusion increases as the surface area increases.


The relative importance of surface diffusion to total transport flux can be estimated from the pore properties and adsorption characteristics of pore surface [Birnboim et al, 1984, Prauser et al, 1985, Rieker, 1985 and Yao, 1990]. A significant contribution from surface diffusion requires that the flux within the surface adsorbed layer be comparable with the flux in the gas phase within the pore. Since the mobility of the surface adsorbed species is generally much lower than that of the gas, a significant surface flux can occur only when the adsorbed layer is thick enough to compensate for the lower mobility. The thickness of the adsorbed layer decreases exponentially with temperature so one may expect that significant surface diffusion can occur only up to temperatures not too much higher than the boiling point of the adsorbate.
4.5 Combination of Various Diffusional and Flow Mechanisms

The above discussed four mass transport modes in porous solids can occur in all sorts of combinations and the problem is to discover how to combine the individual mathematical descriptions in a unified way.

First, the molecular and Knudsen diffusion combination is considered. The relative importance of molecular and Knudsen diffusion in porous solids is determined by the ratio of the pore diameter to the mean free path of the gas molecule. When the pore diameter is greater than ten times the mean free path, molecular diffusion will be dominant. On the contrary, Knudsen diffusion prevails when the mean free path is smaller than ten times the pore diameter. Both diffusion processes are important when the mean free path and pore diameter are of the same order of magnitude. In this situation the diffusivity can be represented by the combination of molecular and Knudsen diffusivities as an effective diffusivity [Scott and Dullien, 1962]

\[
D_e = \frac{1}{\left[ 1 - \left( 1 + \frac{J_B}{J_A} \right) \right] x_A/D_{mi} + 1/D_{Ki}} \quad (1.118)
\]

where \(D_e\) is the effective diffusivity and \(J_A\) and \(J_B\) are the mass fluxes of species A and B and \(x_A\) is the mole fraction of component A. For equimolar counter diffusion \(J_A = -J_B\), and the equation (1.118) reduces to the simple reciprocal addition law:

\[
D_e = \frac{1}{1/D_{mi} + 1/D_{Ki}} \quad (1.119)
\]

If a gradient of total pressure exists, the convective flux must be considered. In contrast to the molecular and Knudsen diffusions, the contributions from convective flow and diffusion are directly additive. The reason for this additivity follows from kinetic theory where there are no convective flow terms in the diffusion equations and also no diffusion terms in the convective flow equations. The two are entirely independent in the sense that there are no direct coupling terms in these equations [Mason and Malinauskas, 1983]. Similarly, the surface flux is also considered and added to the diffusion flux. This additivity is harder to justify than the additivity of the convective flow. Usually it is recognized as a physical assumption. Finally, the total flux including these four contributions for a binary system can be written as:

\[
J_i = -D_{ei} \left[ 1 + \frac{D_{1s}}{D_{ei}} + x_i \frac{D_{1s} - D_{2s}}{D_{mi}} \right] \nabla \rho_i + x_i \delta_i J - x_i \gamma_i \left( \frac{n_i B_0}{v} \right) \nabla P + \frac{x_i}{kT} \left( \frac{D_{2s}}{D_{mi}} \right) \nabla P \quad (1.120)
\]

Where \(D_{ei} = \frac{1}{1/D_{mi} + 1/D_{Ki}}\), \(\delta_i = \frac{D_{Ki}}{D_{Ki} + D_{mi}}\), \(\gamma_i = 1 - \delta_i\)

44
A similar equation holds for $J_2$

$$J_2 = -D_{c2} \left[ 1 + \frac{D_{2S}}{D_{c2}} + x_2 \frac{D_{2S} - D_{1S}}{D_{m1}} \right] \nabla n_2 + x_2 \delta_2 J - x_2 \gamma_2 \left( \frac{nB_o}{\nu} \right) \nabla P + \frac{x_2}{kT} \left( \frac{D_{m1}}{D_{m2}} \right) \nabla P$$

(1.121)

with corresponding definitions of $D_{c2}$, $\delta_2$ and $\gamma_2$.

A complete phenomenological description of isothermal diffusion and flow in a binary mixture over the whole pressure range is given by equations (1.120) and (1.121). These equations exhibit different behavior as different transport mechanisms dominate. The relevance of surface diffusion is explicitly exhibited as the ratio of surface diffusivity to the other diffusivities. Apart from surface diffusion, the behavior in various regions is manifested through the pressure dependence of $D_{c1}$, $\delta_1$ and $\gamma_1$. At very low pressure, $\delta_1 = 0$ and $\gamma_1 = 0$ so $D_{c1} = D_{K1}$. While at high pressure, $\delta_1 = 1$ and $\gamma_1 = 0$ so $D_{c1} = D_{m1}$. The behavior in the transition region shows explicitly that the convective flow term $\left( \frac{nB_o}{\nu} \right) \nabla P$ is only important in the transition region. It vanishes in the Knudsen diffusion region and in the molecular diffusion region is dominated by the term involving $J$ [Evans and Song, 1973].

The main difficulty arises with coupled flow and diffusion, which is nonlinear when the total flux is large. To illustrate the problem, a binary mixture system at constant temperature undergoing simultaneous convective flow and molecular diffusion can be considered (in order to simplify the discussion, the Knudsen diffusion is neglected). The flux equation for component 1 becomes:

$$J_1 = -D_{m12} \frac{\partial c_1}{\partial z} + x_1 J$$

(1.122)

At steady state, $J_1$ and $J$ are constant along the pore length; when $D_{m12}$ is independent of the concentration, equation (1.122) can be integrated over the length of a single pore to yield [Mason and Manilaukas, 1983]:

$$J_1 = x_1^0 J - \frac{J (x_1^1 - x_1^0) \exp(JL/D_{m12}) - 1}{\exp(JL/D_{m12}) - 1}$$

(1.123)

where $x_1^0$ and $x_1^1$ are the mole fractions at the entrance and exit respectively. Clearly $J_1$ is not linear in $J$, so the addition of the fluxes through a collection of pores to find the total flux leads to an equation of apparently radically different form. A nonlinear term results in the denominator.
4.6 Influence of Pore Geometry

The above molecular and Knudsen diffusional processes are related to a straight cylindrical pore structure with unisized diameter. In practice, the commercial adsorbents and catalysts have a much more complex structure composed by an interconnected pore network with variable pore diameter and pore size distribution. Alumina, activated carbon and silica gel have a continuous pore size distribution from several Å to thousands of Å [Suzuki, 1990]. The pore shape is also difficult to be represented by a simple geometric parameter. Both the pore shape and connectivity will affect the diffusion process of molecules in porous media [Ballal and Zygorakis, 1985]. The definition of an effective diffusivity by considering these effects is obviously meaningful. As an example, for a simple three dimensional pore network composed of an elemental unit formed by a spherical cavity with two symmetric pores, the effective diffusivity will vary from the neck to cavity due to the variable pore size. Quantitative results for this case were given by Ballal [Ballal and Zygorakis, 1985]. A detailed pore structure for a practical porous material can not be measured with any certainty by today’s experimental techniques. The ordinary experimental techniques only give the information on porosity, the relative pore size distribution and the specific surface area. In order to describe quantitatively the effective pore diffusivity from transient experimental data and limited pore structure information, usually, an empirical parameter describing the pore structure characteristics is introduced.

The complex pore structure is idealized as a cylindrical pore with a unisized pore diameter, the average pore diameter. The difference between the calculated pore diffusivity by the unisized cylindrical pore diffusional formula and that one obtained from transient experimental data are set by an adjustable parameter $\chi$:

$$D_e = \chi D \quad (1.124)$$

The parameter $\chi$ is usually divided into two parts: the contribution of porosity $\bar{\sigma}$ and the contribution of the increase of the diffusing path and geometrical shape variation $\tau$ (tortuosity).

$$\chi = \frac{\bar{\sigma}}{\tau} \quad (1.125)$$

$\tau$ is basically an empirical parameter. There were a few papers where it was tried to relate with porosity [Yang and Liu, 1982] that successfully predicted some systems. The typical values of $\tau$ are 2 - 6 for alumina and silica gel [Satterfield, 1970], but some published papers showed that they may be greater than 100 [Yang and Liu 1982]. In principle $\tau$ depends on the diffusing molecule, pore connectivity, pore size distribution, porosity and should be independent of temperature.

As an improvement, a parallel pore model was proposed [Johnson and Stewart, 1965]. The real pore structure was simplified by an array of parallel cylindrical pores with varying
pore size and the average diffusivity can be directly calculated from the molecular and Knudsen diffusivities by integrating the Knudsen diffusivity and pore size distribution function from zero to infinity:

$$\bar{D} = \int_0^\infty D_K(r) f(r) \, dr$$

(1.126)

where $D_p(r)$ can be calculated by equation (1.110) and $f(r)dr$ is the pore distribution function between $r$ and $r + dr$. By this definition, the tortuosity, $\tau$, can be represented by:

$$\tau = \frac{\bar{D}}{D_e}$$

(1.127)

The equation is thus a measurement of the error that is likely to be involved in applying the assumption of effective homoporosity to such a heteroporous situation, that is, in replacing the sum of the terms by a single effective term. To investigate this problem, the steady state isotherm binary diffusion in the molecular diffusion region is usually adopted. Although this is not the most general case, it is one of the worst cases possible. Somewhat surprisingly, it turns out that the maximum relative deviation from homoporous behavior results obtained from pore distribution are only moderately large and thus most distributions introduce only small errors [Wendt et al, 1976]. So the heteroporosity can be assumed to be equivalent to an effective homoporosity [Chen and Rinker, 1979]. This is true as long as the fluxes are linear in the overall concentration or pressure range, but not otherwise. In combined flow and diffusion, the species fluxes are a nonlinear function of the total flow or pressure difference and this assumption fails. For parallel pores with different cross-section geometry and different lengths, the analytical and numerical computation of diffusion and flux shows that results are within 4% error in fluxes [Mason and Malinauskas 1983] using the effective homoporosity to replace the heteroporous situation.

4.7 Macropore Diffusion Theories

Due to its importance in theoretical studies, process development and design involving mass transport on porous solids, a model is necessary for the calculation of an effective diffusivity. Several models have been proposed: random walk model [Karger and Ruthven, 1992], effective medium theory [Kirkpatrick, 1973, Sahimi and Hughes, 1983, Benzioni and Chang, 1984, Bugaros and Sotirchos, 1987 and Kapoor and Yang, 1990] and the dusty gas model [Jackson, 1977 and Mason and Malinauskas, 1983].

In the random walk model, the simplest case is a one dimensional system. The diffusing molecule moves in two directions with equal probability and each step length is ± z. When the time (t) between two jumps or the jumps frequency (1/t) is a constant, the self diffusivity can be calculated by using Einstein formula
\[ D = \frac{z^2}{2t} \quad (1.128) \]

For two and three dimensional systems, only one - half and one - third of the jumps occur in a given direction and thus the factor of \( \frac{z}{2} \) in equation (1.128) is changed into 4 and 6 respectively. The step length (z) and frequency (1/t) can be estimated and measured from the pore structure and interactions among diffusing molecules and between diffusing molecules and pore atoms. For complex practical pore networks, the diffusion pores are composed of different sizes, lengths, interaction potential energy fields and intersecive pores and the step length (z) and frequency (1/t) may not be constant and even the walk of a diffusing molecule may have a somewhat preferential bias in some special directions at the beginning of each walk. For example, in a two dimensional square pore network, when in one of the four neighboring nodes there is a diffusing molecule, the jumping probability of a diffusing molecule in the central node along this direction will be smaller than along other three directions. The random walk diffusion theory has been widely applied to the zeolitic intracrystalline diffusion systems since the regular structure of zeolite crystals results in that the micropore networks are also regular and can be well represented spatially. The detailed discussion about this topic, will be carried out in the Chapter III.

The effective medium approximation is a useful method to represent the effective diffusivity in complicated pore networks using some reasonable assumptions for the network. The effective medium theory assumes that a practical heterogeneous pore system can be represented by an equivalent homogeneous medium. In practice two and three dimensional pore networks can be related to the corresponding two and three lattice systems. The diffusion process is focused on a lattice cell whose structure is the minimum repeating unit for forming the whole pore network. Burganos and Sotirchos [1987] shown some basic lattices. The molecular and Knudsen diffusion theories and the convective theory can be directly applied to the subpores of the lattice. The relationships of various fluxes in the subpores of the lattice can be simulated by the corresponding electric circuits.

In the dusty gas model, the solid is considered as a dummy species of very massive molecules constrained by unspecified external forces to have zero drift velocity. The gas kinetic theories are used to the mixture of n components of true gases and the pseudo gaseous component [Mason and Malinauskas, 1983]. The dusty flux is set to zero by a momentum balance. When the concentration of dust increases, the diffusion varies from the molecular diffusion to Knudsen diffusion. Because the pore structure and size distribution factors are not included in the theory the model can not reflect the pore geometry effects on the transport properties.

### 4.8 Micropore Diffusion Theories

All previous discussions on diffusion in porous solids are limited to the case where the pore size is much larger than the molecular dimensions. The pore dimensions of catalyst supports and adsorbents such as zeolites and molecular sieve carbons where the catalysis and adsorption occur are of the same magnitude as molecular dimensions. In such micropores, the motion of diffusing molecules is greatly influenced by the interaction potential energy field due to the presence of the pore wall atoms. In small pore zeolites the free aperture of the window is only slightly greater than the critical diameter of the adsorbate molecule, the activation energy correlates directly with critical molecular diameter which suggests that the rate limiting step should be the passage of the molecule
through the window. In diffusion of gases in zeolite 4A the passage through the window is hindered by a significant repulsive barrier due the presence of a cation and the diffusional activation energies are typically several kcal/mole. From the statistical point of view, there is a translational kinetic energy distribution for each adsorbate molecule inside zeolite cavities. Only these molecules whose kinetic energies exceed the repulsive energy barrier located at the window plane can move to the next cavity.

When the pore dimension is in the range of the diffusing molecule size, the migration of the molecule is strongly influenced by the interaction potential energy between the molecules and the atoms of the pore walls. One of the characteristics of such diffusion is that there is a diffusional energy barrier usually called activation energy, $\mathcal{E}$. Only these molecules with average kinetic energy greater than the potential barrier can migrate from one adsorbed site to the adjacent one. According to the Boltzmann kinetic energy distribution [Bird et al., 1960], the average kinetic energy of a molecule is independent of the interaction potential field and depends on the motion degrees of freedom and on the environment temperature. The functional relationship of each motion degree of freedom with temperature can be expressed as $kT/2$. The corresponding micropore diffusivities are usually conformed to the Arrhenius equation for temperature independent activation energy:

$$D = D^* \exp(-\frac{\mathcal{E}}{RT})$$

(1.129)

where $D^*$ is a temperature independent constant. When the size of micropores is close to the size of the adsorbate molecules, the molecular diffusion in such micropore is affected by the strong interaction between the adsorbate molecules and adsorbent atoms. The migration rate of adsorbate is usually an activated process heavily related to the interaction properties.

For zeolite and carbon molecular sieve adsorbents the adsorption and catalytic active surface is mainly the interior surface of crystals and micropores. The exterior surface of crystals and macropores is negligible when compared with the interior surface. In such porous solids the mass transport processes should include two steps. The molecules in the bulk phase diffuse first into intermicroparticle pores and then into intramicroparticle pores.

Because of the complexity of the interaction potential energy between diffusing molecules and atoms of the pore wall, the theoretical prediction of micropore diffusivities is very limited. Although micropore diffusion in zeolites and carbon molecular sieves has been widely studied, the primary objectives of micropore diffusion studies were focused on the correlation and explanation of experimental results. The data from published literature is a little confusing. The micropore diffusivities obtained by different experimental methods show big differences. Kärger reviewed and gave some reasonable explanation on the differences in experimental results [Kärger and Ruthven, 1989]. In the Chapter III, the diffusion of gases in zeolite A will be discussed in detail.
5 EXPERIMENTAL TECHNIQUES FOR MASS TRANSFER PARAMETER DETERMINATION

Because of the complexity of the pore network structure of practical porous solids, the existing theories for describing and predicting the mass transport mechanisms and parameters still rely greatly on experimental information. The experimental factors related to pore structure can be used to identify pore structure properties such as pore volume, pore dimensional distribution and specific surface area and examine the validity of the theoretical approximation to a practical pore structure. While the experimental results for mass transport parameter determination can provide important information to understand the mass transport mechanisms, to check the correctness of mass transport models and are helpful to process development, design and optimization of operating conditions.

The experimental means for determining the pore structure include pore size distribution by adsorption - desorption and mercury porosimetry and surface area by nitrogen adsorption. The principle of adsorption - desorption measurement of the pore size distribution is based on the observation that the saturation vapor pressure of a liquid increases on a concave surface. When a porous solid is exposed to an adsorbate vapor, the molecules in the vapor phase will partially condense in small pores. When the pore radius decreases the condensation amount increases. The relationship between the saturation pressure, \( p \), of the curved interface and that, \( p_o \), of the flat liquid interface is given by the Kelvin equation (White, 1990):

\[
\ln \left( \frac{p_o}{p} \right) = \frac{2 \kappa V \cos \eta}{r_m R} \quad (1.130)
\]

where \( r_m = 1/r_1 + 1/r_2 \) is the mean radius of curvature for a cylindrical pore (radius is \( r_1 \)) with a spherical closed - end (radius is \( r_2 \)), \( \kappa \) is the surface tension, \( V \) is the adsorbate liquid molar volume, \( R \) is the gas constant and \( \eta \) is the contact angle of the meniscus with the solid. For an open - pore at both ends, \( r_m = r_1 \). When the gas pressure is changed, the condensation amount varies and the average radius of the pore where the adsorption or desorption takes place at each pressure can be obtained from the Kelvin equation. Because there is a neck effect in which the desorption curve is always higher than the adsorption curve in the plots of adsorbed amount against pressure, the calculated results will be different when using the adsorption or the desorption curve. Generally, the desorption branch of isotherms has been used to relate the incremental amount of adsorbate vapor removed with an incremental decrease of the pressure above the sample. In typical experiments, the porous solid is saturated by the adsorbate vapor and the pore is filled with \( p_o/p \) at the beginning of the experiment. The pressure is lowered slightly to a new value and the desorbed amount, the negative volume increment, \( \Delta V \), which is out of the pores is measured by monitoring the change of solid weight or adsorbate volume in gas phase. For this new relative pressure, the radius of the pore remaining full is determined by the Kelvin equation (1.130). The difference in radii for these two relative pressures is calculated as \( \Delta r \). The differential pore size distribution is represented by the ratio \( \Delta V/\Delta r \). The most common used adsorbate is nitrogen and the operating temperature is set to the nitrogen boiling point (77 K). When the pore is within the range of micropores, the state of adsorbate molecules in the adsorbed phase loses the meaning of gas or liquid and thus the Kelvin equation is no longer valid. When the pore is large, the
condensation effect is small. The adsorption - desorption technique is suitable to determine the pore size distribution with pore sizes in the range of 10 - 250 Å [Yang, 1987].

When the pore size is greater than 100 Å, an alternative procedure with the mercury intrusion technique can be used. The basic principle is that the non-wetting liquid, mercury, is forced to fill the pore volume. The force size is proportional to the pore size and thus pore size fraction at each force can be evaluated. From the interface theory the force required to fill a pore with pore radius, r, is \( \pi r^2 \rho \) and the resistance force to compensate the intrusion force results from the surface tension force and is given by \( -2\pi k \cos \eta \). At the equilibrium state these two forces must be balanced and this yields the equation to relating the pressure \( p \) and pore size [White, 1990]

\[
p = -\frac{2\pi k \cos \eta}{r} \tag{1.131}
\]

The experimental procedure is simple. The solid sample is put into a vessel and the zero penetration volume just at the beginning of the process is registered. The pressure acting on the mercury is changed continuously and the mercury volume variation is recorded. Finally, a continuous curve of mercury intrusion volume against pressure can be obtained and thus the pore size distribution can be calculated. This method is limited by the pore stability. For most systems equation (1.131) can be simplified into \( r = \frac{75000}{p} \) (pressure is in atm and \( r \) in Angstrom). For the determination of pores with radius less than 21 Å, pressures as high as 3570 atm are required. At such high pressure, the original pore structure may be already destroyed. The reliable range of pore sizes determined by this method is for pore diameters greater than 100Å [Yang, 1987].

In the case of solids such as zeolites, the micropore dimension is uniform and determined by the crystal structure. The micropore size measurement is carried out by using adsorbate molecules with different dimensions and examining the corresponding adsorption equilibrium and kinetic behavior. For a series of adsorbate molecules the maximum adsorbed molecular dimension is regarded as the micropore size. The cross section dimension is considered for linear adsorbate molecules. The ability of an adsorbate molecule to diffuse through a pore such as the blocked window of 4Å zeolite, is dependent on the adsorbate molecular kinetic energy; some critical molecules hardly diffuse through the pore at low temperature and it may be possible that the molecule can diffuse through the same pore when temperature is raised.

The specific surface area (the pore surface area per unit solid volume) is determined from the adsorption isotherms of nitrogen at the temperature of the nitrogen boiling point (77 K) by the BET isotherm equation correlation. The BET equation has the following form:

\[
\frac{p}{a(p - p_0)} = \frac{1}{a_m c} + \frac{c - 1}{a_m c} \frac{p}{p_0} \tag{1.132}
\]

where \( a \) and \( a_m \) are respectively the adsorbed amounts at \( p \) and at monolayer capacity and \( c \) is a constant. The constant \( c \) and \( a_m \) can be obtained by regressing the experimental isotherm of nitrogen. The surface area is taken as the area for monolayer coverage based on the nitrogen molecular area (16.2 Å²) calculated by assuming liquid density and

51
hexagonal close packing [Yang, 1987]. It should be mentioned that the concept of specific surface area for microporous solids is not clear, specially for the zeolites since the intracrystalline pore size of zeolites is close to the nitrogen molecular dimension and there is no meaning for the monolayer adsorption.

Based on the measurement principle the experimental techniques usually used for determining the transport parameters of gases in porous solids can be classified into two types: microscopic and macroscopic methods. In the microscopic technique, the characteristics of molecular motion are directly measured by means of some special instruments. The macroscopic mass transport parameters can be related to the measured microscopic parameters by some physical and chemical laws. The most commonly microscopic technique is the Nuclear Magnetic Resonance (NMR) with Field Gradient (PFG) [Kärger and Caro, 1977]. In the macroscopic experimental techniques, a macroscopic quantity that changes with time, such as concentration, flux, weight or volume is monitored. The mass transport parameters can be estimated by solving the corresponding mass transport equations. In this type of methods, the determined mass transport parameters are usually dependent on the choices of mass transport equations since the mass transport parameters exist in the mass transport equations as parameters and the relations between experimentally measured variables and mass transport parameters are linked through a set of differential equations called mass transport models. So the mass transport parameters obtained for a system may vary with different experimental processes and mass transport models. Because the macroscopic approaches directly determine the macroscopic quantities and the experimental conditions can be set close to industrial process conditions the results are usually more easily accepted by the requirements of practical process development and design. The adsorption equilibrium data of gases can be obtained simultaneously with the measurement of the mass transport variables in these macroscopic experimental techniques.

5.1 Nuclear Magnetic Resonance Methods (NMR)

Nuclear magnetic resonance (NMR) technique is a rapid, convenient and reasonably accurate method for the determination of macropore and micropore diffusivities. This method has the advantages that it is possible to measure the diffusivities over several orders of magnitude and since there is no need to set up and maintain a concentration gradient and only a small quantity of sample is required, the control of the temperature and pressure is relatively straightforward and can be made as exact as necessary. Originally, it was used to determine liquid phase diffusivities [Tyrrel and Harris, 1984]. There are a number of variants of the method which may be adapted to particular experimental requirements. The commonly used variant for the determination of the gas diffusivities in porous media is the pulse field gradient (PFG). In this method the migrating molecule displacement over a mean distance at a given time interval can be directly measured. According to Einstein formula, the self-diffusivity can be calculated.

The determination of gas effective self-diffusivities in the macropores is easy to be applied and is similar to the liquid systems since the order of magnitude of the effective diffusivity of gases in macropores is close to that of the liquid phase diffusivities. The application of this technique to the determination of micropore diffusivities (intracrystalline diffusivity of zeolites) is somewhat difficult because the diffusivities in micropores are usually much smaller than these in the liquid phase. This means that the use of NMR-PFG requires a large magnetic field gradient. When the diffusion rate is very low, the requirement on the strength of the magnetic field gradient will be beyond the practical limit of the experimental apparatus [Kärger and Caro, 1977, Kärger and Pfeifer, 1989 and Kärger and Ruthven, 1992].
5.2 Macroscopic Experimental Techniques

Based on the bulk phase motion states, the macroscopic experimental methods can be divided into static and dynamic types. In the static methods, there is no gas phase flow. The mass transport rate into porous solid can be expressed by the pressure, concentration and volume changes of bulk phase and solid weight with time. There is a bulk phase flow in the dynamic techniques. The mass transport rate into porous solid is related to the concentration changes between the inlet and outlet. The quantity accumulated inside the solid can be calculated by making a mass balance. In the dynamic techniques the bulk phase flow is helpful to release the heat resulting from adsorption. However, the flow gives rise to more complexity on mass transport parameter estimation.

A. Static Experimental Measurements

In the static techniques, the bulk gas is kept stationary relatively to the solid sample. At time zero, an incremental concentration step of bulk phase is introduced and the existing equilibrium between the adsorbent and adsorbate is broken. The system tends to a new equilibrium. Theoretically, both positive and negative increments of concentration steps can be used. Taking into account the serious tailing for very strong adsorption systems, the negative increment is less used. The mass transport rate into or out of porous solids can be directly related to the experimental measurable changes including: (i) the change with time of the volume of gas around the solid with the condition of constant pressure (constant pressure method); (ii) the change with time of the pressure of gas around the solid with the condition of constant volume (constant volume method); (iii) the change with time of the weight of solid bathed in a constant pressure and volume (gravimetric method).

The mass transport process can be described by the Fick’s second diffusion law (or called mass balance differential equations). For different particle geometric shapes the corresponding equation forms are different, the simplest case is when the diffusion takes place into an isotropic spherical porous solid particle with uniform particle radius \( R_0 \) and mono-disperse pore structure (the solid particle does not contain another small and independent porous subparticle with different pore size distribution); the diffusion equation with the assumption of constant diffusivity has the following form:

\[
\frac{\partial c}{\partial t} = D \text{ div } \text{ grad } c
\]

Depending on the experimental conditions (constant pressure or volume), there are corresponding boundary conditions on the particle external surface. The constant pressure case is simple since constant pressure is equivalent to constant total concentration. The mathematical expressions for initial and boundary conditions are:

I.C. \( t = 0, \ c = c_0 \)

B.C. \( r = 0, \frac{\partial c}{\partial r} = 0; \quad r = r_0, \ c = c_\infty \)

(1.134)
where \( c_{\infty}, c \) and \( c_0 \) are respectively the adsorbate concentrations at the particle external surface, inside the particle at \( t = t \) and at \( t = \infty \). Equations (1.133) and (1.134) can be solved by a variable separation method. The solution gives the relation among the concentration, \( c, \) position, \( r, \) and time, \( t. \) Because the concentration is dependent on the position and is difficult to measure experimentally, the solution function is integrated along the \( r \) direction to obtain the adsorbed amount at time \( t = t \) which is a measurable variable. Finally, the solution has the form expressed by the adsorbed amount as a function of time [Crank, 1975]

\[
\frac{m_t}{m_{\infty}} = \frac{a_t - a_o}{a_{\infty} - a_o} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left( \frac{\pi^2 D t}{r^2} \right)
\]

(1.135)

where \( m_t \) and \( m_{\infty} \) are the incremental adsorbed amounts at \( t = t \) and \( t = \infty \) with a concentration step, \( a_o, a_t, \) and \( a_{\infty} \) are the absolute adsorbed amounts at \( t = 0, t = t \) and \( t = \infty, \) respectively.

Alternatively, the diffusion can occur under constant volume / variable pressure conditions. At \( t = 0, \) an extra amount of gas is introduced into the system and allowed to equilibrate with the solid. When the Henry law governs the equilibrium, the final solution is [Crank, 1975]

\[
\frac{m_t}{m_{\infty}} = 1 - \frac{6 K (K + 1) \exp \left( \frac{-h^2 D t}{r_0^2} \right)}{9 \left[ (K + 1) + \alpha_n^2 K^2 \right]}
\]

(1.136)

where \( K \) is the equilibrium constant and \( \alpha_n^2 \) is the \( n \) th positive root of equation

\[
\tan \alpha = \frac{3 \alpha}{3 + K \alpha^2}
\]

(1.137)

These equations are only valid for spherical particles with uniform isotropic pore structure and constant diffusivities. For other regular simple geometric forms, there are similar solutions [Crank, 1975]. For the porous solid with a bidisperse distribution the solution can also be obtained analytically [Ruckenstein et al., 1971].

It is difficult to obtain particles with uniform shape and size. A size distribution among the particles will distort the experimental plots of \( m_t/m_{\infty} \) against \( t \) as compared with the plot for uniform particles. The curve will initially increase more rapidly ( an effect due to the smaller than average particles ) and finally will increase less rapidly ( because of the larger than average particles ), than the particles with uniform particle size [Kärger and Ruthven, 1992].

The experimental technique to determine intraparticle or micropore diffusivities by these methods is straightforward. The experimental observable variable, the adsorbed amount,
m, needs to be measured accurately. Specially when diffusivity is strongly dependent on concentration, great adsorption heat effect and poor heat releasing, it is desirable that the experimental measurement is carried out over a differential concentration step so that the corresponding adsorbed amount also has a small change. Among the adsorbed amount measurements, the weight change measurement at constant volume and pressure has more advantages [Ruthven, 1984]. First, at the conditions of constant volume and pressure, the experimental data treatment is easy; second, the measurement accuracy of the weight change can be very high. The weight method is limited by the buoyancy force effect and thermal convection of bulk phase when the sample temperature is quite different from the environmental one and bulk phase pressure higher than the atmosphere. So the weight method is suitable for measurements under vacuum. The corresponding experimental apparatus includes a reservoir with relatively large volume in order to keep the pressure approximately constant during a concentration step. By matching the experimental uptake curve to the transient solutions of the diffusion equation the intraparticle diffusivities can be obtained. The validity of the isothermal diffusion model may be confirmed by varying the particle size and the concentration step.

When the porous solids have bidisperse pore size distribution, the experimental data treatment is complex. When the diffusional rate in micropores is much slower than in macropores, the case can be treated in the same way as for the mono-disperse pore size distribution. The most serious disadvantage of static experimental techniques is the adsorption heat releasing rate. The slow releasing of adsorption heat results in a temperature rise of the solid sample and thus the concentration on the external surface of the particle varies due to the adsorption equilibrium constant change and the diffusivity also varies during a concentration step. Theoretically, the static method is mainly applied to systems with slow diffusion rate which reduces the adsorption heat production rate and decreases the effect of heat on the diffusional process.

The adsorption isotherm can be obtained simultaneously by collecting the adsorbed amount at time $t = \infty$ and the corresponding bulk phase concentration. When there is no any inert component in bulk phase, the determined diffusivity is a self-diffusivity.

B. Diffusion Cell Techniques

The diffusion cell technique [Hashimoto and Smith, 1974, Dogu and Smith, 1975 and 1976, Burghardt and Smith, 1979, Cresswell and Orr, 1982, Allawi and Gunn, 1987, Biswas et al, 1987, Alqobah et al, 1988, Jahnke and Radke, 1989 and Patwardhan and Mann, 1991] for determining the effective intraparticle diffusivity of a single particle with a mono-disperse pore size distribution is easy to understand. The particle sample is either sealed into or supported within a custom built cell. The concentration of an adsorbate gas is measured as a function of time at the cell entrances and exits located at both sides of particle, following the imposition of a concentration disturbance upstream the cell entrance. The pressure difference between both sizes of the diffusion cell should be kept at zero in order to eliminate the convective mass transport contribution. When the mass transport reaches equilibrium, the flux in any section area along the gas flow direction should be equal. From the concentration difference between the two sizes of the diffusion cell, the effective diffusivity can be readily obtained. By making a mass balance between the inlet and outlet streams, the accumulated amount inside the solid and thus the adsorbed amount can be obtained. The adsorbate isotherm can be measured by changing the inlet concentration and noting the corresponding adsorbed amount. The method has the advantage that it depends on a steady-state measurement and it is not affected by finite heat transfer. Effective intraparticle diffusivities determined in this way are commonly somewhat smaller than the value derived for the same adsorbent under similar conditions from
transient uptake curve rate measurements. This is because of the presence of blind pores, which contribute to the flux in a transient measurement but make no contribution in a steady state diffusion cell system. In principle, the effective bulk phase diffusivity can be determined by packing uniform size particles in the cell. The method is in principle also applicable to the measurement of micropore or intracrystalline diffusivities, but the difficulties of mounting and sealing a single small zeolite crystal tend to prevent such applications. However, these difficulties have been overcome and the results of two studies have been reported in which diffusion through a single (100 μm) zeolite crystal, mounted in a metal plate, was measured by this method [Paravar and Hayhurst, 1984 and Hayhurst and Paravar, 1988].

For porous solids possessing bidispersed pores, the steady state exit concentration responses at both sides of the diffusion cell can only be used to calculate the macropore effective diffusivity since micropore diffusion does not make any contribution to the steady state concentration responses. In order to describe the mass transport behavior of a diffusing gas in both pore types, the mass transport model must include macropore diffusion and micropore diffusion equations. These two types of equations are related by the boundary conditions of the diffusing gas concentrations at the macropore wall. The experimental transitory behaviors at the exits of both sides of the diffusion cell are recorded and the effective diffusivities are then determined either by matching moments of a suitable mathematical model of the cell with the observed moments, or by directly fitting the analytical or numerical solutions of the model in time domain. The detailed information of the mass transport model and matching technique will be discussed later. Because there is a saturation with carrier gas before experiment the determined diffusivities are counter-diffusivities.

The advantages of diffusion cell technique are the experimental simplicity, no heat effects and the possibility of choosing the experimental conditions close to practical process operating conditions. The diffusion cell technique applies to single particles. When the micropore diffusion resistance is much less than the macropore resistance, the transitory response curves are mainly determined by the macropore diffusion and it is difficult to obtain the micropore effective diffusivity by matching the experimental responses to the model responses. Reducing the thickness of the solid can decrease the macropore diffusion resistance.

By setting a pressure difference between the two sides of the diffusion cell, the convective contribution to the total mass transport rate can be estimated [Dogu et al, 1989 and Biswas et al, 1987]. From Darcy equation we know that the convective mass transport through a porous particle is dependent on the pressure difference. In the two side entrances of the diffusion cell pure component diffusing gas with known flow rate is respectively introduced and the steady state flow rates at the exits of both sides are noted. Comparison of the flow rates at exits of both sizes can give the total flux through the particle. If the diffusivity is known, the convective flux can be calculated and thus the permeability of the porous solid can be obtained.

C. Chromatographic Technique

The most widely used method for quick determination of the effective diffusivity over a wide range of experimental conditions is the chromatographic technique [Haynes 1975, Gangwal et al, 1978 and 1979, Cresswell and Orr, 1982, Chiang et al, 1984, Hyun and Danner, 1985, Valus and Schneider, 1985 and Cooney, 1990]. In the chromatographic method, the non-diffusive rate effects such as external mass transfer resistance and/or heat dissipation can
be further decreased by the choice of a high bulk phase flow. The principle of the chromatographic method is that the diffusion rate can be related to the measurements of the dynamic response of an adsorption column suffering a perturbation in the feed adsorbate concentration.

The experimental procedure includes an inert carrier that is passed through a small column packed with the porous solid at the desired temperature until the response curve at the column exit becomes a steady straight line. Detectors located at the inlet and outlet of the column record the gas stream composition, that is, the concentration curves of the adsorbate as a function of time. At time zero a small pulse of adsorbate gas is introduced at the entrance of column or the carrier stream is turned to a gas mixture stream with a known concentration of adsorbate. The effluent concentration at the column exit is monitored continuously. The equilibrium adsorbed amount can be obtained by making a mass balance during the experimental operation period. The response curves can be used to determine the mass transport parameters.

Because the column is packed with small particles and there is a bulk phase flow, the axial dispersion effect is inevitable and thus will also change the transitory response curve shape and give rise to difficulties in the interpretation of experimental data. Theoretically, the importance of the axial dispersion can be lowered by increasing the bulk phase velocity. But the increase of bulk phase velocity will increase the column pressure drop and thus the bulk phase density becomes a function of column position which will greatly increase the complexity of models. By running the experiments at several bulk phase velocities, it is possible to separate the axial dispersion effects and mass transfer effects. In order to decrease the complexity of the mass transport model describing the chromatographic system it is expected that the adsorbate concentration in bulk phase is low and the adsorption isotherms are in the range of Henry's law. Because there is a saturation with carrier gas before introducing the adsorbate pulse or turning to the mixture stream the determined diffusivities are counter-diffusivities.

The mass transport parameters can be obtained by moment matching between experimental and model calculated moments or by direct fitting of model calculated concentration transitory response curves to these obtained experimentally. The chromatographic method can be carried out at a wide range of temperatures and pressures and has the advantages of quick measurement and it reproduces most correctly the conditions of a real process. A serious drawback of this method is the difficulty to interpret the experimental results. Specially, for the bidisperse pore size distribution particles, several parameters need to be regressed from the transitory response curves, the mathematical treatment is difficult and the accuracy of the obtained parameters is limited. The mathematical model for treating the data must take into account the intracrystalline, intraparticle, interparticle and axial mass transports which greatly complicate the model. Further details about the mass transport models and matching technique are given in Chapter IV.

When the mass transport resistance is located in the macropores, the pore dimension is enough large and the concentration of tracer in the bulk phase is high, the intraparticle convection effect, resulting from the pressure driven flow in the pores, on total mass transport rate must be accounted for [Rodrigues et al, 1982]. As a variant of the chromatographic method, the arrested flow chromatographic technique can be applied to circumvent the effect of intraparticle convection on the estimation of the macropore diffusivities [McCoy and Moffat, 1986]. The arrested flow chromatography is similar to the common one, but the input way is specially adjusted. The input of a band of the tracer is stopped when the band reaches the midregion of the column. The band spreads by stationary diffusion (nonconvective) during the period of the arrested flow and is then eluted by restarting the flow. In the absence of adsorption and reaction, the diffusive and
dispersive processes are linear and the band spreading effects are superimposed. Subtraction of variances for the eluted band, as in the determination of the slope of variances vs. delay time, will cancel axial dispersion and entrance and exit effects. From the slope of this line the effective diffusivity can be calculated [MaCoy and Moffat, 1986 and Park et al, 1987].

D. Zero Length Column Method

The most serious limitation that restricts the application of the ordinary chromatographic technique to determine the intraparticle diffusion is the axial dispersion effect. When the experimental transitory curve is mainly dependent on the axial dispersion rather than on the intraparticle diffusion, that is, the intraparticle diffusion rate is fast, it is impossible to obtain the intraparticle diffusivity from the transitory curve. The zero length column method [Ruthven, 1991 and Kärger and Ruthven, 1992] can retain the basic advantages of the chromatographic method and eliminate the limitations imposed by axial dispersion. The basic principle is that an extremely short column packed with a small amount of adsorbent is initially saturated with an adsorbate gas of known concentration. In order to be easily modeled it is desirable that the initial adsorbed amount is in the range of Henry's law. At time zero, an inert gas is introduced in a very high flow rate to purge the column. The objective of using high flow rates is to reduce the external surface concentration and thus the external mass transport resistance can be maintained at a minimum. The desorption mass transport rate can be obtained by measuring the composition of the effluent gas. The mass transport parameters are calculated by matching the experimental measured transitory curves to the model calculated ones.

The zero length column technique is attractive for the diffusion of small molecular gases in large zeolites. Other macroscopic experimental methods are difficult to be applied since the diffusion rates are too fast [Kärger and Ruthven, 1989]. Although the experimental principle of zero length column technique is simple, the practical application is difficult because of the high bulk phase velocity results in a very low concentration in the effluent stream and thus a very sensitive detector is required. The dead volume of the experimental apparatus will also introduce large errors. The zero length column technique uses inert gas and the determined diffusivities are thus counter diffusivities.

5.3 Comparison among Different Methods

The comparison of experimental results by various methods used by different workers is difficult for macropore diffusivity since there are great differences of the properties of macropore structure among different manufacturers. The intracrystalline diffusivity of vapors or gases in zeolites is comparable because the crystal structures of zeolites are identical among the different manufacturers. Good agreement was found among the results obtained with different experimental methods for zeolite systems [Kärger and Ruthven, 1992]. It must be mentioned that the results obtained by the uptake rate (static methods) are self-diffusivities, while the results from continuous methods are counter-diffusivities. Between these two types of diffusivities there are different physical concepts. In the case of the existence of an inert gas, the opposite direction diffusion process of the inert gas molecules partially blocks the diffusion path of adsorbate molecules. So the self diffusivity should be greater than the counter-diffusivity. Table 1.3 shows some characteristics of the macroscopic methods. The diffusion cell and chromatographic techniques will be discussed in detail in later chapters.
Table 1.3 Advantages and limitations of some experimental methods for measuring micro pore diffusivities [Kärger and Ruthven, 1989]

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Difficulties</th>
<th>Useful for</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uptake Rate Gravimetric Volumetric</td>
<td>Simple and Direct</td>
<td>Heat Effects, Extra-crystalline Mass Transfer, T/D Correction</td>
<td>Relative Slow Diffusivities (D/π² &lt; 10⁻³ s⁻¹) Moderate ΔH</td>
</tr>
<tr>
<td>Chromatography</td>
<td>Good Heat Transfer, Simple and Versatile</td>
<td>Axial Dispersion, For Large K, T, Large and Dax Increased by Intracrystalline Diffusion (Required Conditions May Be Impractical)</td>
<td>Moderate K (K&lt; 10⁵) 10⁻⁵ &lt; D/π² &lt; 10⁻² s⁻¹</td>
</tr>
<tr>
<td>Zero Length Column</td>
<td>Simple, Rapid, Good Heat Transfer. No Axial Dispersion</td>
<td>Only for c = 0 (Desorption)</td>
<td>K &gt; 10⁴ Wide Range of D/π²</td>
</tr>
</tbody>
</table>

6 MASS TRANSFER MODEL SOLUTIONS AND DATA FITTING

Although the practical adsorption and mass transport processes of gases in porous media are complicated, they can be described by means of some mathematical models. The mathematical model fundamentals are the momentum, energy and mass balance equations of the diffusing gas in a differential element in given operating conditions and the apparatus characteristics together with thermodynamic and kinetic equations. Because adsorption and diffusion occur inside the porous solids, the important aspect of model reliability is the description of the pore structure. Because of the lack of knowledge and of detailed mathematical expressions for the pore network structure, the entire mathematical description of the pore network structure is impractical. The samples in our systems include the zeolite A series and activated alumina. The first type has the typical bidisperse distribution. The size distribution of the original crystals of the synthetic zeolite is narrow compared to the macropore size distribution of other adsorbents and thus the macropore size distribution will be also narrow. The micropores of the zeolite are uniformly determined by the crystal framework structure and thus they are of uniform size. The later kind of samples usually shows a pore size distribution that has a certain width.

When the pressure gradient inside the porous media and in the bulk phase is enough small, the momentum balance equations are usually not necessary to be considered and the gas average molecular momentum can be considered as constant. This approximation holds correct for most of gas - solid mass transport experiments. The energy balance
equations are mainly equivalent to the heat balance equations. The adsorbed amount of permanent gases in zeolites at ambient temperature and pressure is small compared to that of the vapors and thus the heat released is not enough to raise the temperature of the solid samples and thus the heat effects on the mass transport rate can be safely dropped out.

Reasonable mass transport models for describing the adsorption and mass transport of gases in a bidisperse pore media and in the bulk phase should include the adsorption equilibrium term, micropore, macropore and film diffusion and axial dispersion (for the flow system). Generally, the models are a set partial differential equations and they are linked by the boundary conditions. When the adsorption equilibrium equations are linear, the various mass transport resistance coefficients are constant and the variation of the bulk phase flow rate is very small, the model equations may be linear. For the linear system, the solution procedure is greatly simplified.

There are several methods to extract the mass transport parameters from the experimental data by matching the theoretically calculated response values to the experimental ones. It is important to mention that all methods except curve fitting in the time domain are restricted in principle to the linear processes [Ramachandran and Smith, 1978].

6.1 Fitting in the Laplace Domain

In the case of the response of a pulse input in a linear process, the Laplace transform is a powerful tool to deal with the time variable. When a process is defined in a half infinite time domain \( [0, \infty) \), the terms related to the time variable in the partial equations can be transformed giving equations that are only position dependent. Thus the one-dimensional mass transport partial differential equations can be simplified to a set of ordinary differential equations. The transformed ordinary differential equations corresponding the original partial differential equations can be solved. If the analytical solutions of the transformed equations can be found, the relationships between the mass transport parameters and the response curves are explicitly established in the Laplace domain. Otherwise a numerical technique must be used to obtain these relationships [Chiang et al, 1984]. The Laplace transform \( C(s) \) of the experimental response values can be determined from the experimental \( C(t) \) data by numerically evaluating the transform for a set of discrete values of the Laplace variable \( s \ (s > 0) \). Adjusting the mass transport parameters, the differences between the calculated and experimental \( C(s) \) can be minimized and the parameters fixed. Theoretically, the fitting technique can extract several parameters from an experimental curve by changing the Laplace variable. When there are more than one parameter, simple relationships between Laplace transform and the parameters are not often obtained and thus an optimization technique has to be used to find the best fitting and the correct values for the parameters. Usually, that matching technique is only suitable in the simple one-parameter system.

The relationships between the time domain response concentrations at \( t = 0 \) and \( t = \infty \) and Laplace domain response concentrations at \( s = \infty \) and \( s = 0 \) can be easily obtained by the initial and final value theorems for a pulse input [Seborg et al, 1989]. These two values can be used to check the theoretical Laplace domain response concentration values at \( s = 0 \) and \( s = \infty \) points.

Similarly, the Fourier transform method can also be used in the original mass transport equation to eliminate the time variable. The solutions in the Fourier domain are obtained analytically or numerically. The experimental values in the Fourier domain can be
calculated from the time domain data. The comparison between experimental and theoretical values in the Fourier domain gives the mass transport parameters [Bashi and Gunn, 1977 and Gangwal et al., 1979].

6.2 Moment Fitting

All adsorption parameters, equilibrium constants, bulk phase diffusivity, film mass transport coefficient, macropore diffusivity and microparticle diffusivity can be easily obtained from the calculation of the moments of the response to a pulse input [Chiang et al., 1984, Hyun and Danner, 1985, Valus and Schneider, 1985, de Lasa et al., 1986, Schneider, 1986, Allawi and Gunn, 1987, Biswas et al., 1987, Burghardt et al., 1988 and Dogu et al., 1989]. The $n$th noncentral moment, $\mu_n$, of a response curve to an impulse input is defined as:

$$\mu_n = \int_0^\infty t^n C(t) \, dt$$  \hspace{1cm} (1.138)

Various experimental moments can be calculated by this definition. Theoretical expressions for the moments can be related to the response in Laplace domain by the relation [Smith, 1970]:

$$\mu_n = (-1)^n \lim_{s \to 0} \frac{d^n C(s)}{ds^n}$$  \hspace{1cm} (1.139)

The various moments include the adsorption equilibrium constant, axial dispersion parameters and effective diffusion parameter inside the porous media. In practice, only the zeroth, first and second moments are useful since higher moments can rarely be determined accurately from experimental response curves. When matching an experimental response curve, the adsorption equilibrium constant may be unambiguously determined from the first moment fitting. Matching the second moment provides one relationship to link two mass transport parameters, axial dispersion coefficient and a lumped mass transport coefficient. By changing the experimental operating conditions it is possible to split the lumped mass transport coefficient. In principle it is possible to derive $n$ model parameters by solving the expressions for the first $n$ moments of the response curves [Boniface and Ruthven, 1985]. In practice, however, the equations are almost degenerate in terms of the mass transport coefficient, the macropore and micropore diffusivities [Gangwal et al., 1978 and Wakao et al., 1980]. This means that although it is possible to separate the contributions from the axial dispersion and mass transport, it is not possible to distinguish between the different mass transport resistances except by studying the effect of variables such as particle size and gas velocity. Although the adsorption parameters can be calculated in theory by the moment fitting technique, process response curves can not be simulated from these parameters. In addition, the accuracy of moment fitting heavily depends on the response curve form. Even if there is only small tailing, calculations of the higher moments suffer from large errors [Hashimoto and Smith, 1974]. The moment technique is principally applied to linear systems, that is, all terms in the mass transport equations are linear. Dogu [1986] developed an iterative moment expression for a nonlinear adsorption process in a slurry adsorber.
6.3 Laplace Domain Solutions and Time Domain Fitting

In order to overcome the disadvantages of moment fitting and Laplace domain fitting techniques, the best way is the time domain matching. If the inverse functions of the solutions in Laplace domain can be analytically found, the solutions in time domain become analytical. When the adsorption equilibrium isotherm is linear and the interstitial velocity is considered constant then the solutions of the mass transport equations can be obtained using Laplace transform methods and further inverted analytically [Rasmussen and Neretnieks, 1980 and Rasmussen, 1982]. In these time domain solutions there is an infinite integral which is usually slowly convergent [Hsu and Dranoff, 1987]. When the mass transport equations include micropore and macropore diffusion resistances and film resistance, the solutions in Laplace domain will be very complicated and the approach to find out the analytical inversions is quite difficult. As an alternative, a numerical inversion technique can be applied [Chen and Hsu, 1987].

There are a couple of numerical inversion methods [Bellman et al, 1966, Weeks, 1966, Wing, 1967, Dubner and Abate, 1968, Krylov and Skoblya, 1977 and Hsu and Dranoff, 1987]. Each technique has its own specialty. Comparably, the inversion technique based on the Fast Fourier Transform (FFT) is easy to program, quick, accurate and efficient [Hsu and Dranoff, 1987]. The principle of the Fast Fourier Transform inversion is discussed in the following.

The inverse function $f(t)$ of a function $F(s)$ in Laplace domain can be calculated according to the Mellin’s inversion formula [Bracewell, 1987]:

$$f(t) = L^{-1}\{F(s)\} = \frac{1}{2\pi i} \int_{a-i\infty}^{a+i\infty} e^{st} F(s) \, ds$$

(1.140)

where $\alpha$ is a real constant greater than the real part of all function poles and $i$ is the imaginary unit, $\sqrt{-1}$. Equation (1.140) can be rewritten using a variable substitution, $s = \alpha + i \omega$.

$$f(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{(\alpha+i\omega)t} F(\alpha + i \omega) \, d\omega$$

(1.141)

The integration of equation (1.141) can be approximated by using the trapezoidal rule with the variable substitution $\omega = n\pi/T$ and $\Delta\omega = \pi/T$

$$f(t) = \frac{e^{\omega}}{2T} \sum_{n=-\infty}^{\infty} [F(\alpha + i \frac{n\pi}{T}) \exp(i \frac{n\pi t}{T})]$$

(1.142)
Assuming \( t = j\Delta T \) (\( j = 0, 1, 2, \ldots, N \); \( N = 2T/\Delta T \)), this equation can be put into the following form:

\[
f(j\Delta T) = \frac{e^{j\omega\Delta T}}{2T} \sum_{n=0}^{N-1} \left[ A(n) \exp\left(i \frac{2\pi nj}{N}\right) \right] \quad j = 0, 2, \ldots, N - 1
\]  \hspace{1cm} (1.143)

where

\[
A(n) = \sum_{n=-\infty}^{\infty} F \left[ \alpha + i \left(\frac{n+nN}{T}\pi \right) \right]
\]  \hspace{1cm} (1.144)

The most convenient choice of \( \alpha \) in equations (1.141) and (1.142) is zero when all function poles of \( F(s) \) are located in the left half plane, otherwise the input conditions in time domain should be converted so that all function poles of \( F(s) \) in right plane can be eliminated.

The evaluation of equation (1.141) can be achieved by using the algorithm of Fast Fourier Transform which saves about \( N^2/N \log_2 N \) operations compared with the conventional direct computation [Cooley and Tukey, 1965].

When the original function \( f(t) \) is real, from the theorem of Fourier transform the imaginary function \( F(s) \) must be of the Hermitian type which satisfies the following properties [Bracewell, 1987]:

\[
F(\alpha + i \frac{2n\pi}{T}) = F^*(\alpha - i \frac{2n\pi}{T})
\]  \hspace{1cm} (1.145)

\[
F(\alpha + i \frac{2n\pi}{T}) = F^*[\alpha + i \frac{2(N - n)\pi}{T}]
\]  \hspace{1cm} (1.146)

Where \( F^*(s) \) is the complex conjugate of \( F(s) \). So only the half values of \( A(n) \) in equation (1.141) from \( n = 0 \) to \( n = N/2 \) need to be computed and the other half values from \( n = N/2 + 1 \) to \( n = N - 1 \) can be immediately obtained from the symmetry relationships (1.145) and (1.146) because the real part of the imaginary function is an even function and the imaginary part is an odd function. The main computation time for the numerical inversion is consumed in calculating \( A(n) \). For many situations the equations (1.141) and (1.142) can be further simplified by selecting \( N/2 > T\omega_{\text{max}}/\pi \), where \( \omega_{\text{max}} \) is the largest frequency for which \( F(\alpha + i \omega_{\text{max}}) \) is less than a desired value; equation (1.141) becomes:

\[
f(j\Delta T) = \frac{e^{j\omega\Delta T}}{2T} \sum_{n=0}^{N-1} \left[ F \left[ \alpha + i \frac{n\pi}{T} \right] \exp\left(i \frac{2\pi nj}{N}\right) \right] \quad j = 0, 2, \ldots, N - 1
\]  \hspace{1cm} (1.147)
Such simplification will greatly reduce the computational work. The choice of half period T depends on the system properties where the period 2T must cover all unsteady experimental points. If it is too large or too small, the inversion accuracy will be reduced. The number of FFT points, N should be reasonably selected by balancing the calculation work and accuracy requirements. FFT algorithm can be found in most of the computer mathematical libraries. In IMSL (International Mathematical and Statistical Library) there is a subroutine named FFT2C which carries out the task. When FFT2C subroutine is called, the complex function values of A(n) are passed to subroutine and after execution the transformed values at different times which are the results of f(jΔT) multiplied by $\exp(j\omega T/2T)$ are obtained. As a comparison, in next the part the numerical solution by orthogonal collocation will be focused.

Because the Laplace transforms of nonlinear terms are not a simple function in the Laplace domain, the above discussed method is mainly applied to linear systems. [Chen and Hsu, 1989] extended the method to some nonlinear cases. If the nonlinear terms only appear in the bulk phase equations, a special technique was developed [Sun and Costa, 1992]. The intraparticle diffusion equations are solved in Laplace domain and this solution is the product of two functions: one is only dependent on model parameters and can be inverted by the Fast Fourier Transform method and the other is just the time derivative of the axial bulk concentration. The mass transfer rate of solute into particle can then be calculated by the convolution integral of those two functions. Finally the nonlinear one region equations are solved by the method of lines using global orthogonal collocation for the axial coordinate.

6.4 Solving by Orthogonal Collocation

When the adsorption equilibrium isotherm equations are nonlinear and/or the mass transport coefficients are dependent on the unknown functions as well as the bulk phase velocity is variable all of previous methods fail to obtain the solutions of the theoretical models. It is necessary to solve the mass transport equations directly in the time domain.

For the semi-linear and quasi-linear cases of fixed bed adsorption equilibrium processes an analytical or semi-analytical solution can be obtained by the method of characteristics [Rhee et al, 1986] whereas the nonlinear case requires a numerical solution [Loureiro and Rodrigues, 1991]. If the isotherm is nonlinear and the process is at non-equilibrium the usual way to solve the problem is the method of lines. The spatial variables are discretized by finite differences [Sun and Meunier, 1991], orthogonal collocation [Costa and Rodrigues, 1985 and Raghavan and Ruthven, 1985] or finite elements [Sereno et al, 1991], and the resulting set of ordinary differential equations (ODE) solved by the Gear method [Hindmarsh, 1980]. This way can be used to solve various adsorption models mostly in multiregions.

The orthogonal collocation method for solving partial differential equations has been well discussed in several books [Villadsen and Michelsen, 1978 and Finlayson, 1980]. It belongs to the method of weighted residuals. The main principles of the method of weighted residuals are that the unknown functions in partial differential equations and boundary conditions are expanded in a series of known functions of spatial variables with unknown coefficients, function of the time variable. These coefficients are determined to satisfy the equations and boundary conditions in some best sense. The criterion used to choose this best sense determines the method. The orthogonal collocation method has several advantages over other collocations. First, the collocation points are calculated...
automatically, they are taken as the roots of orthogonal polynomials, thus avoiding the arbitrary choice (usually a poorer one) by the user and the error decreases much faster as the number of terms increases. Second, the dependent variables are the solution values at the collocation points rather than the coefficients in the expansion.

6.5 Relationship between the Pulse and Step Inputs

Different inputs result in different response curves. In principle, the same information on adsorption equilibria and mass transport resistances can be extracted from various input types.

The pulse input has the advantage of simple mathematical handling, but the experimental technique to produce an ideal pulse input is difficult. The nonideal pulse injection results in some contribution to spreading of the response. Boniface and Ruthven [1985] and Raghavan and Ruthven [1985] proposed that the injection system can be approximated by a mixed cell with a time constant $t_o$.

$$C(t) \bigg|_{z=0} = C_o \exp(-t/t_o) \tag{1.148}$$

A complete time domain solution for the case of a finite injection pulse has been given by Carta [1988]. The step input is easy as experimental technique and the sensitivity of the experimental moments to long-time tailing region of the pulse input response can be reduced [Gibilisco and Waldram, 1972 and 1973].

REFERENCES


Chen, T. L. and J.T. Hsu, Prediction of Breakthrough Curves by the Application of Fast Fourier Transform, AIChE J., 33, 1387, 1987


Cooney, D.O., External Film and Particle Phase Control of Adsorber Breakthrough Behavior, AIChE J., 36, 1430, 1990


Cowling, T.C., Molecules in Motion, Hutchinson, 1950


Dogu, T., Extension of Moment Analysis to Nonlinear Systems, AIChe J., 32, 849, 1986


Fick A., Phil. Mag., On Diffusion, 10, 30, 1855


Guerin de Montgareuil, P. and D. Domine, French Patent 1223261, 1957


Huizenga, D.G. and D.M. Smith, Knudsen Diffusion in Random Assemblages of Uniform Spheres, AIChE J., 32, 1, 1986


Kärger, J. and D.M. Ruthven, On the Comparison between Macroscopic and NMR Measurements of Intracrystalline Diffusion in Zeolites, Zeolite, 9, 267, 1989


Kirkpatrick, S., Percolation and Conduction, Rev. Mod. Phys., 45, 574, 1973


Pruess, S. and C. Fulton, SLEDGE/NETLIB Release 2.11, spruess@mines.colorado.edu, 1991


Satterfield C.N., Mass Transfer in Heterogeneous Catalysis, MIT Press, 1970


Tyrrell H.J.V. and Harris K.R., Diffusion in Liquids, Butterworth & Co Ltd, 1984


Weisz, P.B., Diffusion and Chemical Transformation. An Interdisciplinary Excursion, Science, 179, 433, 1973


White, M. G., Heterogeneous Catalysis, Prentice Hall Inc., 1990


Yang, R.T., J.B. Fenn and G.L. Haller, Modification to the Higashi Model for Surface Diffusion, AIChE J., 19, 1052, 1973


II. THEORETICAL PREDICTION OF PERMANENT GASES ADSORPTION EQUILIBRIA IN ZEOLITE A SERIES

The macroscopic adsorption thermodynamics and kinetics deal with macroscopic systems only. From some basic thermodynamic and kinetic laws or postulates and a few experimental facts, a variety of relationships among the observed macroscopic properties of a system were derived. These derivations only involve the macroscopic characteristics of systems and thus can only explain and predict macro phenomena. It is recognized that they are in principle unable to explain why a system has the properties it does.

With the development of modern physics and chemistry, the nature of micro particles was deeper understood. The macro characteristics of a system can be related to its micro states. An explanation of this can be found in statistical mechanics which applies the results of quantum mechanics to the evaluation of the properties of a macroscopic system from the properties of its constituent particles. Statistical mechanics enable us to calculate the bulk properties of a system from fundamental constants and microscopic properties. Since the number of adsorbate molecules and adsorbent crystalline cells in a system is extremely large, it is understood that the calculation must be of a statistical nature and all results only represent statistical averages.

The adsorptive macroscopic properties of gases on zeolites, such as the equilibrium relationship, diffusion mass transfer, thermal effects, etc. can be related to microscopic interactions among adsorbate molecules and adsorbate molecules and zeolites. The adsorbate molecule motion microstates determine its macro properties. By studying the microscopic characteristics, the macro properties can be explained and predicted.

Zeolites are a special type of adsorbents which have regular crystalline structure. The adsorption active surface of zeolites is composed by \( \text{AlO}_4 \) and \( \text{SiO}_2 \) tetrahedrons. The number and spatial arrangements of these tetrahedrons in a basic crystal cell are well identified. These tetrahedrons produce a local electrostatic field and a local electrostatic field gradient. In addition, compared with other tetrahedrons which are fixed on non-adsorptive surfaces, the tetrahedrons located on the adsorptive surface have a potential force field to catch the adsorbate molecules in order to compensate the unbalanced forces. The exchangeable ions will also produce some local electrostatic field and field gradient. When an adsorbate molecule is caught by the zeolite crystal adsorptive surface, the interaction potential distribution on the surface of a crystal cell will significantly vary. The ability of the surface to adsorb other molecules will be far different from the first one. So zeolite adsorption appears highly heterogeneous. The interaction potential field and field gradient are determined by the crystal structure of the zeolites and that is quite regular throughout the whole crystal (all crystals are completely identical except for the crystal imperfections). In the case of very low occupation, that is, the adsorbate molecules are in random distribution among the crystal cells and the probability of more than one molecule in a cell can be neglected the macroscopic features of adsorption of gases in zeolites are similar to those on the surface of a non-porous crystal [Kiselev, 1971]. This similarity shows that it is possible to apply the molecular theory to porous zeolites. The high reproducibility of zeolite crystal structures allows us to just pay attention to the calculation of the adsorption properties in a cavity.

The macroscopic effects of adsorbate in adsorbed phase can be calculated directly from the interaction potential and the thermodynamic statistical functions.
Among the widely used zeolites, zeolites A, X and Y are the most suitable to microscopic analysis. The crystal structure including the position of AlO₄ and SiO₄ tetrahedrons and of the exchangeable ions, is well known. These three types of zeolites have similar structural features. The adsorption active surface is composed by cavities linked by windows which have relatively small dimensions. Because of the presence of the window, the interaction between different cavities can be approximately considered as negligible. Baksh and Yang [1991] used a uniform distribution of atoms and ions on cavity walls for 5A, 13 X and Y zeolites to describe cavity structure; the interaction potential between adsorbate molecules and wall atoms was simply integrated over all cavity surface. Experimental isotherms were then related to these interaction parameters. The model has simplicity and clear physical meaning but is dependent on experimental isotherm data for the calculation of potential field parameters. Their calculation results on adsorption heats agree well with the experimentally determined ones.

For non-noble gas molecules, Barrer et al [1971] and Sargent et al [1971] studied the adsorption of H₂O and CO₂ in 5A zeolite, respectively. In their models, the interaction potential between adsorbate molecules and wall atoms and other adsorbate molecules was calculated by summing all pairs of interaction potentials. Then they used the average potential to calculate the adsorption heats. Nowak et al [1987] simulated the adsorption of benzene and toluene in the zeolites theta-1 and silicalite. The interaction potential between a zeolite atom and an adsorbate molecule was calculated by summing the interaction between all atoms composing the adsorbate molecule and the zeolite. Because these two zeolites are high - silica and the quantity of aluminum can be neglected and thus no exchangeable ions exist, the interaction potential only includes the Lennard - Jones terms. The total interaction potential of adsorbate molecules at any spatial point was obtained by summing all pairs of interaction potentials. The average interaction potential calculated using the Boltzmann distribution was taken as the adsorption heat.

The Monte Carlo simulation technique is a tool also used to predict adsorption properties [Karvias and Myers, 1991]. Razmus and Hall [1991] used grand canonical Monte Carlo simulation to calculate adsorption isotherms and adsorption heats of Ar, O₂ and N₂ in 5A zeolite. The interaction potential inside cavity was simulated by adding all site - site interactions between adsorbate - adsorbate and adsorbate - wall atoms. They left an adjustable parameter in the potential model to fit the experimental adsorption heats.

One of the most important adsorption systems is the adsorption of oxygen, nitrogen and argon in zeolite A including 4A and 5A. The difference on adsorption isotherms of the individual components in 5A is fundamental for the production of oxygen from air by PSA. While in production of nitrogen from air by PSA using 4A zeolite, the favorable adsorption of nitrogen over oxygen results in a lower efficiency. The improvement of the oxygen adsorption isotherm in 4A will highly increase the corresponding separation efficiency. Most PSA techniques usually operate in the low coverage region. So the theoretical studies of adsorption equilibria at low coverage can be useful to provided an effective tool to improve process design and development.

To study the nature of adsorption mechanics it is necessary to obtain a model based on molecular level relationships. The microscopic adsorption mechanics can explain the macroscopic facts and understanding of the adsorption nature. The zeolite regular crystalline structure creates the possibilities to predict the adsorption characteristics from the basic physical and chemical properties of adsorbate molecules, adsorbent atoms and crystalline structure. The importance of such predictions is that they can theoretically support a tool to adjust the adsorbent selectivity. On the other hand, a good microscopic model can be used to optimize the adsorbent separation characteristics prior to the
necessary experimental determinations. To support a reliable microscopic methodology, a successful model must satisfy the following requirements:

* The model should include the molecular and crystal classical or quantum statistical basis and the interaction potential between adsorbate molecules and adsorbent atoms. All parameters in that model must have a clear physical meaning. The model should be able to describe the relationship between some calculated and macroscopically observable variables.

* As a predictive model, the calculated macroscopic adsorption properties must explain well the observable facts and the model parameters should be independent of the experimental data.

At low cavity occupation in zeolite A the interaction potential among adsorbate molecules can be neglected and the potential field between adsorbate molecule and cavity wall atoms can be simulated using an additive site - site potential model [Barrer, 1978]. This potential function is then substituted into the Schrödinger equation [ter Haar, 1969] that describes the adsorbate molecular motion states. A set of second order ordinary differential equations are obtained and numerically solved. The solution of this Sturm-Liouville problem gives an infinite set of eigenvalues and the corresponding eigenfunctions. The eigenvalues stand for the adsorbate molecular total energies at different microscopic states. The eigenfunctions determine the probability density of an adsorbate molecule with given total energy being found at various spatial positions. The partition function describing the number of microscopic states can be calculated from the eigenvalues and the degeneracy which shows the number of possible microscopic states at a given energy. Furthermore, the average total potential and kinetic energies and the average position of an adsorbate molecule inside a cavity can be evaluated at given macroscopic system conditions such as temperature and pressure. With the aid of partition functions, all thermodynamic properties of the macroscopic state can be obtained. This truly predictive model does not depend on experiments and each energy term has a clear physical meaning.

We applied this methodology to the adsorption of He, Ar, O₂ and N₂ in 5A and 4A zeolites. The potential field was calculated assuming that the nonnegligible interactions were of the repulsion-dispersion, induction and field quadrupole types. It is worthwhile to mention that some of the parameters used in these calculations are affected by uncertainty which reflects on the quality of the potential field prediction. In the particular case of the 5A and 4A zeolites, due to the spherically symmetrical location of wall atoms and of most of the exchangeable ions this potential field can be considered as spherically symmetrical which allows for a separation of variables of the Schrödinger equation and to its solution. These results are then substituted in the partition function that can be related to the macroscopic thermodynamic state functions. In the following section, a predictive methodology for calculating the adsorption isotherm of gases in zeolite A at low occupation will be discussed.

The Henry adsorption constants, isosteric adsorption heats and adsorption thermodynamic state functions including internal energy ΔU, enthalpy ΔH, entropy ΔS, Helmholtz free energy ΔF and Gibbs free energy ΔG of He, Ar, N₂ and O₂ in 5A and 4A zeolites were calculated for various temperatures by this method. In the region of low occupancy (less than 0.2 molecules/cavity) these results compare very well with experimental results taken from the literature [Miller et al, 1987].
The principal disadvantage of this methodology is associated with the form of the potential field function that can prevent the solution of the Schrödinger equation. This is the case when lateral interactions are considered.

Another possible use of the proposed method is as a reference for Monte Carlo simulation.

1. CRYSTAL STRUCTURE OF 4A AND 5A ZEOLITES

Zeolites are porous, crystalline aluminosilicates. Their well defined lattice structures contain cavities and / or channel intersections connected to each other by channels ( also called windows or pores ) of molecular dimensions. Due to their uniform micropore distribution and good industrial production reproducibility, synthetic zeolitic molecular sieves have been widely used since they were introduced in 1950's. The discovery of aluminophosphate materials has opened a new dimension in molecular sieves [ Flanigen et al, 1986 ]. The successful synthesis of new aluminophosphate materials with 18 membered ring large micropore dimension has broadened the molecular sieve applications to the potential separation of some large molecular mixtures [ Flanigen et al, 1988 ].

The important data on adsorption isotherms and other thermodynamic functions for theoretical studies and industrial process development are strongly dependent on experimental determinations. In recent years, more attention has been paid to the prediction of adsorption equilibria and adsorption heats by means of available microscopic properties of adsorbate molecules and adsorbents. Among these, the most successful examples are noble gas adsorption in A, X and Y zeolites [ Baksh and Yang, 1991 and Raznus and Hall, 1991 ].

The behavior of zeolites as a diffusion, adsorbent and molecular sieve medium is regulated by the crystalline structure, by the topology of the anionic framework and by the size, charge and the location of the exchangeable ions. Accordingly, structural knowledge is important in understanding the characteristics of zeolite adsorbents. There have been various reviews on zeolite structures [ Meier, 1968, Breck, 1974, Meier and Olson, 1971, Barrer, 1978 ]. The classification of zeolites is mainly based on two categories:

* Those which have the same framework topology, but have different chemical compositions ( cations or Si/Al ratios ) and in which as a result there may be minor framework adjustments and also differences in chemical, crystalline structure, Si/Al ratios and types and amounts of exchangeable ions. Examples of this kind of zeolites are Zeolite X and Zeolite Y.

* Those with a framework containing one or more common structural elements linked together. These different linking ways give different framework types like ZSM - 5 and ZSM - 11, zeolite A and zeolite X or Y.

The fundamental structural groups of zeolites are AlO₂ or SiO₂ tetrahedrons. The Al or Si atoms in each tetrahedron link with four oxygen atoms. The linking ways among different tetrahedrons by common bridges of oxygen atoms form secondary building units ( SBU ). The valence of Si atom is four so SiO₂ tetrahedrons are neutral. But the AlO₂ tetrahedron charge is -1, which must be neutralized by nonframework cations. The SBU is used to identify structural elements of zeolites [ Meier, 1968 ]. The different linking ways in spatial directions of different SUBs result in the formation of different
polyhedral building blocks. The zeolite crystalline framework can be constructed by stacking one or more types of polyhedra in simple coordinations. The channels and cavities inside zeolite crystals are frequently the internal free space of polyhedra or the voids among different polyhedra. The free diameter of channels and cavities is determined by the polyhedra and the linking ways. The size and location of cations balancing the framework charges also will affect the free diameter. The distortion in the structure of SUB and polyhedra will reduce the free diameter.

Zeolites can be classified into several groups based on the channel size: large pore zeolites of 12-membered oxygen rings, such as X and Y; intermediate pore zeolites of ten-membered rings, such as ZSM series; small pore zeolites of eight-membered rings, such as A series, erionite and chabazite; and six-membered rings, such as sodalite. There are at least two ways to characterize the size of zeolite channels [Breck, 1974, Barrer, 1978 and Ruthven, 1984]. The free diameter of a zeolite channel can be calculated from the structural model of the oxygen rings forming the channel openings, based on an assumed diameter for the oxygen atom. The channel size of a zeolite can also be characterized by the dimension of the adsorbed guest molecules. The effective diameter of the zeolite channel is determined experimentally by submitting the zeolite to guest molecules with different kinetic diameters.

The structure of zeolite A is one of the most well known. Its framework is composed of silica and alumina tetrahedrons, in which the silicon and aluminum atoms are surrounded by four oxygen atoms. These tetrahedrons are joined together through shared oxygen atoms to form the truncated octahedron, or sodalite. Zeolite A also contains exchangeable cations, most commonly Na$^+$ and Ca$^{2+}$, which serve to offset the negative charge introduced by the (AlO$_4$) groups. The cations are not part of the framework and instead partially sit near the six-membered oxygen rings in 5A zeolite as indicated in Figure 2.1. The structure of zeolite A is a simple cubic arrangement of sodalite units with lattice constant $a_0 = 12.29$ Å. The sodalite units are connected by the four oxygen atoms at the square face of the truncated octahedron. A simplified diagram of this structure is shown in Figure 2.1. This arrangement forms a nearly spherical cavity, which is surrounded by eight sodalite units. The shape of zeolite 5A cavity is shown in Figure 2.1. All the aluminum and silicon atoms are buried in tetrahedrons of oxygen atoms and are not exposed to the cavity surface. Therefore the surface is composed of oxygen atoms and cations. The cavity free diameter is 11.4 Å and the cavity volume is reported to be 775 Å$^3$ [Breck, 1974]. The pore structure is a lattice of interconnected cavities. The cavities lie on a cubic lattice, in which each cavity is connected to the six adjacent cavities. The window between the cavities is an eight-membered oxygen ring with a free diameter of about 4.3 Å [Barrer, 1978] in zeolite 5A. The differences between 5A and 4A zeolite are the number, type and location of the exchangeable cations.

Three distinct cation sites exist: in the centers of the six-membered rings in the eight corners of the central cavity (site I), in the eight-membered ring window (site II) and on the cavity wall in close proximity to a four-membered ring (site III). The occupation order is such that all of site I are preferentially occupied, followed by the site II and the site III is filled only after all sites I and II have been occupied. In 4A zeolite, there are 12 Na$^+$ cations per cell and these are accommodated in the following way: eight in site I, three in site II (the six eight-membered rings share one cation between two cavities) and one cation in site III. All windows are therefore partially obstructed by one Na$^+$ cation and the effective aperture of the path is therefore reduced from 4.3 Å to 3.8 Å. When partial exchangeable Na$^+$ cations are replaced by Ca$^{2+}$ cations with 67% ideal exchange amount, there are only 8 cations (4 Na$^+$ and 4 Ca$^{2+}$ per cell) and all cations can be preferentially accommodated in sites I. So the diffusional windows are not obstructed.
This is the case of 5A zeolite [Ruthven, 1984]. These differences result in different interaction potentials between adsorbate molecules and wall atoms in zeolite A.

The adsorption of gases occurs in these spherical cavities. The identical structure over all zeolite A crystals allow that the calculation of interaction between adsorbate molecules and cavity wall atoms is only concentrated on one cavity.

![Diagram of 5A zeolite structures]

Figure 2.1 Framework structure of 5A zeolite

2 CALCULATION OF THE POTENTIAL ENERGY OF A MOLECULE INSIDE A CAVITY

Although the framework crystalline structures of 5A and 4A zeolites are the same, the cation location, number and type are different. For a typical 5A, all cations (4 Ca** and 4 Na* in each cavity) sit near the centers of the six membered rings to balance the negative charges of (AlO2)^+ and there are no free cations inside the cavity. In 4A there are 12 Na* in each cavity where 8 Na* sit near the centers of the six membered rings. Other 3 Na* are located near the 8 eight membered ring plane which will affect the free diameter of window and the last Na* is located in a position close to the 4 eight-membered ring plane near the 8 eight membered ring window. Because of the sharing of
ions among neighboring cavities, in each cavity of 4A zeolite, there are a total of 15 Na+ and 72 O-. The differences on cation location, number and type result in different potential energy distributions inside the cavities of 4A and 5A zeolites.

The atoms and ions forming the walls of the cavities in 5A zeolite lie in polyhedral shells that may be approximated by a collection of identical cavities [Brouard and Shoemaker 1960 and Break, 1974]. The adsorption of gases in these zeolites can be approximately considered as sorption in spherical cavities.

The following four kinds of interactions between adsorbate molecules and wall atoms of the cavity will be considered here:

* The dispersion potential \( \mathcal{U}_{\text{disp}} \) which results from the instantaneous configurations of two interacting molecules, ions or atoms, \( a \) and \( b \). The asymmetrical configuration of moving electrons in molecule, ion or atom, \( a \), induces an instantaneous dipole (even if it possesses no permanent electric moment). This instantaneous dipole induces a dipole in \( b \). The interaction between these two dipoles results in an attractive potential between them. The dispersion potential is then this potential averaged over all instantaneous configurations of electrons in \( a \). In the adsorption of gases on zeolites, the dispersion potential always plays an important role and can be expressed as [Barrer, 1978]:

\[
\mathcal{U}_{\text{disp}}^{ik} = A_{ik} \rho_{ik}^6
\]

(2.1)

where subscript \( i \) and \( k \) represent wall atoms and adsorbate molecule respectively, \( A_{ik} \) are dispersion constants for the interaction of \( i \) and \( k \) and \( r_{ik} \) is the separation between particles \( i \) and \( k \). The most widely used equations for calculating \( A_{ik} \) are London, Slater-Kirkwood and Kirkwood-Muller [Barrer, 1978]:

\[
A_{\text{London}}^{ik} = 1.5 \alpha_i \alpha_k \frac{I_i I_k}{I_i + I_k}
\]

(2.2)

\[
A_{\text{Slater-Kirkwood}}^{ik} = \frac{3Z_e h \alpha_i \alpha_k}{4\sqrt{m_e} (\sqrt{\alpha_i/n_{ei}} + \sqrt{\alpha_k/n_{ek}})}
\]

(2.3)

\[
A_{\text{Kirkwood-Muller}}^{ik} = \frac{6mc^2 \alpha_i \alpha_k}{\alpha_i/\chi_i + \alpha_k/\chi_k}
\]

(2.4)

where \( I \) is the ionization potential, \( \alpha \) is the polarizability, \( Z_e \) is the electron charge, \( m_e \) is the mass of the electron, \( n_e \) is the number of outer shell electrons, \( c \) is the speed of light and \( \chi \) is the magnetic susceptibility. For many kinds of gases, the values calculated by equations (2.2) - (2.4) may have differences of several times. Usually the London equation underestimates and the Kirkwood-Muller equation overestimates. Taking into account the importance of the dispersion potential contribution to the total potential, we used the average of the results obtained with the three equations.
* Repulsion potential $U_{\text{rep}}$ is related to the electrostatic repulsive effects between the electrons and nuclei of two interacting molecules, ions or atoms when then are close enough and can be approximated by [Barrer, 1978]:

$$U_{\text{rep}}^{ik} = B_{ik}/r_{ik}^{12} \quad (2.5)$$

where $B_{ik}$ are repulsion constants that can be estimated by considering the derivative of the potential to distance as zero at the minimum point of the potential function between two molecules, ions or atoms; they can be obtained as the sum $r_e$ of the van der Waals radii $r_i$ and $r_k$ (*van der Waals radius equals to $2^{1/6}$ * Lennard - Jones radius) of the two particles:

$$B_{ik} = \frac{A_{ik} r_{ik}^6}{2} + \frac{\alpha_i Z_{ik}^2}{6} \quad (2.6)$$

where $Z$ is the charge of the ion. The repulsion potential is a short distance interaction potential compared to other van der Waals potentials.

The combination of dispersion and repulsion potentials shows the total effects between two non-polar molecules. At large separations ($r >> r_e$) where $r_e$ is the distance when the interaction potential between two atoms or molecules is zero), the inverse sixth-power term of the dispersion attractive component is dominant and the molecules are attracted to one other with a force which is proportional to the inverse seventh power of the separation. At small separations ($r << r_e$), the inverse twelfth-power repulsive component is dominant and the molecules are repelled from one other with a force which is proportional to the inverse thirteenth power of the separation. At $r = r_e$ the potential energy is zero ($r_e$ is usually called the Lennard - Jones radius), and therefore $r_e$ is the distance of closest approach of two molecules which collide with zero initial relative kinetic energy. For such potential function, there is a minimum potential point and its location, $r_{\text{min}}$, can be calculated as $r_{\text{min}} = 2^{1/6} r_e$ by the condition that the derivative of the sum of dispersion and repulsion potentials in order to separation be zero.

* Induction potential $U_{\text{ind}}$ which is related to a charged particle (for example, an ion) that interacts with a neutral molecule; the charged particle induces a dipole moment in the neutral molecules that can be determined by [Barrer, 1978]:

$$U_{\text{ind}}^{ik} = -\frac{\alpha_i Z}{2} \left( \frac{r_i - r_k}{r_{ik}} \right)^2 \quad (2.7)$$

where $r_i$ and $r_k$ are the position vectors.

* Electrostatic potential $U_{\text{ele}}$ which results from the interactions of various multipole moments (mainly, dipole and quadrupole moments) in molecules. The quadrupole moment of a molecule is really a second-order tensor with nine components. Only in the case of molecules with cylindrical symmetry this tensor can be specified by a single
scalar quantity. A direct application of the Coulomb law gives the formula for the interaction potential between a linear quadrupole and a charge [Hirschfelder et al., 1954]:

\[ U_{ik}^{fq} = -\frac{\Theta Z (3 \cos^2 \eta - 1)}{4r_{ik}^3} \]  

(2.8)

where \( \Theta \) is the quadrupole moment of the adsorbate molecule and the \( \eta \) is the angle between the direction of the electrostatic field produced by the charge and the quadrupole direction. The angular dependence of the above expression is somewhat complicated. For a given value of the intermolecular separation, there are relative orientations of the molecules for which the potential energy is a maximum or a minimum. In practical calculation, it is sometimes useful to use an effective average spherical symmetrical potential function over all orientations under Boltzmann distribution [Barret, 1978]:

\[ \overline{U}_{ik}^{fq} = \frac{\int U_{ik}^{fq} \exp(-U_{ik}^{fq}/RT) \sin \eta \, d\eta}{\int \exp(-U_{ik}^{fq}/RT) \sin \eta \, d\eta} \]  

(2.9)

In this averaging process the Boltzmann weighting factor \( \exp(-U_{ik}^{fq}/RT) \) is included in order to take into account the fact that statistically, the molecules spend more time in these orientations for which the energy is small. Physically the use of this average value corresponds to the assumption that the quadrupole moment interaction potential does not change appreciably as the molecule undergoes a rotation [Hirschfelder et al., 1954]. Substituting equation (2.8) into (2.9) we have:

\[ \overline{U}_{ik}^{fq} = -\frac{(3BkT/\pi)^{1/2} \exp(-3B/kT)}{\text{erf}[(3B/kT)^{1/2}]} + B + kT/2 \]  

(2.10)

where \( B = -QZ/4r_{ik}^3 \) and \( \text{erf}(z) \) is the error function of complex argument. For the anion \( B > 0 \) (anion), \( (3BkT/\pi)^{1/2} \) and \( \text{erf}[(3B/kT)^{1/2}] \) are real functions. When \( B < 0 \) (cation) \( (3BkT/\pi)^{1/2} \) and \( \text{erf}[(3B/kT)^{1/2}] \) become pure imaginary functions but the \( \overline{U}_{ik}^{fq} \) is still a real number.

Equations (2.1) - (2.7) are in cgs units and independent of temperature in a wide temperature range. After taking the average, the interaction potential between a linear quadrupole and an adsorbate molecule is dependent on temperature.

The above potential functions are derived for one adsorbate molecule interacting with an isolated ion (or atom) at the wall of the zeolite cavity. Because of the complicated structure and charge distribution of a cavity, the accurate theoretical evaluation of the interaction potential among all ions (atoms) and adsorbate molecules is impractical without any approximation. The following reasonable assumptions can considerably simplify the complex calculation of the potential field:
* All framework oxygen atoms are at the cavity wall and are located at the same spherical shell and their relative positions are kept invariable during adsorption.

* All negative charges are averagely distributed over all oxygen atoms (O\(^{-0.25}\)) and all positive charges are in exchangeable ions (Ca\(^{++}\) and Na\(^{+}\)).

* Exchangeable ions are located at the centers of the six membered rings for 5A or and also at the center of the windows and inside the cavity for 4A zeolite.

* All potential functions between adsorbate molecule and ions or wall atoms can be added; the interaction potential between the adsorbate molecules and framework atoms located in different cavities can be ignored.

* The contribution to the interaction potential from the aluminum (or silicon) atoms can be neglected since they are shielded by the four oxygen atoms.

* The adsorbate molecule is considered as being rigid in its equilibrium geometry. The assumption of no interaction between adsorbate molecules implies that the calculations are valid in the low coverage region.

The additive assumption results in the direct sum of dispersion, repulsion and quadrupole interaction potentials between different framework ions (atoms) and adsorbate molecule:

\[
\mathcal{U}_{\text{disp}} = \sum_{k=1}^{n} q^{\text{disp}}_{ak} 
\]

\[
\mathcal{U}_{\text{rep}} = \sum_{k=1}^{n} q^{\text{rep}}_{ak} 
\]

\[
\mathcal{U}_{\text{fq}} = \sum_{k=1}^{n} q^{\text{fq}}_{ak} 
\]

where \(n\) is the number of framework ions (atoms) and exchangeable ions. While the induction interaction potential is a vector addition instead of an algebraic addition:

\[
q^{\text{ind}}_{ak} = -\frac{\alpha Z}{2} \sum_{k=1}^{n} \frac{(r_{i} - r_{k})}{r_{ik}^3} 
\]

The accuracy of the partition function calculation depends largely on the accuracy of the potential energy field models. For adsorption at low concentration the interaction between adsorbate molecules can be neglected. The total potential energy field contributions inside the cavity include the dispersion \(\mathcal{U}_{\text{disp}}\), repulsion \(\mathcal{U}_{\text{rep}}\), induction \(\mathcal{U}_{\text{ind}}\) and ion quadrupole \(\mathcal{U}_{\text{fq}}\) between the adsorbate molecules and the zeolite framework atoms and cations.
\[ U = U_{\text{disp}} + U_{\text{rep}} + U_{\text{ind}} + U_{\text{iq}} \]  

Among these four interaction potentials, the dispersion and repulsion always play an important role for He, Ar, O_2 and N_2 in 5A and 4A zeolites. He and Ar have no permanent quadrupole moment, O_2 has a very weak one and N_2 has a strong one.

Since the zeolite is electrically neutral, the total negative charge of the framework oxygens must be balanced by the positive charges of the cations. To model the electrostatic interactions, the way in which the negative charges are distributed on the framework oxygen atoms must be estimated. Several previous investigators have suggested distributing the negative charge evenly over all of the framework oxygen atoms [Derrah and Ruthven, 1975]. In the 5A and 4A structures, this even distribution leads to a -1/4 charge on each oxygen atom.

It must be mentioned again that the uncertainty on the physical parameters of adsorbate molecules and cavity atoms brings in uncertainty on the calculated results for the potential functions. Specially, the parameters for O^{2-} which cannot be directly measured and that have been estimated by some researchers display great differences. The most effective parameter is the polarizability \( \alpha \) which greatly affects the dispersion and repulsion coefficients. Sargent and Whitford [1971] compared the effect of two values, 3.90 \times 10^{-24} \text{ and } 1.65 \times 10^{-24} \text{ on adsorption heats for CO}_2 \text{ in 5A and the difference between the adsorption heats calculated by using these two different numbers was 20 - 30\%.} \ We examined these two values and the calculated isotherms and adsorption heats are too large for 3.90 \times 10^{-24} \text{ and too small for } 1.65 \times 10^{-24}. \text{ May be an average value is the better selection.} \text{ In addition, the values of quadrupole moments for nitrogen are 1.29 - 1.60 \times 10^{-26} \text{ esu by microwave determination and } 2.51 \times 10^{-26} \text{ esu was reported by theoretical evaluation} [\text{Kington and Madeod, 1959}], \text{ the average value } 2.0 \times 10^{-26} \text{ esu was used in our calculations. Other parameters have weaker effects on potential field calculation.}

The parameters used in calculating the adsorbate - zeolite potential are summarized in Table 2.1. Table 2.2 shows the dispersion and repulsion constants \( A_{vk} \) and \( B_{vk} \) at 298.15K by three equations and the average values.

The interaction potential function between adsorbate molecule and adsorbent atoms calculated by the above site - site summation is dependent on the radial position. Later the validity of a spherically symmetrical field approximation by an average value over all angular orientations will be discussed.

3 EVALUATION OF ADSORBED PHASE PARTITION FUNCTION BY QUANTUM MECHANICS

The states of motion of an adsorbate molecule in the cavities of zeolites 5A and 4A at equilibrium are similar to those of a particle in a potential energy field. The total energy \( \epsilon_{\text{total}} \) of each molecule in a cavity can be represented by

85
Table 2.1 Physical parameters

<table>
<thead>
<tr>
<th></th>
<th>O^{0.25}</th>
<th>Na^+</th>
<th>Ca^{++}</th>
<th>He</th>
<th>Ar</th>
<th>N_2</th>
<th>O_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>l ev</td>
<td>13.624</td>
<td>47.29</td>
<td>51.21</td>
<td>24.48^a</td>
<td>15.755</td>
<td>15.576</td>
<td>12.063</td>
</tr>
<tr>
<td>α x10^{-24} cm^3</td>
<td>2.78</td>
<td>.19^b</td>
<td>.51^b</td>
<td>.79^a</td>
<td>1.63^c</td>
<td>1.67^c</td>
<td>1.57^c</td>
</tr>
<tr>
<td>χ x10^{-29} cm^3</td>
<td>20.9^b</td>
<td>7.00^b</td>
<td>14.95^b</td>
<td>1.88^a</td>
<td>31.0^c</td>
<td>19.8^c</td>
<td>24.0^c</td>
</tr>
<tr>
<td>n</td>
<td>6.25</td>
<td>8</td>
<td>8</td>
<td>2</td>
<td>8</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>r_nm</td>
<td>0.152^b</td>
<td>0.095^b</td>
<td>0.099^b</td>
<td>0.132^a</td>
<td>0.171^d</td>
<td>0.185^d</td>
<td>0.179^d</td>
</tr>
<tr>
<td>Z_e</td>
<td>-0.25</td>
<td>+1</td>
<td>+2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Θ x10^{-38} esu</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.4^d</td>
<td>2.0</td>
</tr>
</tbody>
</table>

^a [Weast, 1973 ]
^b [ Barrer, 1978 ]
^c [ Kington and Madeo, 1959 ]
^d [ Hirschfelder et al, 1954 ]
^e is in electronic charge ( 1 electronic charge = 1.6024 x 10^{-19} C )
^f 1 esu = 3.336 x 10^{-14} C.m^2

Table 2.2 Dispersion and Repulsion Constants

<table>
<thead>
<tr>
<th>Equation</th>
<th>He</th>
<th>Ar</th>
<th>N_2</th>
<th>O_2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A^*</td>
<td>B^*</td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>London</td>
<td>O^{-0.25}</td>
<td>Na^+ cations</td>
<td>0.195</td>
<td>0.0157</td>
</tr>
<tr>
<td>Slater - Kirkwood</td>
<td>O^{-0.25}</td>
<td>Na^+ cations</td>
<td>0.426</td>
<td>0.0460</td>
</tr>
<tr>
<td>Kirkwood - Muller</td>
<td>O^{-0.25}</td>
<td>Na^+ cations</td>
<td>0.461</td>
<td>0.0135</td>
</tr>
<tr>
<td>Average values</td>
<td>O^{-0.25}</td>
<td>Na^+ cations</td>
<td>0.361</td>
<td>0.0207</td>
</tr>
<tr>
<td></td>
<td>A^*</td>
<td>B^*</td>
<td>A</td>
<td>B</td>
</tr>
</tbody>
</table>

*Units for A and B are respectively, erg cm^{-6} molecule^{-1} x 10^{58} and erg cm^{-12} molecule^{-1} x 10^{102}  
**The parameters for the exchangeable ions were taken as the geometric average of Ca^{++} and Na^+

\[ \epsilon_{\text{int, pot}} = \mathcal{U}^* + \epsilon_{\text{total}} \quad (2.16) \]

Where \( \mathcal{U}^* \) is the average potential energy of a molecule and \( \epsilon_{\text{int}} \) is the sum of internal energies including translational energy \( \epsilon_{\text{tr}} \), rotation energy \( \epsilon_{\text{rot}} \), vibration energy \( \epsilon_{\text{vib}} \) of molecular atoms, electronic energy \( \epsilon_{\text{ele}} \) and nuclei energy \( \epsilon_{\text{nuc}} \), that is:
\( \epsilon_{\text{total}} = \epsilon_{\text{tr}} + \epsilon_{\text{rot}} + \epsilon_{\text{vib}} + \epsilon_{\text{ele}} + \epsilon_{\text{nu}} \)  \hfill (1.43)

When the equilibrium amount is far less than the average of one molecule per cavity of zeolite, we can neglect the probability of more than one molecule per cavity and assume that there are no interactions among any adsorbed molecules located at different cavities. Each adsorbed molecule is thus subjected to the same potential energy field. The acting force on adsorbed molecules is only dependent on the molecule and zeolite cavity properties and on the position inside the cavity. In such a system, the motion status of each adsorbed molecule can be described by quantum mechanics.

Under physical adsorption conditions, no chemical properties of the adsorbed molecules are changed and so vibration and rotation energies are considered as being the same as those of a free molecule. All translational energy levels of an adsorbed molecule can be evaluated by solving the stationary state Schrödinger equation. Then the molecular and system partition functions can be obtained.

According to statistical thermodynamics theory, the changes of adsorption thermodynamic functions, such as internal energy \( \Delta U \), enthalpy \( \Delta H \), entropy \( \Delta S \), Helmholtz free energy \( \Delta F \), Gibbs free energy \( \Delta G \) and adsorption Henry constant can be directly related to the molecular and/or system partition functions. Based on the classical statistical theory, the molecular partition function of an adsorbate molecule in an adsorbent potential field can be expressed as the product of two parts, one being the kinetic or translational part and another is the configurational part which accounts for the adsorbent potential functions:

\[
\varphi_v = \left( \frac{\sqrt{2\pi M_k T}}{h^3} \right)^3 \int \exp\left(-\frac{\mathcal{U}(r)}{kT}\right) dr
\]  \hfill (2.17)

where \( \mathbf{r} \) is the position vector. Equation (2.17) is only valid for systems in which the kinetic energy of a molecule is independent of the molecule spatial position and under this condition the integration in equation (1.60) can be divided into two independent parts. In the adsorption of gases in zeolite A series, the interaction potential between an adsorbate molecule and adsorbent wall atoms is strongly dependent on the position of the adsorbate molecule inside the cavity. If the classical mechanics is still valid to describe the motion of the adsorbate molecule, this motion is under a potential field that varies with position. The molecule velocity will vary with position and initial velocity. Only when the motion is along an equipotential surface, the kinetic energy will remain constant.

According to the Heisenberg uncertainty principle the momentum and position of an adsorbate molecule moving inside the cavity cannot be identified simultaneously. When an adsorbate molecule inside the cavity under a given translational quantum number, the total energy of the molecule is fixed (the total energy of a moving particle is only dependent on the quantum number in a given system) and then it is independent of the spatial position. The potential energy of the molecule is dependent on the spatial position and so the kinetic energy also changes with the spatial position.
In classical adsorption statistical thermodynamics, the prediction of the Henry constant is established on the base of the equation (2.17) and is simply equal to the ratio between gas and adsorbed phase molecular partition functions. At low pressure, the adsorbate behavior in gas phase can be approximately considered as ideal and the prediction of the adsorption Henry constant is reduced to the calculation of the configuration integral:

$$K = \int_v \exp\left( - \frac{U(r)}{kT} \right) \, dr$$  \hspace{1cm} (2.18)$$

The calculation of adsorption Henry constants when considering that the kinetic energy of adsorbate molecules inside the cavity is dependent on the spatial position must start from the fundamental definition of the molecular partition function of an adsorbate inside the cavity. Although for most adsorbate gases at common temperatures, the quantum effects of electronic spin are negligible and the classical statistical mechanics can be assumed as valid, the integration of equation (1.59) is difficult to be carried out because the explicit relationship between momentum of the adsorbate molecule inside the cavity and spatial position is difficult to be obtained by classical mechanics. As a good alternative, the various energy levels in the definition (1.28) of the molecular partition function can be easily obtained by directly solving the corresponding Schrödinger equation that is possible for special interaction potential functions. As long as the total energy levels for different quantum numbers and the corresponding probability distribution functions, that is, the wavefunctions are known, all other average microscopic and macroscopic quantities such as kinetic energy and position can be calculated. The technique of solving the steady state Schrödinger equation with a spherical symmetrical interaction potential has been already discussed in detail in Chapter I.

### 4 THEORETICAL PREDICTION OF ADSORPTION ISOOTHERMS, ADSORPTION HEATS AND THERMODYNAMIC FUNCTIONS

#### 4.1 Calculation of the Potential Field

The calculation of the interaction potential functions between adsorbate molecules and cavity wall atoms was carried out by the site-site pairwise additive model. Taking account of the symmetry of the structure of the 5A zeolite cavity and that the properties of Na\(^+\) and Ca\(^{2+}\) can be averaged and the average values are chosen as the values of Na\(^+\) or Ca\(^{2+}\), the calculation is concentrated on the spatial area $0 \leq r \leq r_w$, $0 \leq \eta \leq \pi/2$ and $0 \leq \xi \leq \pi/2$ ( $r_w$ is the radius of cavity shell.). In practical numerical calculations the radial variable was divided into 100 points and $\eta$ and $\xi$ into 50 points each and so the total network points for potential functions are $100 \times 50 \times 50$. The detailed calculation procedure is shown by an example in the Appendix.

The calculation of the interaction potential for the 4A cavity is more complicated, due to the position of one of the Na\(^+\) ions that is located inside the cavity thus destroying the structural symmetry. Due to the very strong electrostatic attractive force between Na\(^+\) and O\(^{-0.25}\) on cavity wall compared with the attractive interaction force between that ion and the adsorbate molecule, the most probable location of Na\(^+\) is in a place at equal
distance from each O\(^{-0.25}\) in one of the four membered rings and the distance is approximately equal to the sum of the Lennard-Jones radii of O\(^{-0.25}\) and Na\(^+\). So the interesting spatial region for 4A cavity calculations should include all spherical volume. In practical numerical calculations, the radial variable was divided into 100 points and \(\eta\) and \(\xi\) into 60 points each. The total network points for potential functions are 100 x 60 x 60. At these points the interaction potential energies between the adsorbate molecule and the cavity atoms including dispersion, repulsion, induction and quadrupole moment (for O\(_2\) and N\(_2\)) were calculated.

As already discussed in Chapter I the numerical solution technique for the steady state Schrödinger equation is only applicable to spherically symmetrical potential distributions. In order to utilize this solution technique, the interaction potential acting inside the cavity must be carefully examined. Figures 2.2 to 2.5 show the potential function distributions of He, Ar, O\(_2\) and N\(_2\) in 5A zeolite cavity at \(\xi = 0\) (equatorial plane) at 297.15 K. In these figures, the vertical axis represents the potential energy of the adsorbate molecule and the two axes on the horizontal plane stand for the radial coordinate. In the central region of the cavity the interactions are weaker due to the distance between the adsorbate molecule and wall atoms. When the molecule is close to the cavity wall, the dispersion interactions quickly increase and dominate over the repulsion interactions. When the adsorbate molecule is very close to the wall atoms, repulsion interaction becomes the dominant component and the total potential undergoes a change of sign and rapidly increases. The quadruple moment contribution to total potential is obvious in the nitrogen system and it results in a deeper well in the potential distribution of nitrogen and increases the width of the potential well. In each figure there are four regions where the repulsion potential extends a bit more. The existence of these regions results from the sparse atom density in the region of the 8 membered ring windows.

When the adsorbate molecule is close to these areas, the repulsion interactions are weaker than in other areas. If we take the average properties of Na\(^+\) and Ca\(^{2+}\) cations, the potential contribution from the wall atoms is symmetrical along the three coordinate axes. Figure 2.6 to 2.9 show the corresponding potential distributions of He, Ar, O\(_2\) and N\(_2\) in 5A zeolite cavity in the region of \(0 < \eta < \pi/2\) and \(0 < \xi < \pi/2\) of \(\eta = 0\) or \(\xi = 0\) planes at 297.15 K. The cross points in these figures are the calculated network points. These points were chosen at equal distances in \(\eta = 0\) or \(\xi = 0\) planes according to the requirements of the graphic software. The choice of real network points for potential calculation is different. When the potential is greater than zero these figures, display different high peaks at the same radial position, that shows that the potential has a non-spherically symmetrical distribution.

The potential distribution is nearly spherically symmetrical within the region \(r \leq r_z\). Sargent and Whitford [1971] showed similar results for CO\(_2\) in 5A zeolite. In this region, the repulsion interaction is small and dispersion, induction and electrostatic actions are present as long range effects. Around the shell of the cavity, there are 72 O\(^{-0.25}\), 4Na\(^+\) and 4Ca\(^{2+}\). Within this region, the effects of these atoms acting on adsorbate molecule are close to these of a uniform distribution. But when \(r \geq r_z\), the repulsion action becomes dominant and it is very sensitive to the separation distance. Due to the discrete distribution of atoms on the cavity shell, the separation distances at different points on the same calculation shell will change with orientation. So potential distribution is strongly dependent on the position.
Figure 2.2 Potential distribution of helium in cavity of 5A zeolite

Figure 2.3 Potential distribution of argon in cavity of 5A zeolite
Figure 2.4 Potential distribution of oxygen in cavity of 5A zeolite

Figure 2.5 Potential distribution of nitrogen in cavity of 5A zeolite
Figure 2.6 Potential distribution of helium in 5A zeolite in the region of \(0<\eta<\pi/2\) and \(\xi = 0\)

Figure 2.7 Potential distribution of argon in 5A zeolite in the region of \(0<\eta<\pi/2\) and \(\xi = 0\)
Figure 2.8 Potential distribution of oxygen in 5A zeolite in the region of $0 < \eta < \pi/2$ and $\zeta = 0$

Figure 2.9 Potential distribution of nitrogen in 5A zeolite in the region of $0 < \eta < \pi/2$ and $\zeta = 0$
All of these adsorbate potential distribution functions have the same form. Owing to its small molecular diameter and weak interaction, the potential distribution of helium is even and has a wider range of attractive potential. Nitrogen has a strong quadrupole moment and thus the potential distribution function has a deeper well than others. An increase of the molecular diameter results in the decrease of the attractive potential region.

The structure of the 4A cavity and the number of framework atoms are the same as for the 5A. All exchangeable ions in 4A are Na⁺. The variation of cation type and number in 4A zeolite results in the existence of a free Na⁺ inside the cavity. There are totally 12 four membered rings in each cavity. It is not important to know that this cation is close to a defined 4 membered ring plane because the position of all 12 four membered rings on cavity shell is symmetrical. In practical calculations we can artificially choose any one after defining the coordinate system. Figures 2.10 to 2.13 show the potential function distributions of He, Ar, O₂ and N₂ in 4A zeolite cavity in ξ = 0 plane at 297.15 K. In these potential distribution calculations, the coordinate system was chosen such that the three axis origins coincide with the center of cavity and the directions of the three coordinates are perpendicular to the six eight membered ring planes. The free cation was fixed in the position of the diagonal line η = ξ = π/4 plane. The potential distributions in 5A cavity have a convexity along the direction of the eight membered ring windows, whereas the potential distributions in 4A cavity are concave in these directions. This is due to the presence of a cation in each window. The average position of this cation should be in the center of window. The distance between the centers of window and cavity is shorter than the radius of the cavity. This cation increases the repulsion interaction range and gives rise to an attraction potential decreasing along the window direction. All of these four figures show that the symmetry of the potential distributions in ξ = 0 plane is somewhat destroyed. The potential distribution in ξ = 0 is an extreme situation compared with other planes because there are four windows and thus four cations in this plane. The situations in η = 0 and ξ = π/2 planes are the same as the ξ = 0 plane. It is worthy to mention that there is a concavity of the potential distribution in this plane along the diagonal line. This concavity results from the repulsion interaction of the additional free cation. In order to show the effect of these cations on the potential distribution in this plane, figures 2.14 to 2.17 illustrate the potential function distributions of He, Ar, O₂ and N₂ in the region of η = 0 and 0 ≤ ξ ≤ π/2 in this plane at 297.15 K. Comparing with figures 2.6 to 2.9, it is easy to see the differences on the potential distributions around the region close to the windows and that the regions of attractive potential are smaller than in 5A cavity, specially, for Ar, O₂ and N₂. Except for the potential distribution of N₂, deepness of the potential wells of other adsorbates becomes smaller than in 5A.

In the previous discussion on the solution of Schrödinger steady state wave equation, it was concluded that the variable separation technique is suitable if the potential distribution is spherically symmetrical. From the definition of partition functions of adsorbate inside cavity, we know that the values of partition functions are primarily determined by these eigen energies whose values are less than zero. Because the partition function is a sum of exponential functions of the eigen energies, it will quickly converge when the eigen energy increases at a given quantum number. In our calculations, the first several eigen energies of adsorbate molecules inside cavity are mainly determined by the potential well deepness. The part of the potential distribution greater than zero mainly affects the eigen energies whose values are greater than zero and that make very small contribution to the partition functions.
Figure 2.10 Potential distribution of helium in cavity of 4A zeolite

Figure 2.11 Potential distribution of argon in cavity of 4A zeolite
Figure 2.12 Potential distribution of oxygen in cavity of 4A zeolite

Figure 2.13 Potential distribution of nitrogen in cavity of 4A zeolite
Figure 2.14 Potential distribution of helium in 4A zeolite in the region of $0 \leq \eta \leq \pi/2$.

Figure 2.15 Potential distribution of argon in 4A zeolite in the region of $0 \leq \eta \leq \pi/2$. 

97
Figure 2.16 Potential distribution of oxygen in 4A zeolite in the region of $0 \leq \eta \leq \pi/2$

Figure 2.17 Potential distribution of nitrogen in 4A zeolite in the region of $0 \leq \eta \leq \pi/2$
Figures 2.6 to 2.9 show that all interaction potential distribution functions of He, Ar, O₂ and N₂ in 5A cavity are spherically symmetrical in the region of \( r < r_0 \), so it is reasonable that we use a spherically symmetrical potential energy field to approximate the real one. The average values at a given radial position \( r \) over all spatial angular variables \( \eta \) and \( \xi \) for 5A cavity can be expressed as:

\[
\overline{\mathcal{U}}(r) = \frac{\int \int \mathcal{U}(r, \eta, \xi) \sin \eta \, d\eta \, d\xi}{\int \int \sin \eta \, d\eta \, d\xi}
\]  

(2.19)

The integrations in equation (2.19) can be numerically carried out. The average potential distribution curves of He, Ar, N₂ and O₂ in 5A zeolite cavity along the radial variable are shown in Figure 2.18. The size of N₂ and O₂ molecules is close to each other. Owing to the strong quadrupole moment interaction of nitrogen with cations and anions, the potential distribution of nitrogen in the cavity is different. The potential well is deeper than for O₂. O₂ has a very weak quadrupole moment and its contribution to total interaction potential is small. There is no great difference between the molecular properties of O₂ and Ar utilized to calculate potential functions and so the potential distributions are similar. Molecular size and dispersion potential constant of He are greatly different and the potential distribution of He is even and close to zero potential. The differences among the potential distributions of He, Ar, O₂ and N₂ result in differences of partition functions and therefore on the adsorption properties. All these potential curves become very steep when the potentials change sign and small variations on separation distance will give rise to great variations on potentials. The characteristics of potential distribution functions determine the adsorption properties.

In order to illustrate the error introduced by the use of a spherically symmetrical potential approximation for the region of \( r > r_0 \), we artificially increased and reduced the potential functions 10 times in this region. The corresponding variation on the partition function values related to "correct potential function" are less than 0.2% and the errors on other calculated results such as average energy and average coordinate are even smaller because the partition function values are an exponential function of the eigen values. Such tests ensure that the error in the calculation of partition functions resulting from the asymmetrical potential distribution in the region of \( r > r_0 \) can be neglected. The closer to wall atoms the adsorbate molecule is, more obvious the asymmetry of the potential function is, but smaller the effect on the partition function calculation. This approximation makes it possible to separate the variables of the Schrödinger equation and solve it.

Due to the differences of the number, kind and location of cations between in 4A and 5A cavities, the potential distribution functions in Figures 2.10 to 2.17 show the effects of 7 cations (six in windows and one inside cavity). Because Na⁺ size and attractive interaction coefficient with adsorbate molecules are small when compared to O⁻0.25, these cations do not make significant attractive potential contributions to the total attractive potential. But the positions of these cations are not in the cavity shell, specially the location of the additional free cation. The cavity radius is in the order of molecular dimensions and due to the repulsive force of these cations the region for motion of the adsorbate molecule inside cavity will be limited. Repulsive potential is a short distance potential and when the adsorbate molecule is close to this cation the potential variation will be very sensitive to the separation distance between them. When we use equation (2.19) directly to evaluate the orientation-independent average potential function, the

99
effect of the repulsive potential of these cations on the average value may be over
determined because the high repulsive potential values in the vicinity of this cation will
cancel out all attractive potential values in the spherical surface out of this vicinity where
the average value is calculated. Taking into account that the probability of the adsorbate
molecule being in different positions is proportional to the Boltzmann weight function,
we may consider the use of this function to weight the interaction potential between
adsorbate molecule and these cations at various locations for all repulsion interactions,
that is,

\[ \bar{U}_{\text{rep}}(r) = U_{\text{rep}} \exp(-U_{\text{rep}}/kT) \]  \hspace{1cm} (2.20)

Figure 2.18 Radial average potential energy distribution in the cavity of 5A zeolite

By using such weights, the repulsion contribution of the cation in the four membered
ring to total potential energy is reduced. Figure 2.19 shows the average potential
distribution curves of He, Ar, N2 and O2 on 4A zeolite cavity along the radial coordinate
at 297.15 K. The comparison of the average potential distribution curves between 4A
and 5A cavities shows the effects of cation type, number and position on the adsorbate
potential distribution. The potential well width in 4A cavity is narrower than in 5A cavity
due to the window and free cation repulsion interaction. The deepest points of the
interaction potential well in 5A cavity are close to the place where repulsive force just
makes a sensible contribution. The existence of the window and free cations in 4A
reduces the attractive potential region and the deepness of the well. For non-polar and
very weak polar molecules (He, Ar and O2) the dominant contributions to total attractive
potential result from the dispersion interactions. The dispersion interaction constants of
O^{-0.25} are much larger than these of cations (Na^+ and Ca^{++}) and the number of O^{-0.25} in
each cavity is several times the number of cations, so the changes of the kind and the number of cations between 4A and 5A do not significantly affect the dispersion potential. The situation is different for N₂. The quadrupole moment interaction between wall cations and molecule makes a great contribution to the total attractive potential. Although the number of cations and total charges affecting the molecule in each 4A cavity is greater than in 5A, the quadrupole moment interaction is greatly dependent on the number and charge of single ion. In 5A cavity, the average charge of each cation is 1.5, while in 4A cavity is 1. This difference results in that there is a more obvious reduction of the interaction potential of N₂ in 4A zeolite than for He, Ar and O₂.

![Figure 2.19 Radial average potential energy distribution in the cavity of 4A zeolite](image)

The dispersion, repulsion and induction interaction potentials are independent of temperature in a large region. The average interaction potential between ion and molecule quadrupole moment varies with the temperature due to the Boltzmann weight function. So the potential functions of Helium and Argon in 5A cavity are independent of temperature and the temperature effect on the potential of oxygen is very small owing to the weak quadrupole moment. The temperature dependency of the nitrogen interaction potential in 5A zeolite cavity is shown in Fig. 2.20. Although the temperature variation covers a wide range the difference on potential distributions at two temperatures is still small. For the 4A cavity, because we took the Boltzmann average for the cations located at the window plane and inside cavity, all potential distributions for He, Ar, O₂ and N₂ are temperature dependent. The calculated results show that the temperature effects resulting from Boltzmann averaging of cation interaction on total potential can be neglected since we only consider the Boltzmann weight for the repulsion interaction of these cations which are located at the window and inside the cavity and thus the temperature dependency only appears in the repulsion potential region. The small variation of potential distribution in the repulsion region makes little contribution to the eigen energy.
In the Schrödinger equation, except for the potential term, all other terms are independent of temperature and thus when the potential function is independent of temperature the corresponding Schrödinger equation only need to be solved once for the calculation of the eigen energies. Due to the strong quadrupole moment, the potential function of nitrogen depends on the temperature. Because the small variation of potential distribution in the attractive region will greatly affect the energy spectrum and so the partition function, the Schrödinger equation must be solved for each individual potential function at each temperature respectively. The adsorbed phase partition functions at different temperatures can be calculated from the eigenvalues obtained from the solution of the corresponding Schrödinger equation. Although the potential functions of Helium, Argon and Oxygen are independent of temperature, the average properties including the position, potential, kinetic and total energies of an adsorbate molecule inside the cavity are really dependent on temperature since the calculation of average values includes the temperature effect. When temperature increases, molecular kinetic and total energies increase too.

4.2 Molecular Partition Function inside the Cavity

From the Sturm - Liouville theory, we know that the lowest translational eigen energy is the energy for which the quantum number, \( \ell \), is zero and the index, \( \lambda \), of eigenvalues is zero too. When the quantum number increases, the term in equation (1.91) \( \mathcal{U}(r) + \)
\[ \frac{h^2 \ell (\ell + 1)}{2M r^2} \] increases, which results in an eigen energy decrease. Because there is \( 2\ell + 1 \) fold degeneracy of microscopic states at the same eigen energy, the term \( (2\ell + 1)^* \exp(-\varepsilon_i/kT) \) shows a peak value with different quantum numbers, \( \ell \), at the same index of eigenvalues. The effect of quantum number, \( \ell \), on microscopic states makes the average properties of the system to deviate from these in which the adsorbate molecule is close to the position with minimum potential energy. Due to the degeneracy of the eigen energies, not only the lowest eigen energies but also the distributions of eigen energies make contributions to the partition function. For the slow convergent distribution of eigen energies, the degeneracy weight, \( (2\ell + 1) \), causes the partition function to be more heavily dependent on the distribution of the eigen energies. When the potential energy distribution is steeper and the region of attractive energy is narrower, the corresponding distribution of eigen energies is steeper. The partition function is a sum of various exponential functions of eigen energies where a small variation of the eigen energy distribution at low eigenvalues will result in large partition function changes. Table 2.3 shows the calculated results for the partition functions of He, Ar, N\(_2\), and O\(_2\) in cavities of 5A and 4A zeolites.

### Table 2.3 Adsorbed Phase Partition Function Values at Different Temperatures

<table>
<thead>
<tr>
<th></th>
<th>203.15K</th>
<th>233.15K</th>
<th>297.15K</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>5A</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>He</td>
<td>5.602 x 10(^4)</td>
<td>4.226 x 10(^4)</td>
<td>2.034 x 10(^4)</td>
</tr>
<tr>
<td>Ar</td>
<td>1.687 x 10(^7)</td>
<td>9.612 x 10(^6)</td>
<td>3.721 x 10(^6)</td>
</tr>
<tr>
<td>N(_2)</td>
<td>5.714 x 10(^7)</td>
<td>2.407 x 10(^7)</td>
<td>4.293 x 10(^6)</td>
</tr>
<tr>
<td>O(_2)</td>
<td>1.526 x 10(^7)</td>
<td>9.329 x 10(^6)</td>
<td>3.288 x 10(^6)</td>
</tr>
<tr>
<td><strong>4A</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>He</td>
<td>4.065 x 10(^4)</td>
<td>3.238 x 10(^4)</td>
<td>1.657 x 10(^4)</td>
</tr>
<tr>
<td>Ar</td>
<td>1.411 x 10(^7)</td>
<td>7.723 x 10(^6)</td>
<td>3.484 x 10(^6)</td>
</tr>
<tr>
<td>N(_2)</td>
<td>2.168 x 10(^7)</td>
<td>9.842 x 10(^6)</td>
<td>4.382 x 10(^6)</td>
</tr>
<tr>
<td>O(_2)</td>
<td>1.041 x 10(^7)</td>
<td>6.194 x 10(^6)</td>
<td>2.787 x 10(^6)</td>
</tr>
</tbody>
</table>

The potential changes from negative to positive when the variable \( r \) increases, the eigenvalues also vary from negative to positive with increasing the index of eigenvalues under a given quantum number \( \ell \). From the partition function equation, the value of the term \( \exp(-\varepsilon_i/kT) \) quickly decreases when \( \varepsilon \) increases. In practical calculations we set the stop conditions based on the ratio \( \exp(-\varepsilon_i/kT) / \max[\exp(-\varepsilon_i/kT)] < 10^{-5} \). Similarly, for a different quantum number \( \ell \), the calculation is stopped when \( (2\ell + 1) \exp(-\varepsilon_i/kT) / \max[(2\ell + 1)\exp(-\varepsilon_i/kT)] < 10^{-5} \).

Compared with the partition functions of other adsorbates, the partition function of helium is much smaller and the temperature dependency is also small due to its weak interaction potential. Weak interaction potential results in that the lowest values of the eigen energy spectrum are close to zero and thus the partition function temperature dependency is small. The difference between Ar and O\(_2\) in 5A zeolite is very small, while in 4A it is a bit larger. The comparisons of partition functions in 4A and in 5A show that the differences between helium and argon are smaller than for O\(_2\) and N\(_2\) and that with the increase of temperature the differences decrease. The dimensions of He
and Ar are small and the positions of cations have small effects on their potential distribution functions.

4.3 Energy Terms

Although the total energy of an adsorbate molecule inside the cavity varies with the quantum numbers, the average potential energy is nearly constant. This means that the corresponding kinetic energy of an adsorbate molecule inside the cavity at different quantum numbers varies with similar trends as the total energy. The lowest kinetic energy value is the state at which \( t \) and \( \mathcal{E} \) are zero and it must not be equal to zero otherwise the Heisenberg uncertainty principle will be violated. In the classical statistical theory, when the integration of equation (1.61) is carried out, the lower limit for the momentum integral is negative infinity and the upper limit is positive infinity and thus the corresponding kinetic energy lower limit is zero. This shows why the smallest translational energy is chosen as zero in the classical treatment.

Table 2.4 shows the calculated results using quantum mechanics for average kinetic and potential energies and coordinates. At all three temperatures, the average molar kinetic energies of adsorbed phase are almost equal to those of bulk gas phase. This is in agreement to the requirement of the equipartition principle that states that the average kinetic energy of a molecule is determined by the motion degrees of freedom and temperature and is independent of the potential field [Atkins, 1986]. Inside the cavity, adsorbate molecules have localized three-dimensional translational motion and so the motion degrees of freedom are the same as in gas phase. In this situation the average kinetic energies of the adsorbed and gas phases should be the same. This similarity does not mean that the kinetic energy distribution is also the same. The detailed discussion of the kinetic energy distribution of an adsorbate molecule will be carried out in Chapter III.

<table>
<thead>
<tr>
<th></th>
<th>203.15 K</th>
<th></th>
<th></th>
<th></th>
<th>233.15 K</th>
<th></th>
<th></th>
<th></th>
<th>297.15 K</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>r</td>
<td>( E_a )</td>
<td>( E_{ad} )</td>
<td>( \psi )</td>
<td>r</td>
<td>( E_a )</td>
<td>( E_{ad} )</td>
<td>( \psi )</td>
<td>r</td>
<td>( E_a )</td>
<td>( E_{ad} )</td>
</tr>
<tr>
<td>He</td>
<td>0.396</td>
<td>2.533</td>
<td>2.563</td>
<td>-6.512</td>
<td>0.393</td>
<td>2.908</td>
<td>2.929</td>
<td>-6.394</td>
<td>0.387</td>
<td>3.706</td>
<td>3.712</td>
</tr>
<tr>
<td>Ar</td>
<td>0.368</td>
<td>2.533</td>
<td>2.524</td>
<td>-12.22</td>
<td>0.367</td>
<td>2.908</td>
<td>2.903</td>
<td>-12.21</td>
<td>0.363</td>
<td>3.706</td>
<td>3.707</td>
</tr>
<tr>
<td>N₂</td>
<td>0.363</td>
<td>2.533</td>
<td>2.525</td>
<td>-15.58</td>
<td>0.361</td>
<td>2.908</td>
<td>2.901</td>
<td>-15.44</td>
<td>0.358</td>
<td>3.706</td>
<td>3.703</td>
</tr>
<tr>
<td>O₂</td>
<td>0.359</td>
<td>2.533</td>
<td>2.529</td>
<td>-11.92</td>
<td>0.357</td>
<td>2.908</td>
<td>2.902</td>
<td>-11.81</td>
<td>0.352</td>
<td>3.706</td>
<td>3.698</td>
</tr>
<tr>
<td>5Å</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>He</td>
<td>0.388</td>
<td>2.533</td>
<td>2.577</td>
<td>-5.368</td>
<td>0.385</td>
<td>2.908</td>
<td>2.944</td>
<td>-5.265</td>
<td>0.379</td>
<td>3.706</td>
<td>3.730</td>
</tr>
<tr>
<td>Ar</td>
<td>0.359</td>
<td>2.533</td>
<td>2.519</td>
<td>-10.67</td>
<td>0.356</td>
<td>2.908</td>
<td>2.893</td>
<td>-10.54</td>
<td>0.352</td>
<td>3.706</td>
<td>3.686</td>
</tr>
<tr>
<td>N₂</td>
<td>0.308</td>
<td>2.533</td>
<td>2.527</td>
<td>-13.13</td>
<td>0.306</td>
<td>2.908</td>
<td>2.905</td>
<td>-13.00</td>
<td>0.303</td>
<td>3.706</td>
<td>3.710</td>
</tr>
<tr>
<td>O₂</td>
<td>0.352</td>
<td>2.533</td>
<td>2.533</td>
<td>-9.171</td>
<td>0.349</td>
<td>2.908</td>
<td>2.913</td>
<td>-9.050</td>
<td>0.345</td>
<td>3.706</td>
<td>3.712</td>
</tr>
</tbody>
</table>

One of the most important parameters for process development and design, is the isosteric adsorption heat that was calculated at three temperatures by considering equal to \( \Delta \mathcal{H} \) are shown in Table 2.5. For comparison the experimental results obtained from literature are also shown. All calculated results for isosteric adsorption heats in 5Å zeolite agree well with the experimental ones [Miller et al., 1987]. In our model, the interaction potential between adsorbate molecules is neglected and so it is only valid for
low coverage. The experimental adsorption heats of Ar and O₂ are independent of adsorbed amount in a wide range. But for nitrogen, adsorption heat decreases with increasing adsorbed amount [Miller et al., 1987]. The kinetic energies of adsorbate molecules in gas and adsorbed phases are almost the same and thus the isosteric adsorption heat can be evaluated simply by taking the average potential energy plus RT [Ruthven, 1984]. This rough estimation gives a relative error less than 10% for these systems.

Table 2.5 Adsorption Heats (KJ/mol) at Different Temperatures

<table>
<thead>
<tr>
<th></th>
<th>203.15 K</th>
<th>233.15 K</th>
<th>297.15 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>calculation</td>
<td>experiment</td>
<td>calculation</td>
</tr>
<tr>
<td>5A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>He</td>
<td>-8.201</td>
<td></td>
<td>-8.332</td>
</tr>
<tr>
<td>Ar</td>
<td>-13.93</td>
<td></td>
<td>-14.15</td>
</tr>
<tr>
<td>N₂</td>
<td>-17.28</td>
<td></td>
<td>-17.38</td>
</tr>
<tr>
<td>O₂</td>
<td>-13.61</td>
<td></td>
<td>-13.75</td>
</tr>
<tr>
<td>4A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>He</td>
<td>-7.057</td>
<td></td>
<td>-7.203</td>
</tr>
<tr>
<td>Ar</td>
<td>-12.36</td>
<td></td>
<td>-12.48</td>
</tr>
<tr>
<td>N₂</td>
<td>-14.82</td>
<td></td>
<td>-14.94</td>
</tr>
<tr>
<td>O₂</td>
<td>-10.86</td>
<td></td>
<td>-10.99</td>
</tr>
</tbody>
</table>

Experimental data for 5A from Miller [Miller et al., 1987] and experimental data for 4A from Ruthven and Derrah [1975]

1 Kiselev [Kiselev, 1971]

4.4 Adsorption Thermodynamic Functions

With the aid of the partition function, all thermodynamic state functions can be calculated. At a given pressure, the coverage and therefore system partition functions of adsorbed phase can be calculated. Table 2.6 gives the calculated results for the thermodynamic state functions obtained by quantum mechanics.

Table 2.6 Adsorption Thermodynamic Functions (at 1000 Pa)

<table>
<thead>
<tr>
<th></th>
<th>203.15 K</th>
<th>233.15 K</th>
<th>297.15 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔUᵣ</td>
<td>ΔSᵣ</td>
<td>ΔFᵣ</td>
</tr>
<tr>
<td>He</td>
<td>-12.28</td>
<td>-51.95</td>
<td>-35.08</td>
</tr>
<tr>
<td>N₂</td>
<td>-11.92</td>
<td>-50.14</td>
<td>-34.53</td>
</tr>
<tr>
<td>4A</td>
<td>-10.67</td>
<td>-46.06</td>
<td>-35.10</td>
</tr>
<tr>
<td>He</td>
<td>-13.13</td>
<td>-55.94</td>
<td>-34.24</td>
</tr>
<tr>
<td>Ar</td>
<td>-9.171</td>
<td>-36.68</td>
<td>-34.53</td>
</tr>
</tbody>
</table>

The units of ΔUᵣ, ΔSᵣ, ΔFᵣ, and ΔGᵣ are respectively KJ/mol, J/mol K, KJ/mol and KJ/mol.

ΔU is the differential adsorption heat at constant volume and temperature. The number of molecular motion states is more restricted after adsorbing, so the ΔS is less than zero.
In the view of statistical thermodynamics, the entropy decrease means that the total number of probable molecular microscopic states is reduced.

The decrease of \( \Delta U \) with increasing temperature can be simply explained as follows. At low temperature, the adsorbate molecule has low translational kinetic energy and so moves close to the position of minimum interaction potential in the adsorbed phase. The total energy of the molecule is low, so the change in internal energy \( \Delta U \) is large in absolute value. Rising the temperature results in an increase of the adsorbate molecular translational kinetic energy, the molecule has more probability to appear in the high interaction potential region and \( \Delta U \) decreases in absolute value. The enthalpy change \( \Delta H \) is different. There is a term, \(-RT\), which also contributes to the \( \Delta H \) temperature dependency and this contribution acts in opposite direction to \( \Delta U \); the total results of \( \Delta H \) temperature dependency are dependent on the relative contributions of these two terms.

### 4.5 Adsorption Isotherms

The adsorption isotherms at low coverage are readily obtained from the partition functions. Figures 2.21 to 2.23 show the results of Ar, N\(_2\) and O\(_2\) in 5A. The experimental data were evaluated using the Miller’s regression parameters [Miller et al., 1987] and the adsorbed amount was expressed in unit number of molecules (N) per cavity. All predicted results agree fairly with the experimental values. When the pressure tends to the zero limit, the experimental and calculated slopes of adsorption isotherms should be coincident. When adsorbed amount exceeds 0.2 molecules/cavity, the calculated curves deviate from the experimental ones. This effect is expected. With the adsorbed amount increasing, the interaction between adsorbate molecules may not be negligible. In our model the adsorption isotherms were expressed in the Langmuir form even at low pressure and only when pressure tends to the zero limit the isotherms become truly linear. Table 2.7 shows the experimental and calculated adsorption Henry constants at these three temperatures. In order to show the uncertainty of the experimental values we collected two sets of experimental data from different sources. For the systems of argon, nitrogen and oxygen in 5A at three temperatures (except nitrogen at 203.15 K) the calculated Henry constants well agree with the published experimental data obtained from two sources. Whereas the two sets of experimental Henry constants for nitrogen in 5A at 203.15 K have quite difference. Our predicted values are within the uncertainty range of the experimental results.

The experimental adsorption Henry constants for nitrogen and oxygen in 4A zeolite were collected from the Ruthven and Derrah [1975] and Ruthven [1976] studies and also listed in Table 2.7. The data at the same experimental conditions for argon in 4A were rarely obtained. The predicted data for nitrogen at 203.15 K in 4A is quite poor compared with the experimental result and the difference between calculated and experimental results for 4A is greater than for 5A. The existence of the free cation inside the 4A cavity affected the calculation precision.

It may be pointed out that the precision of the determination of the adsorbed amount of permanent gases at very low pressure is limited since the accurate measurement of a small variation of adsorbent weight or gas volume or pressure is difficult. The experimental adsorption Henry constants are usually obtained by extrapolating the isotherms at low pressure to zero pressure.
The dashed lines are experimental results and the solid lines are the results calculated by this work.

Figure 2.21 Adsorption isotherms of Ar in 5A zeolite

The dashed lines are experimental results and the solid lines are the results calculated by this work.

Figure 2.22 Adsorption isotherms of N₂ in 5A zeolite
The dashed lines are experimental results and the solid lines are the results calculated by this work.

Figure 2.23 Adsorption isotherms of O₂ in 5A zeolite

Table 2.7 Adsorption Henry constants (molecule.cavity⁻¹.Pa⁻¹ x 10⁵) at different temperatures

<table>
<thead>
<tr>
<th></th>
<th>203.15 K</th>
<th></th>
<th>233.15 K</th>
<th></th>
<th>297.15 K</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>calc</td>
<td>expt ¹</td>
<td>expt ²</td>
<td>calc</td>
<td>expt ¹</td>
<td>expt ²</td>
</tr>
<tr>
<td>5A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>He</td>
<td>0.459</td>
<td></td>
<td></td>
<td>0.246</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>4.372</td>
<td>4.559</td>
<td>3.215</td>
<td>1.766</td>
<td>1.565</td>
<td>1.102</td>
</tr>
<tr>
<td>N₂</td>
<td>25.29</td>
<td>32.08</td>
<td>62.91</td>
<td>7.549</td>
<td>10.82</td>
<td>12.78</td>
</tr>
<tr>
<td>O₂</td>
<td>5.527</td>
<td>4.848</td>
<td>3.944</td>
<td>2.359</td>
<td>1.712</td>
<td>1.377</td>
</tr>
<tr>
<td>4A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>He</td>
<td>0.333</td>
<td></td>
<td></td>
<td>0.188</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>3.657</td>
<td></td>
<td></td>
<td>1.419</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>9.594</td>
<td>22.99</td>
<td></td>
<td>3.087</td>
<td>5.769</td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>3.771</td>
<td>2.558</td>
<td></td>
<td>1.590</td>
<td>0.922</td>
<td></td>
</tr>
</tbody>
</table>

1. [Miller et al., 1987]; 2. [Ruthven and Derrah, 1975 and Ruthven, 1976]

5 COMPARISON OF THE RESULTS CALCULATED BY CLASSICAL AND QUANTUM MECHANICS

The calculations of adsorption thermodynamic functions and adsorption isotherms are dependent on the molecular partition functions. The difference between using classical mechanics and quantum mechanics on the calculation of molecular partition functions of
the adsorbed phase is discussed in the following. In classical mechanics, the translational molecular partition functions inside the cavity can be evaluated by replacing the summation by a continuous integral and assuming that the total energy can be divided into kinetic and potential energies and that the kinetic energy is independent of the spatial position. This independence allows the separation of the configurational integral into two parts and the integral related to kinetic energy can be solved analytically. So the calculation of the molecular partition functions is reduced to the evaluation of the configuration part:

$$\mathcal{Z}_c = \int \exp\left(-\frac{\mathcal{U}(r)}{kT}\right) \, dr$$  \hspace{1cm} (2.21)

When the kinetic energy of an adsorbate molecule inside the cavity is dependent on the spatial position, the calculation of the molecular partition function by classical mechanics has a difficulty in the calculation of the configurational integral. In quantum mechanics, the molecular partition functions can be obtained from the energy levels which are the eigenvalue spectrum of the steady state Schrödinger equation.

The results for the molecular partition functions of helium, argon, nitrogen and oxygen on 5A and 4A zeolite cavities using classical and quantum mechanics show that the maximum relative differences are within the 5 - 20 % in the temperature range of 183.15 K to 297.15 K. At least part of the difference can result from the numerical procedures. The configurational integral $\mathcal{Z}_c$ of classical mechanics can be expressed in a spherical coordinate system by:

$$\mathcal{Z}_c = \int \exp\left(-\frac{\mathcal{U}(r)}{kT}\right) \, dr = \int_0^{2\pi} \int_0^\pi \int_0^{r_w} \exp\left(-\frac{\mathcal{U}(r,\eta,\xi)}{kT}\right) \, d\eta \, d\xi \, dr$$  \hspace{1cm} (2.22)

The calculated interaction potential between adsorbate molecule and adsorbent atoms shows that $\mathcal{U}(r,\eta,\xi)$ is strongly dependent on the angles $\eta$ and $\xi$ at a given shell when the distance between the adsorbate molecule and the wall atom is close to the separation between wall atoms. Equation (2.21) will greatly weight the potential in the positions where $\mathcal{U}(r,\eta,\xi)$ is minimum at a given shell. The average potential at a given shell is taken as the average over all $\eta$ and $\xi$ in equation (2.19). In order to illustrate the classical mechanics applicability and exclude the orientation effects on the numerical evaluation of the integral, we take an angle-independent potential function to show the differences.

We take a potential function in the form of a polynomial and keep the real shape of interaction potential inside the cavity:

$$\mathcal{U}(x) = \frac{a_0 + a_1 x + a_2 x^2}{1 - x^2}$$  \hspace{1cm} (2.22)
where \( x \) is the dimensionless radial variable, \( x = r/r_w \). The following potential values are taken at \( x = 0 \), \( \mathcal{U}(0) = -2 \times 10^{-14} \) erg/molecule; at \( x = 0.6 \), \( \mathcal{U}(0.6) = -1.3 \times 10^{-13} \) erg/molecule and at \( x = 0.65 \), \( \mathcal{U}(0.65) = 0 \). The corresponding constants are \( a_0 = -2 \times 10^{-12} \), \( a_1 = -1.73856 \times 10^{-12} \) and \( a_2 = 2.72205 \times 10^{-12} \). The differences on the results calculated for helium by both methods are shown in Table 2.8.

<table>
<thead>
<tr>
<th>( r_w = 7.05 \text{Å} )</th>
<th>Classical Mechanics</th>
<th>Quantum Mechanics</th>
<th>Relative Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>297.15 K</td>
<td>3.583 \times 10^6</td>
<td>3.544 \times 10^6</td>
<td>1.1</td>
</tr>
<tr>
<td>183.15 K</td>
<td>2.268 \times 10^8</td>
<td>2.217 \times 10^8</td>
<td>2.3</td>
</tr>
<tr>
<td>83.15 K</td>
<td>4.254 \times 10^{15}</td>
<td>3.988 \times 10^{15}</td>
<td>6.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( r_w = 3.00 \text{Å} )</th>
<th>Classical Mechanics</th>
<th>Quantum Mechanics</th>
<th>Relative Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>297.15 K</td>
<td>2.765 \times 10^5</td>
<td>2.657 \times 10^5</td>
<td>4.1</td>
</tr>
<tr>
<td>183.15 K</td>
<td>1.751 \times 10^7</td>
<td>1.602 \times 10^7</td>
<td>9.3</td>
</tr>
<tr>
<td>83.15 K</td>
<td>3.287 \times 10^{14}</td>
<td>2.363 \times 10^{14}</td>
<td>39.1</td>
</tr>
</tbody>
</table>

The configurational integration in equation (2.21) was numerically carried out by using Simpson technique with 10000 equal spatial discrete points in the interval \( x \in [0,1] \) and the solutions from SLEDGE software package are controlled until the ratio of \( \exp(-\varepsilon_f/kT)/\max[\exp(-\varepsilon_f/kT)] \) and \( (2E + 1)\exp(-\varepsilon_f/kT)/\max[(2E + 1)\exp(-\varepsilon_f/kT)] < 10^{-9} \). We believe that the numerical accuracy is enough. The results in Table 2.8 show that classical mechanics is applicable to the adsorption systems in the moderate temperature range. Decreasing the volume of the cell, the difference between classical mechanics and quantum mechanics becomes obvious. Theoretical studies on the nature of the adsorption equilibrium are sometimes performed in conditions of low temperature such as at the nitrogen boiling point so that the effect of factors of non-adsorption nature is reduced. In this case the classical mechanics approach is questionable. Specially when the adsorption system is a small molecular gas in a \( \beta \) cage of zeolite A series, the dimension of the \( \beta \) cage is close to molecular dimension and the classical mechanics treatment may be invalid.

6 CONCLUSIONS

In this section, a methodology for predicting the adsorption isotherms, adsorption heats and adsorption thermodynamic functions at low coverage was developed. The model is independent of the experimental data and no any adjustable parameter exists, thus the model is truly predictive. The calculated results of adsorption isotherms and adsorption heats for argon, oxygen and nitrogen in 4A and 5A zeolites are in good agreement with the published experimental data. The central work of the theoretical model is the calculation of the molecular partition function of the adsorbate in the adsorbed phase.
The steady state Schrödinger equation was applied to describe the motion of the adsorbate molecule inside the zeolite A cavity. The interaction potential between the adsorbate molecule and adsorbent wall atoms is calculated by pairwise summation of the various individual interactions including dispersion, repulsion, induction and quadrupole moment. The solutions of the steady state Schrödinger equation using the interaction potential in the spherically symmetrical form give the eigen energy spectrum. Different quantum numbers correspond to different molecular energy levels. The molecular partition functions of adsorbate inside the cavity of zeolite A can be calculated from the eigen energy spectrum. All adsorption thermodynamic functions, adsorption heats and adsorption Henry constants can be directly related to the molecular and system partition functions. The main objective of this work was to develop this predictive methodology.

The comparison of the molecular partition functions calculated by classical and quantum mechanics shown that the differences are negligible for moderate temperatures and relative large cavities. At low temperatures the classical method loses applicability, specially for small size cavities where the deviation becomes more serious.

The drawback of this methodology is that the model can only deal with cases for the adsorbed amount is less than in average one molecule per cavity in order to be able to use the spherically symmetrical potential distribution. One of the potential applications of this methodology is as a criterion for theoretical design and improvement of adsorbent separation characteristics prior to any experimental determinations.

**APPENDIX**

**PROCEDURE FOR THE CALCULATION OF THE INTERACTION POTENTIAL**

1. **Position of O\(^{-0.25}\) Anions and Na\(^+\) Cations**

The interaction potentials at each point inside the cavity were calculated by pairwise summation of dispersion, repulsion, induction and quadrupole moment interactions between different wall atoms and the adsorbate molecule. Based on the structure of 4A zeolite, all wall atoms (72 O\(^{-0.25}\) and 15 cations) in each cavity can be located after fixing the coordinate system. The coordinate system was chosen such that the origins of the three axes coincide with the center of the cavity and the directions of the three coordinates are perpendicular to the six eight membered ring planes. The coordinates of 72 wall atoms and 15 cations are shown in Table A2.1 and Table A2.2.

In Table A2.1 r8ring is the radius of the eight membered ring (r8ring = 3.65 Å), r8toc is the distance between the eight membered ring plane and the center of the cavity (r8toc = 6.05 Å), rmid is equal to 0.5(r8ring + r8toc) = 4.85 Å, rpi8 = rmid * sin(π/8) and rpi4 = r8ring * sin(π/4). O\(^{-0.25}\) anions of numbers 1 to 48 are located at the four membered rings and 49 to 72 are located at the eight membered rings.
Table A2.1 Positions of O\(^{0.25}\)

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0</td>
<td>r8ring</td>
<td>r8toc</td>
<td>37</td>
<td>m3id</td>
<td>rpi8</td>
<td>m3id</td>
</tr>
<tr>
<td>2</td>
<td>0.0</td>
<td>r8toc</td>
<td>r8ring</td>
<td>38</td>
<td>m3id</td>
<td>rpi8</td>
<td>m3id</td>
</tr>
<tr>
<td>3</td>
<td>0.0</td>
<td>r8ring</td>
<td>r8toc</td>
<td>39</td>
<td>m3id</td>
<td>rpi8</td>
<td>m3id</td>
</tr>
<tr>
<td>4</td>
<td>0.0</td>
<td>r8toc</td>
<td>r8ring</td>
<td>40</td>
<td>m3id</td>
<td>rpi8</td>
<td>m3id</td>
</tr>
<tr>
<td>5</td>
<td>0.0</td>
<td>-r8ring</td>
<td>r8toc</td>
<td>41</td>
<td>m3id</td>
<td>m3id</td>
<td>rpi8</td>
</tr>
<tr>
<td>6</td>
<td>0.0</td>
<td>-r8toc</td>
<td>r8ring</td>
<td>42</td>
<td>m3id</td>
<td>m3mid</td>
<td>rpi8</td>
</tr>
<tr>
<td>7</td>
<td>0.0</td>
<td>-r8ring</td>
<td>r8toc</td>
<td>43</td>
<td>m3id</td>
<td>m3id</td>
<td>rpi8</td>
</tr>
<tr>
<td>8</td>
<td>0.0</td>
<td>-r8toc</td>
<td>r8ring</td>
<td>44</td>
<td>m3id</td>
<td>m3id</td>
<td>rpi8</td>
</tr>
<tr>
<td>9</td>
<td>r8ring</td>
<td>0.0</td>
<td>r8toc</td>
<td>45</td>
<td>m3id</td>
<td>m3id</td>
<td>rpi8</td>
</tr>
<tr>
<td>10</td>
<td>r8toc</td>
<td>0.0</td>
<td>r8ring</td>
<td>46</td>
<td>m3id</td>
<td>m3id</td>
<td>rpi8</td>
</tr>
<tr>
<td>11</td>
<td>r8ring</td>
<td>0.0</td>
<td>r8toc</td>
<td>47</td>
<td>m3id</td>
<td>m3id</td>
<td>rpi8</td>
</tr>
<tr>
<td>12</td>
<td>r8toc</td>
<td>0.0</td>
<td>r8ring</td>
<td>48</td>
<td>m3id</td>
<td>m3id</td>
<td>rpi8</td>
</tr>
<tr>
<td>13</td>
<td>-r8ring</td>
<td>0.0</td>
<td>r8toc</td>
<td>49</td>
<td>rpi4</td>
<td>r8toc</td>
<td>rpi4</td>
</tr>
<tr>
<td>14</td>
<td>-r8toc</td>
<td>0.0</td>
<td>r8ring</td>
<td>50</td>
<td>rpi4</td>
<td>r8toc</td>
<td>rpi4</td>
</tr>
<tr>
<td>15</td>
<td>-r8ring</td>
<td>0.0</td>
<td>r8toc</td>
<td>51</td>
<td>rpi4</td>
<td>r8toc</td>
<td>rpi4</td>
</tr>
<tr>
<td>16</td>
<td>-r8toc</td>
<td>0.0</td>
<td>r8ring</td>
<td>52</td>
<td>rpi4</td>
<td>r8toc</td>
<td>rpi4</td>
</tr>
<tr>
<td>17</td>
<td>r8ring</td>
<td>r8toc</td>
<td>0.0</td>
<td>53</td>
<td>- rpi4</td>
<td>r8toc</td>
<td>rpi4</td>
</tr>
<tr>
<td>18</td>
<td>r8toc</td>
<td>r8ring</td>
<td>0.0</td>
<td>54</td>
<td>- rpi4</td>
<td>r8toc</td>
<td>rpi4</td>
</tr>
<tr>
<td>19</td>
<td>r8ring</td>
<td>-r8toc</td>
<td>0.0</td>
<td>55</td>
<td>- rpi4</td>
<td>r8toc</td>
<td>rpi4</td>
</tr>
<tr>
<td>20</td>
<td>r8toc</td>
<td>-r8ring</td>
<td>0.0</td>
<td>56</td>
<td>- rpi4</td>
<td>r8toc</td>
<td>rpi4</td>
</tr>
<tr>
<td>21</td>
<td>-r8ring</td>
<td>r8toc</td>
<td>0.0</td>
<td>57</td>
<td>r8toc</td>
<td>rpi4</td>
<td>rpi4</td>
</tr>
<tr>
<td>22</td>
<td>-r8toc</td>
<td>r8ring</td>
<td>0.0</td>
<td>58</td>
<td>r8toc</td>
<td>rpi4</td>
<td>rpi4</td>
</tr>
<tr>
<td>23</td>
<td>-r8ring</td>
<td>-r8toc</td>
<td>0.0</td>
<td>59</td>
<td>r8toc</td>
<td>rpi4</td>
<td>rpi4</td>
</tr>
<tr>
<td>24</td>
<td>-r8toc</td>
<td>-r8ring</td>
<td>0.0</td>
<td>60</td>
<td>r8toc</td>
<td>rpi4</td>
<td>rpi4</td>
</tr>
<tr>
<td>25</td>
<td>rpi8</td>
<td>m3id</td>
<td>m3id</td>
<td>61</td>
<td>r8toc</td>
<td>rpi4</td>
<td>rpi4</td>
</tr>
<tr>
<td>26</td>
<td>rpi8</td>
<td>m3id</td>
<td>m3id</td>
<td>62</td>
<td>r8toc</td>
<td>rpi4</td>
<td>rpi4</td>
</tr>
<tr>
<td>27</td>
<td>rpi8</td>
<td>m3id</td>
<td>m3id</td>
<td>63</td>
<td>r8toc</td>
<td>rpi4</td>
<td>rpi4</td>
</tr>
<tr>
<td>28</td>
<td>rpi8</td>
<td>m3id</td>
<td>m3id</td>
<td>64</td>
<td>r8toc</td>
<td>rpi4</td>
<td>rpi4</td>
</tr>
<tr>
<td>29</td>
<td>-rpi8</td>
<td>m3id</td>
<td>m3id</td>
<td>65</td>
<td>r8toc</td>
<td>rpi4</td>
<td>rpi4</td>
</tr>
<tr>
<td>30</td>
<td>-rpi8</td>
<td>m3id</td>
<td>m3id</td>
<td>66</td>
<td>r8toc</td>
<td>rpi4</td>
<td>rpi4</td>
</tr>
<tr>
<td>31</td>
<td>-rpi8</td>
<td>m3id</td>
<td>m3id</td>
<td>67</td>
<td>r8toc</td>
<td>rpi4</td>
<td>rpi4</td>
</tr>
<tr>
<td>32</td>
<td>-rpi8</td>
<td>m3id</td>
<td>m3id</td>
<td>68</td>
<td>r8toc</td>
<td>rpi4</td>
<td>rpi4</td>
</tr>
<tr>
<td>33</td>
<td>m3id</td>
<td>rpi8</td>
<td>m3id</td>
<td>69</td>
<td>r8toc</td>
<td>rpi4</td>
<td>rpi4</td>
</tr>
<tr>
<td>34</td>
<td>m3id</td>
<td>rpi8</td>
<td>m3id</td>
<td>70</td>
<td>r8toc</td>
<td>rpi4</td>
<td>rpi4</td>
</tr>
<tr>
<td>35</td>
<td>-m3id</td>
<td>rpi8</td>
<td>m3id</td>
<td>71</td>
<td>r8toc</td>
<td>rpi4</td>
<td>rpi4</td>
</tr>
<tr>
<td>36</td>
<td>-m3id</td>
<td>rpi8</td>
<td>m3id</td>
<td>72</td>
<td>-r8toc</td>
<td>-rpi4</td>
<td>-rpi4</td>
</tr>
</tbody>
</table>

In Table A2.2 rcavpi4pi4 = rcavity * sin(\(\pi/4\)) * sin(\(\pi/4\)), rcavpi4 = rcavity * sin(\(\pi/4\))

( rcavity is the radius of cavity shell ) and rlen = \(\sqrt{\frac{rionoxy^2 - r_m^2}{2}}\)  ( rionoxy is the
sum of radii of cation and O\(^{0.25}\) and \(r_m\) is \(\sqrt{2} \times \) radius of O\(^{0.25}\). Na\(^+\) cations of numbers
1 to 8 are located near the center of the six membered ring plane. 9 to 14 are located at the
center of the eight membered ring plane and number 15 is located at the site III. This free
cation was fixed in the position of the diagonal line along x >0 and y >0 in z = 0 plane
with equal distances to four O\(^{0.25}\) anions. In 5A zeolite there are only eight cations,
number 1 to 8 and they are located near the center of the six membered ring plane.
Table A2.2 Positions of Na⁺ cations

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>rcaypi4pi4</td>
<td>rcaypi4pi4</td>
<td>rcaypi4</td>
</tr>
<tr>
<td>2</td>
<td>rcaypi4pi4</td>
<td>-rcaypi4pi4</td>
<td>-rcaypi4</td>
</tr>
<tr>
<td>3</td>
<td>rcaypi4pi4</td>
<td>rcaypi4pi4</td>
<td>rcaypi4</td>
</tr>
<tr>
<td>4</td>
<td>rcaypi4pi4</td>
<td>-rcaypi4pi4</td>
<td>rcaypi4</td>
</tr>
<tr>
<td>5</td>
<td>-rcaypi4pi4</td>
<td>rcaypi4pi4</td>
<td>rcaypi4</td>
</tr>
<tr>
<td>6</td>
<td>-rcaypi4pi4</td>
<td>rcaypi4pi4</td>
<td>-rcaypi4</td>
</tr>
<tr>
<td>7</td>
<td>-rcaypi4pi4</td>
<td>-rcaypi4pi4</td>
<td>rcaypi4</td>
</tr>
<tr>
<td>8</td>
<td>-rcaypi4pi4</td>
<td>-rcaypi4pi4</td>
<td>-r8toc</td>
</tr>
<tr>
<td>9</td>
<td>0.0</td>
<td>0.0</td>
<td>r8toc</td>
</tr>
<tr>
<td>10</td>
<td>0.0</td>
<td>0.0</td>
<td>-r8toc</td>
</tr>
<tr>
<td>11</td>
<td>0.0</td>
<td>r8toc</td>
<td>0.0</td>
</tr>
<tr>
<td>12</td>
<td>0.0</td>
<td>-r8toc</td>
<td>0.0</td>
</tr>
<tr>
<td>13</td>
<td>r8toc</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>14</td>
<td>-r8toc</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>15</td>
<td>0.0</td>
<td>rmid - rlen</td>
<td>rmid - rlen</td>
</tr>
</tbody>
</table>

2. Calculation of the Interaction Potential Coefficients

The dispersion and repulsion coefficients between adsorbate molecule and adsorbent wall atoms and cations are chosen as the average values of London, Slater - Kirkwood and Kirkwood - Muller equations (2.2) to (2.4). The induction and quadrupole moment interaction coefficients in equation (2.7) and (2.10) are collected together. All these coefficients are calculated once and are put in an array to be passed to the subroutine in which the interaction potential calculation is carried out.

3. Summation of Various Individual Interaction Potential Terms

The cavity of zeolite 4A is divided into 100 subshells along the radial direction and 60 subintervals along η and ξ directions at each subshell. Totally there are 100 × 60 × 60 = 360000 network points. The interaction potential at each network point can be calculated by summing the various individual interactions including dispersion, repulsion, induction and quadrupole moment. Depending on the ion charge, the calculation of the interaction between ion and quadrupole moment in equation (2.10) involves the evaluation of the error function of complex argument. The calculation of the error function of complex argument can be found by using an approximate method [Gautschi, 1965]. The calculation of the interaction potential of an adsorbate molecule in the eight membered ring window is similar. The window is divided into 100 equal spatial circles and 60 angular areas.

There are totally 100 × 60 = 6000 network points. Exception for eight O⁻0.25 anions and one cation in the window plane, the contributions of other anions and cations in the adjacent two cavities must be considered. For the 4A zeolite window, the cation is fixed in the position of the most packed state with the two O⁻0.25 anions in the same window plane. The distances between the two O⁻0.25 anions and the cation are the sum of O⁻0.25 and Na⁺ radii.

The average values of interaction potential at a given subshell can be evaluated by using equation (2.19) and the integral is carried out numerically. For the 4A zeolite the
contribution of repulsion from the free cation to total interaction potential is reduced by using a Boltzmann weighted average equation (2.20).

REFERENCES


Breck, D.W., Zeolite Molecular Sieves, Wiley, 1974


Gautschi,W., Error Functions and Fresnel Integrals, in Handbook of Mathematical Functions, ed. by M Abramowitz and I. A. Stegun, Dover Publications, Inc., 1965


Kiselev, A.V., Vapor Adsorption on Zeolites Considered as Crystalline Specific Adsorbents, Molecular Zeolites - II, Advances in Chemistry Series No. 102, Amer. Chem. Soc., p37, 1971


Weast, R. C., Handbook of Chemistry and Physics, 54th ed., CRC Press, 1973
III. INTRACRYSTALLINE DIFFUSION AND DIFFUSIVITIES

The successful use of 4A zeolite for producing nitrogen from air by PSA has stimulated the researcher to pay more attention to the theoretical studies on adsorption equilibrium and intracrystalline diffusion. In this process the effects on the separation efficiency of equilibrium and diffusion of individual components to be separated are in opposite directions. The adsorption isotherm is favorable to nitrogen. The requirements for producing nitrogen by PSA imply that the adsorbent must have a favorable adsorption behavior to oxygen and thus when the air stream flows through the adsorption columns, the oxygen is adsorbed and pure nitrogen is obtained at the column outlet. This favorable adsorption characteristic is achieved by adjusting the operating conditions in order to favor the faster intracrystalline diffusional process of oxygen. In other words, the separation is carried out by means of the diffusional rate difference between the individual components to be separated [ Shin and Knaebel, 1987, Kärger and Ruthven, 1992 ]. The production of oxygen from air by PSA utilizes the difference on the adsorption equilibrium characteristics between oxygen and nitrogen in 5A zeolite. In this case the difference between intracrystalline diffusivities is small.

Due to its importance in adsorption studies and process development, the intracrystalline diffusion of gases in zeolites has been one of the main topics for adsorption studies. The diffusional behavior in zeolites has been studied by many researchers in the last decades using various techniques [ Barrer, 1941, Satterfield, 1970, Theodorou and Wei, 1983, Mo and Wei, 1986, Patwardhan, 1989, Yeh and Yang, 1989, Chen and Yang, 1991, Faux and Hall, 1991, Kapoor and Yang, 1990, Lane, 1991, Tsikoyiannis and Wei, 1991 and Xiao and Wei, 1992 ]. The steric and diffusional constraints imposed by the zeolite structure can discriminate among molecules according to the molecular shapes favoring the production of desirable products. The diffusion of molecules in zeolite pores of comparable size plays an important role in this shape selective process. The understanding of its mechanism can greatly facilitate the design of zeolite adsorbents.

The study of intracrystalline diffusion processes is greatly dependent on the experimental techniques. A fundamental peculiarity of the macroscopic adsorption methods including gravimetric uptake, volumetric uptake and pulse and step chromatographic techniques is a non-equilibrium process, that is, when diffusion occurs, there is a concentration gradient within the crystal. This non-equilibrium peculiarity results in the existence of heat effects due to the finite rate of heat release, external mass transfer resistance and diffusional resistance on the crystal surface. This influences the intracrystalline diffusivity calculation from experimental data and the interpretation of the experimental results. When the intracrystalline diffusion is not the mass transfer controlling step the macroscopic methods are not suitable to the determination of the intracrystalline diffusivity [ Kärger and Ruthven, 1989 ]. The microscopic methods are mainly the N.M.R. technique and its modifications. In this method, the average time between molecular jumps is measured indirectly or directly and the intracrystalline self-diffusivities can be related to average time. The most usually used modification of the N.M.R. method is the field gradient technique [ Kärger and Pfeifer, 1987 ]. Due to the restrictions on the field gradient pulse width and field gradient intensity, the lower limit of self-diffusivities measurable by the N.M.R. technique is typically in the range of $10^{-8}\text{ cm}^2/\text{s}$ [ Kärger and Ruthven, 1989 ]. In addition, a special large crystal sample is necessary. These two conditions limit the application of the N.M.R. technique.
One of the early kinetic theories for the diffusion in zeolites was offered by Barrer [Barrer, 1941]. The diffusion rate of a molecule with sufficient energy to jump from one site to another depends on the chance of finding a vacant site. The self-diffusivity is therefore reduced by the factor \((1 - \theta)\) if the probability of a site being occupied by a molecule is \(\theta\). Rieckert [1985] used a lattice model and concluded that in single-component diffusion in zeolites the diffusivity is concentration independent. The transient state method [Ruthven and Derrah, 1976] is able to explain diffusional processes where relatively large adsorbate molecules diffuse through a relatively small window such as paraffins in zeolite A, in other words, the minimum kinetic diameter of the adsorbate molecule is slightly larger than the free dimension of the adsorbent diffusion path. The molecule must overcome the strong repulsive energy in window and only these adsorbate molecules which have an average kinetic energy greater than the window potential can cross the window. Ruthven and Derrah [1976] used the transition state principle successfully to explain the intracrystalline diffusion of \(\text{CH}_4\) and \(\text{CF}_4\) in \(4\)A zeolite. This theory fails to explain the diffusion of small molecules through relatively large windows where the interaction potential at the window plane is minimum or the minimum kinetic diameter of the adsorbate molecule is smaller than the free dimension of the adsorbent diffusion path. Nitsche [Nitsche and Wei, 1991] successfully used the theory of Brownian motion over a potential barrier to explain the phenomena in which the diffusivities of normal paraffins in zeolite T do not decrease monotonically with increasing carbon number.

The Monte Carlo approach has been widely used [Faux and Hall, 1991]. In this method, the molecular random thermal motion is numerically simulated and a large number of calculations are carried out until a stable calculated system is reached. Palekar [Palekar and Rajadhynaksha, 1985 a, b and 1986] carried out simulations for one and two-component diffusion in a one-dimensional, parallel, noninteracting lattice. Aust et al. [1989] extended the work to a two-dimensional lattice by similar Monte Carlo simulations. They found a rising trend of diffusivity with adsorbed amount under the assumption that a molecule would jump if there is at least one vacant neighboring site. An almost concentration-independent trend was observed when the assumption was changed so that the molecule would not jump if the first assigned direction led to an unsuccessful jump. In the Monte Carlo simulation technique, there is a parameter representing the hopping of the adsorbate molecule that need to be determined from some kinetic or dynamic adsorption experimental data or assumption, which results in that the method is not truly predictive. Theoretically, this method can deal with various systems as long as the probabilities of adsorbate molecular motion in various directions can be reasonably specified [Baron et al, 1992].

The intracrystalline diffusivity can be illustrated by means of Fick’s diffusional law:

\[
J = -D \text{ grad } C
\]  
(1.107)

This equation shows that the transport flux of adsorbate through any unit area crystal section results from the adsorbate concentration gradient within the crystal. When the adsorption process reaches the equilibrium state, the macroscopic concentration gradient disappears. From the statistical point of view, individual adsorbate molecules within crystals have different energies and the energy of the same molecule varies with time. Such energy changes result in the random diffusion of the adsorbate molecule.

One important issue in studying the intracrystalline diffusion is the concentration dependency of diffusivity. The size of adsorption and diffusional pores of zeolites is of
the same order of magnitude as the size of the molecules, the adsorbed molecules in the cavity will greatly affect the diffusion of other molecules. In order to eliminate such factor, we only consider the situation of free initial adsorbed amount. Usually, the dependency of diffusivity on adsorbate concentration is described by the Darken's equation [Darken, 1948]:

\[ D = D_0 \frac{\partial \ln P}{\partial \ln c} \quad (3.1) \]

where \( P \) and \( c \) are respectively the pressure in bulk phase and the concentration in the adsorbed phase and \( D_0 \) is the diffusivity when the adsorbed amount tends to zero. In many systems, \( D_0 \) is considered to be independent of concentration [Rudin, 1984]. There are also cases in which \( D_0 \) is concentration-dependent. When adsorption occurs within the Henry region, \( D \) is directly equal to \( D_0 \). According to equation (3.1), the concentration dependency results from the nonlinearity of the adsorption isotherm. This macroscopic approach gives no mechanistic reasons to decide whether \( D_0 \) is dependent or independent of concentration since the details of molecular motion were ignored in the formulation of this equation [Xiao and Wei, 1992]. In the following section, we concentrate our interest on the development of a theoretical model to predict \( D_0 \). Because we only consider the diffusivity at zero coverage, \( D_0 \) becomes the same as \( D \).

It is worthy to mention the differences between self and counter-diffusivities. When the adsorption diffusion system contains more than two adsorbable components, the adsorbent reaches an equilibrium state with one or all components. If the concentration in the bulk phase of one of the adsorbates undergoes a pulse or step, the original equilibrium is broken and the molecules of the corresponding component will diffuse from the crystal surface to the central region by crystalline diffusion until a new equilibrium is established. Simultaneously, other component molecules will diffuse out of the crystal. These two diffusional processes are in opposite directions. The dimension of the diffusional path in zeolites is of the same order of magnitude as adsorbate molecules and thus the molecules diffusing out of the crystal will temporarily block the diffusional path for other component molecules diffusing towards the central region. A typical example is the chromatographic measurement technique for diffusivity. In this system, the adsorbent packed in a column is saturated by the carrier gas, usually helium. When an adsorbate component is suddenly introduced, the diffusion of adsorbable component into the crystals implies that the carrier gas molecules diffuse out of the crystals. If the carrier gas is strongly adsorbed, counter-diffusion is obvious. In practical calculations of diffusivities, the interaction of the carrier gas in adsorption equilibrium and blocking effects is usually neglected. The so-called self-diffusion is the case in which the adsorption system only contains one adsorbate component. The calculation of self-diffusivity is much easier than that of counter-diffusivity. In the gravimetric and volumetric techniques, the determined diffusivities are self-diffusivities.

1 THEORETICAL EVALUATION OF DIFFUSIVITIES

The dimension of diffusional paths in zeolite adsorbents is in the range of molecular size. Adsorbate molecules and zeolite channels can not be considered as rigid and thus their characteristic dimensions usually vary with temperature. The molecular dimensions can be characterized by means of the minimum kinetic diameter [Breck, 1974] or the Lennard Jones parameter (or its corresponding van der Waals diameter). The minimum kinetic
diameter can be calculated from the minimum equilibrium cross-sectional diameter and it characterizes the difficulty experienced by a molecule to cross the zeolite channel. The Lennard Jones parameter can be calculated from either the transport properties or from the second virial coefficients [Hirschfelder et al., 1954]. The Lennard Jones parameter is equivalent to the spherical representation of a real molecule. For the purpose of discriminating diffusion difficulties, the Lennard Jones parameter is less useful than the minimum kinetic diameter. Nevertheless, the Lennard Jones parameter can be used to calculate the interaction potential since the important component of the interaction potential between two molecules or atoms is expressed in the Lennard Jones parameter [Hirschfelder et al., 1954]. The zeolite channel dimension can be estimated by means of the oxygen atom dimension, number of oxygen atoms in the ring and the degree of distortion of the channel.

Based on the relative dimensions of adsorbate molecules and zeolite channels, the intracrystalline diffusion processes can be divided into three types. When the minimum kinetic diameter of the adsorbate molecule is smaller than the size of the zeolite channel, the molecule might experience a net attractive interaction and the diffusion is facilitated. If the minimum kinetic diameter of the adsorbate molecule is slightly larger than the size of the zeolite channel, the molecule experiences a net repulsive interaction and the diffusion undergoes an activated process where only when the adsorbate molecule accumulates enough energy to exceed the energy barrier will be able to pass. When the minimum kinetic diameter of the adsorbate molecule is much larger than the size of the zeolite channel, it will be almost impossible to cross the channel due to the too strong repulsion interaction.

The structure of zeolite A is one of the most well known. The diffusional path is through the eight-membered rings. The free diameter of the eight-membered ring is 4.3 Å [Breck, 1974]. All cations in 5Å are located inside the cavity and the free dimension of the diffusional path is not affected. The calculation of the interaction potential between small molecule gases, such as oxygen, nitrogen, argon and helium and adsorbent atoms shown that the interaction in the vicinity of the window center is minimum when compared with the interaction inside the cavity. In this case, the diffusional process of an adsorbate molecule from cavity to window is along a decreasing potential field. Whereas in 4Å zeolite there is a cation in each window that partially blocks the channel. If the distance between O$^{0.25}$ and Na$^+$ is adopted as 2.4 Å [Barer, 1978], the free dimension of the window blocked by Na$^+$ is reduced to about 2.5 Å. The minimum kinetic diameters of almost all kinds of molecules are greater than this value and the interaction potential between adsorbate molecule and adsorbent atoms in the window region of 4Å zeolite is strongly repulsive. The interaction between the cation and the eight-membered ring is principally the electrostatic force and the interaction among O$^{0.25}$ is a chemical bonding force through co-linked Al or Si atoms. The later force is much stronger than the former. When an adsorbate molecule strikes the eight-membered ring window, as long as the molecule has enough translational kinetic energy, the eight-membered ring window structure will change. Compared with other possible structure variations which are helpful to enlarge the diffusional path dimension, the deviation of the cation needs smaller energy. When the cation in the eight-membered ring window deviates from the window plane, the free dimension of the diffusional path increases. The deviation of cations from the window plane needs that the adsorbate has enough molecular kinetic energy. From the point of view of classical statistical thermodynamics, the translational kinetic energy of an adsorbate molecule has a continuous distribution and only a small fraction of the translational kinetic energy distribution has a value greater than the required to change the cation position. When an adsorbate molecule inside the cavity strikes the window and it has enough translational kinetic energy it can cross the window, otherwise it will be
bounded back to the original cavity. In this case the diffusion is obviously an activated process.

In quantum mechanics, the motion of any microscopic particle has a wave nature. Based on the classical mechanics only when the adsorbate molecule has a translational kinetic energy greater than the energy barrier of the window the molecule can cross the window. Whereas the wave nature of molecular motion shows that even if the translational kinetic energy of an adsorbate molecule is less than the energy barrier of the window there is a probability of the molecule penetrating the window plane. The magnitude of the probability is not only dependent on the magnitude of the energy barrier but also dependent on the thickness of the energy barrier. When the thickness of the energy barrier is greater than several angstrom, the contribution of wave natural penetration is negligible. On the other hand, when the energy barrier is thin, the wave natural contribution to total diffusivity plays in principle an important role. The calculated interaction potential in the cavity and at the window shown that the width of energy barrier is close to the cation dimension (about 2 angstrom) and thus the wave contribution to the permeation of an adsorbate molecule through the window energy barrier is negligible.

According to the equal distribution of the average translational kinetic energy on the motion degrees of freedom, the average translational kinetic energy of an adsorbate molecule at a given temperature is independent of the type of adsorbate. On the other hand, for different adsorbates their average translational kinetic energies are the same as long as they have the same number of motion degrees of freedom. Increasing the dimension of the minimum kinetic diameter, when larger adsorbate molecules cross the window, the cation in the eight membered ring window must deviate more from the window plane and this requires more translational kinetic energy. In this case the probability of the molecule to penetrate the window plane with kinetic energy less than the energy barrier is smaller. So the total probability of large adsorbate molecules to cross the window is smaller than that of small molecules.

The classical statistical mechanics shows that the kinetic energy distribution with different kinetic energy levels can be expressed by means of the Maxwell - Boltzmann relationship. In fact, the Maxwell - Boltzmann distribution is an approximation of quantum energy spectrum by a continuous function. In Chapter I we already shown that this approximation is very rough at high kinetic energy values. The intracrystalline diffusion of gases in the blocked eight membered ring window of 4A zeolite is a strongly activated process. Even if we only consider the classical kinetic behavior, the energy barrier of the blocked window is much higher than the average kinetic energy of the molecule. Only a very small fraction of the molecular kinetic energy distribution is higher than this barrier and thus the calculation of the probability of an adsorbate molecule to cross the barrier involves only the region of high kinetic energies. The calculated results presented in this chapter confirm that the Maxwell - Boltzmann distribution is not applicable to these cases.

These reasons justify the use of quantum mechanics for evaluating the various energy levels and the average macroscopic properties. In our system, the diffusion mechanisms of gases in the blocked and non-blocked windows of zeolite A series are different. In the following sections the two different diffusional mechanisms will be developed.

1.1 Small Molecules Diffusion in Relatively Large Pores

The diffusional processes of small molecular gases, such as, helium, oxygen, argon and nitrogen inside the crystal at low occupation can be imagined by considering the case in
which a molecule in thermal motion inside a cavity has a few chances to escape the cavity to form a temporary state in the window plane. The adsorbate molecule in the intermediate state can diffuse into the next cavity, or return to the original one. The probabilities of these two possibilities should be equal at low coverage. The relative stability of molecules in the cavity and at the window can be expressed by means of the ratio of the corresponding molecular partition functions. The whole diffusional process of an adsorbate molecule from a cavity to another cavity undergoes three steps, the molecule diffuses to the window, temporarily moves at the window plane and then diffuses to the next cavity or returns to the original one. In the case of small molecules diffusing in 5A zeolite, the calculated interaction potential energy shows that at the center of the eight membered ring the interaction potential energy is minimum. But in the window plane the degrees of freedom of adsorbate molecules reduce to two dimensions from a localized three dimensions inside cavities. From the point of view of statistical thermodynamics, the stability of a microscopic state is not only dependent on the system energy but also on the motion degrees of freedom. The stability ratio shows that the probability of a molecule staying at the window plane is much smaller than inside the cavity. So in all three steps, the contribution of the intermediate state at the window plane to the total diffusional resistance can be neglected. The overall self diffusivity \( D_o \) from a cavity to another cavity can be expressed as:

\[
D_o = \frac{1}{\frac{1}{D_{cw}} + \frac{1}{D_{wc}}} \tag{3.2}
\]

where \( D_{cw} \) and \( D_{wc} \) represent the self diffusivities of adsorbate molecule from cavity to window and from window to cavity.

From the principles of non-equilibrium thermodynamics, the transport coefficients can be defined in the terms of the response of a system to a perturbation. The diffusivity relates the flux to the concentration gradient. By introducing such perturbations into the Hamiltonian (quantum view) or into the motion equations (classical view), their effect on the energy distribution function may be calculated by the corresponding quantum or classical mechanics. Generally, a time-dependent distribution is produced and thus any time-independent average (in particular the desired responses) may be calculated. By retaining the linear terms in the perturbation response and comparing this equation with a macroscopic transport equation, the transport coefficient can be identified. This is usually an infinite time integral of a time-dependent correlation function. In the so called Einstein relation the infinite time integral is replaced by a large but finite time and the corresponding diffusivity can be expressed as [Allen and Tildesley, 1987]:

\[
D_o = \frac{1}{6t} < |r(t) - r(0)|^2 > \tag{3.3}
\]

Where \( r(t) \) and \( r(0) \) are the molecular position vectors, \( t \) is the observation time and the \( < > \) means the average value. In the situation of a stiff cavity wall and window and of an elastic bound between the adsorbate molecule and the wall, if no any energy lost, this self diffusivity can be described by the Einstein equation [Xiao and Wei, 1992]:

121
\[ D_0 = \frac{\kappa^2}{6t} \]  

(3.4)

where \( \kappa^2 \) is the molecular mean square displacement. The factor 1/6 comes from the fact that only the motion in one direction contributes to the diffusivity. In fact, the definition of diffusivity in the above equation is equivalent to the definition in Fick's law \[ \text{Kärger and Pfeifer, 1987} \]. In a zeolitic diffusional system, an adsorbate molecule that diffuses from one cavity to the next one, covers an average length which is equal to the crystal cell dimension. So \( \kappa \) can be chosen as this dimension. In zeolite A this is the dimension between two opposite windows in a cavity.

The real case of intracrystalline diffusion of gases is much more complex. The cavity wall and window are not stiff and there is an interaction potential between the cavity wall and window ring atoms and the adsorbate molecule. So the adsorbate molecule moves under an interaction potential. The adsorbate molecule must overcome the average potential differences between cavity and window when it diffuses to window or out of window. For the diffusion of Ar, N\(_2\) and O\(_2\) in 5A, the average potential of adsorbate molecule in the cavity is higher than in window. There is no energy barrier when it diffuses to window, but in the opposite direction there is such a barrier. The situation of diffusion of large molecule in 5A or small molecules in 4A may be quite different.

The motion of the adsorbate molecule inside the cavity under the spherically symmetrical potential field can be assumed to be along the radial direction. The molecular motion properties, \( \kappa \), was calculated at the cavity center thus assuming that it represents well the average properties. Under these conditions the adsorbate molecule self diffusivity from cavity to window can be calculated by multiplying the Einstein diffusivity by the probability \( (P_{cw}) \) of an adsorbate molecule escaping the cavity. It yields:

\[ D_{cw} = \frac{\kappa^2}{t} P_{cw} \]

(3.5)

The calculated interaction potential distributions shown that the interaction potential in the vicinity of the window center is minimum. In the line linking the centers of the cavity and the window the potential gradually decreases when the adsorbate molecule approaches the center of the window. Out of the vicinity of the window center the potential quickly increases and becomes a strong energy barrier due to the repulsion that comes from the O\(-0.25\) in the 8 membered ring. If the adsorbate molecule inside the cavity hits this area it can escape the cavity and form a temporary state at the window plane. Otherwise it will be bounded back. The solutions of the stationary state Schrödinger equation applied to the adsorbate molecule at the window plane allow the calculation of the average radius \( \bar{r} \) and of the average interaction potential energy \( \bar{U}_{win} \). The average radius can be considered as the radius inside which the interaction potential is lower than the average potential. Because the potential distribution is very steep when the potential changes sign, this radius can also be considered as the critical dimension. For an effective hit the probability \( (P_{cw}) \) of an adsorbate molecule escaping the cavity can be expressed as the ratio of the areas of this region and the total surface area of the cavity shell.
\[
\mathcal{P}_{cw} = \frac{r^2}{4\Gamma_x^2} \quad (3.6)
\]

The detailed discussion on how to calculate these average properties by quantum mechanics has already been carried out in Chapter I.

The stability ratio between the states of the adsorbate molecule located at the window plane and located inside the cavity can be expressed as the ratio of the corresponding partition functions \( \mathcal{Q}_w/\mathcal{Q}_c \). The results shown later show that the temporary state at the window plane is very unstable due to the decrease of the motion degrees of freedom and of the region of motion and thus the contribution of this temporary state to the total diffusion resistance can be neglected.

The adsorbate molecule at the intermediate state only has two possible diffusional directions to escape the window. One is to go into the next cavity and only this one makes a contribution to diffusivity. Another is to return to original one. The probability of these two ways may be different depending on the adsorbate concentration in these two cavities. When the initial adsorbed amount inside the zeolite crystal is zero and only a differential amount of adsorbate in bulk phase is introduced into the system, both adjacent cavities are free of adsorbate molecules after the intermediate state is formed. In this case the probabilities of both directions are equal to 1/2. Since the average total energy of an adsorbate molecule inside the cavity is higher than at the window plane, the diffusional process of an adsorbate molecule from the window plane to the next cavity or returning to the original one has to overcome an energy barrier. Only these adsorbate molecules whose translational kinetic energy is greater than the energy barrier can pass through it and finish a diffusional process. For an adsorbate molecule, if the fraction of translational kinetic energy exceeding the barrier is \( \mathcal{P}_{wc} \) then the self diffusivity from window to cavity can be expressed as:

\[
D_{wc} = \frac{x^2}{t} \mathcal{P}_{wc} \quad (3.7)
\]

According to the Boltzmann energy distribution principle [Atkins, 1986], \( \mathcal{P}_{wc} \) can be represented by:

\[
\mathcal{P}_{wc} = \frac{\sum_{i=i_M}^{\infty} g_i \exp(-\bar{\epsilon}_i/kT)}{\sum_{i=0}^{\infty} g_i \exp(-\bar{\epsilon}_i/kT)} = \frac{\sum_{i=i_M}^{\infty} g_i \exp(-\bar{\epsilon}_i/kT)}{\mathcal{Q}_w} \quad (3.8)
\]

where \( \mathcal{Q}_w = \sum_{i=0}^{\infty} g_i \exp(-\bar{\epsilon}_i/kT) \) is the molecular partition function of adsorbate molecule at the window plane. \( i_M \) represents the index of the eigen energy greater than a given energy value \( \Delta \bar{\epsilon} \). The summation in the nominator includes only the terms with
translational kinetic energy exceeding the barrier. The wave natural penetration of adsorbate molecule when the kinetic energy is less than the energy barrier has to be neglected because the energy barrier is thick and thus the penetration will be very small.

The total energy of an adsorbate molecule inside the cavity and at the window plane includes potential energy, translational kinetic energy, molecular rotation kinetic energy, vibration energy and other internal motion energies of the molecule. In the range of physical adsorption, the interaction forces between adsorbate molecules and adsorbent atoms are primarily of the van der Waals and electrostatic types that are much lower than the chemical bonding forces and the cavity space is large when compared to the adsorbate molecule. In these conditions the internal motion states including vibration, electronic and nuclei, are almost not affected. But the translational and the rotation kinetic energies are different inside the cavity and at the window plane. The motion of an adsorbate molecule inside the cavity is a localized three-dimensional motion with three degrees of freedom. According to the energy equipartition principle, the corresponding translational kinetic energy inside the cavity is equal to $3kT/2$. Whereas at the window plane the adsorbate molecule only takes a localized two-dimensional motion with two degrees of freedom and thus the corresponding translational kinetic energy is equal to $kT$.

Oxygen and nitrogen are linear diatomic molecules. Their dimensions are respectively $2.8 \times 3.9$ Å and $3.0 \times 4.1$ Å at the cross section diameter and length respectively [Barrer, 1978]. We consider that these molecules are composed by two atomic mass points and that the distance between these points is equal to the bond length. When such adsorbate molecules take different configurations at the window plane the interaction potentials acting on the molecules are quite different. When the molecule is orthogonal to the window plane, the interaction potential is minimum. The free dimension of the eight membered ring window is close to the length of the oxygen and nitrogen molecules. When the molecules are at the window plane, the adsorbate molecules will be subjected to a strong repulsion potential that makes this configuration impossible. The molecule staying at the window plane can take different orientations that correspond to different repulsion potentials. Only when the axis of the molecule coincides with the linking line of two opposite $O^{2-}$ anions the repulsion potential will be maximum.

The energy barrier between cavity and window states includes the average translational and rotation kinetic energy differences, $\Delta \bar{E}_{tr}$ and $\Delta \bar{E}_{rot}$ respectively, and the potential energy difference $\Delta \bar{U}$. Based on the energy equidistribution principle, each degree of freedom has energy $kT/2$. Inside the cavity the average translational kinetic energy is $3kT/2$ and at the window plane $kT$. So $\Delta \bar{E}_{tr} = kT/2$. In the case of noble gases molecular rotation does not make any energy contribution to total internal energy. The linear diatomic molecules rotate with two degrees of freedom in a zero potential field and later calculations show that the rotation probabilities for oxygen and nitrogen molecules at the window plane are almost negligible. So the average rotational kinetic energy in free rotation is $\Delta \bar{E}_{rot} = kT$. The average potential energy of an adsorbate molecule at the window plane and inside the cavity can be obtained from the solution of the stationary state Schrödinger equations corresponding to these two states. If we assume that the motion properties of the adsorbate molecule inside the cavity and located at the cavity center are equivalent, the potential energy difference will be equal to the difference between the average potential at the cavity center and at the window plane $\Delta \bar{U} = \bar{U}_c - \bar{U}_w$. So the energy barrier $\Delta e$ is equal to

124
\[ \Delta \varepsilon = \frac{3kT}{2} + \Delta \bar{U} \] (3.9)

Up to now the problem of calculating intracrystalline self diffusivity was focused on the evaluation of interaction potential energy and average properties of the molecule at the window plane.

1.2. Activated Diffusion

The cation located at the 8 membered ring window in 4A zeolite greatly reduces the window aperture from 4.3Å in 5A to about 2.6 Å [Barer, 1978]. The minimum kinetic dimension of most gases is greater than this number and so diffusion will be an activated process. In this case the calculation methodology for the intracrystalline diffusivity is different from that used for the 5A zeolite.

The cavity structure of 4A is similar to 5A except for the existence of one free cation. The dimension of 4A zeolite cavity is larger than the molecule dimension and thus the adsorbate molecule inside the cavity moves in a thermal localized random three dimensional way. The average position of the molecule which can be found from the solutions of Schrödinger equations is located in a spherical shell with radius \( \frac{r}{r} \) (discussed in the Chapter I).

The probability (\( \mathcal{P}_{cw} \)) of an adsorbate molecule hitting each 8 membered ring window can be assumed as being the ratio between the areas of the 8 membered ring windows and the total cavity area.

\[ \mathcal{P}_{cw} = \frac{r_{\text{win}}^2}{4r_c} \] (3.10)

where \( r_{\text{win}} \) is the radius of the eight membered ring window. Only when the adsorbate molecule has translational kinetic energy greater than the energy barrier located at the 8 membered ring window, it will be able to cross and finish a hop. Otherwise it will be bounded back to the original cavity. The existence of a cation in each window implies an asymmetrical interaction potential distribution, that is, at different radial and angular positions the energy barrier is different.

According to the Boltzmann energy distribution principle [Atkins, 1986], the fraction \( \mathcal{P}_j \) of adsorbate molecule that have translational kinetic energies greater than an energy barrier \( \Delta \varepsilon_j \) (\( \Delta \varepsilon_j \) is the difference between the potential in \( j \) th window differential area and the average cavity potential \( \bar{U} \)) can be represented by:

125
\[ P_j = \frac{\sum_{i=m}^{\infty} g_i \exp(-\varepsilon_i/kT)}{\sum_{i=0}^{\infty} g_i \exp(-\varepsilon_i/kT)} = \frac{\sum_{i=m}^{\infty} g_i \exp(-\varepsilon_i/kT)}{\psi_c} \] (1.30)

where \( \psi_c = \sum_{i=0}^{\infty} g_i \exp(-\varepsilon_i/kT) \) is the translational molecular partition function of an adsorbate molecule inside the cavity. The summation in nominator includes these terms with translational kinetic energy exceeding the energy barrier \( \Delta \varepsilon_i \). This energy barrier is assumed constant inside each differential element which implies that the potential inside the same element is considered constant too. Inside a differential area, \( s_j \), of the 8 membered ring window, the probability of an adsorbate molecule hitting and crossing this element is \( s_j P_j/4r_w^2 \). The total fraction of adsorbate molecules hitting and crossing the 8 membered ring window should be the sum of \( s_j P_j/4r_w^2 \) over all differential elements.

The combination of above factors yields the diffusivity expression:

\[ D_o = \frac{\alpha^2}{t} \sum_{j=1}^{\infty} \frac{s_j P_j}{4r_w^2} \] (3.11)

From the principle of equal distribution of the energy with the motion degrees of freedom, the adsorbate molecule moves in random thermal three dimensional motion inside the cavity and so the translational kinetic energy is equal to \( 3kT/2 \). The average velocity of the molecule and thus the observation time \( t \) can be calculated. The length was calculated by the distance between two adjacent cavity centers.

2 RESULTS AND DISCUSSION

2.1 Potential Functions

The calculation of the interaction potential functions between adsorbate molecules and the cavity wall atoms and/or the window ring atoms were carried out using the site-site pairwise additive model discussed in Chapter II. All wall atoms of the two adjacent cavities will make contributions to the interaction potential at the window plane. Due to the symmetry of wall atoms in both cavities, except for the atoms located in the 8 membered ring, we only need to calculate the interaction contributions from one cavity. Taking into account the symmetry of the structure of the cavity wall, the calculation of the interaction potentials in window plane between adsorbate molecule and adsorbent atoms were carried out in the region of \( 0 \leq \eta \leq \pi/2 \) for 5A zeolite. The region was divided into 100 equal size points along the radius and 50 points along \( \eta \) direction. Figures 3.1 to 3.4 show the potential function distributions of Ar, He, N2 and O2 at the window plane of 5A zeolite at 298.15 K.

126
The potential distribution is almost radially symmetrical within the region of negative potential. In this region, the repulsion interaction is small and dispersion, induction and electrostatic interactions are the more important effects. Within this region, the resulting effect of these atoms acting on an adsorbate molecule is close to a uniform distribution.

But when \( r \geq \bar{r} \) ( \( \bar{r} \) is the average motion radius at the window plane ), the repulsion interaction becomes dominant and very sensitive to distance. So potential distribution is strongly dependent on the position even at the same ring. The free diameter of 8 membered rings in 5A zeolite is close to molecular dimensions and thus the interaction potential acting on the adsorbate molecule quickly varies with the molecule position. Even for small molecular gases such as He, Ar, O\(_2\) and N\(_2\), the potential is only negative close to the center of the window. When the adsorbate molecule deviates from the center about 0.2 - 0.3 Å it feels a strong repulsion force and the region immediately becomes almost unreachable.

In our calculation, the partition functions of adsorbate at the window are primarily determined by the eigen energies with values less than zero. So it is reasonable that we use a spherically symmetrical field of potential energy to approximate the real one. The average values at a given radial position, \( r \) over all angles, \( \eta \), can be expressed as:

![Figure 3.1 Potential distribution of helium at the window of 5A zeolite](image)
Figure 3.2 Potential distribution of Argon at the window of 5A zeolite

Figure 3.3 Potential distribution of oxygen at the window of 5A zeolite
Figure 3.4 Potential distribution of nitrogen at the window of 5A zeolite

$$\bar{U}_i(r) = \frac{\int \mathcal{U}(r,\eta) \, d\eta}{\int \, d\eta}$$  \hspace{1cm} (3.12)

This approximation makes it possible the separation of variables in the steady state Schrödinger equation and to solve it.

The average potential distribution curves of Ar, He, N\(_2\) and O\(_2\) over all angles at the window plane of 5A zeolite along the radial variable are showed in Figure 3.5. The curves in these figures confirm that the potential distributions are very steep out of the vicinity of the window center. So when we calculate the probability that an adsorbate molecule escapes from the cavity to the window, the dimension of this vicinity can be chosen as the escaping aperture.

The calculation of interaction potentials inside the cavity is similar to the calculations at the window plane and was already discussed in Chapter II.
Figure 3.5 Potential distribution at the window of 5A zeolite

Figure 3.6 Temperature dependency of potential for nitrogen at the window of 5A zeolite
The potential functions for helium and argon are independent of temperature and the temperature effect on the potential function of oxygen is small and negligible due to the very weak quadrupole moment. The steady state Schrödinger equation only needs to be solved once for each of these three systems. All eigenvalues are independent of temperature and can be used to calculate the partition function at different temperatures. Nitrogen has a strong quadrupole moment and the potential function depends on temperature. Figure 3.6 shows the interaction potentials for nitrogen at 5A window at 183.15 and 297.15 K. The steady state Schrödinger equation has to be solved for each temperature. Although the potential functions of helium, argon and oxygen are independent of temperature, the average values of the potential, kinetic and total energies are really dependent on temperature since the averaging weight, \( \exp(-\varepsilon_i/kT) \), is a function of temperature. When temperature increases, molecular kinetic energy increases too.

2.2. Calculation of Average Properties at the 5A Window

The interaction potential functions were substituted into steady state Schrödinger equation that was numerically solved. The translational eigen energies and the corresponding eigenfunctions for an adsorbate molecule at the window, strongly depend on the potential distribution and escaping aperture. The partition function quickly converges with increasing eigen energies \( \varepsilon_i \). Specially the values less than zero mainly determine the partition function. When the interaction potential is negative, the dispersion and induction interactions are dominant. These interactions are long range and not so sensitive to the angular position as repulsion; so the interaction potential is almost independent of the angular position at the window plane. But it becomes dependent on angular position when the molecule deviates from the vicinity of the window center and when the potential becomes greater than zero. In order to confirm the validity of using an angular independent interaction potential to approximate the real one, we examined the effect of changing the positive part of the interaction potential distribution on the eigenvalues and partition functions. The results show that the maximum relative variation of eigenvalues with negative sign is less than 1% and less than 0.3% for the partition functions, when potential function values with positive sign increased or reduced 10 times. This numerical test ensures that the approximation is reasonable. At the window plane, when the adsorbate molecule is close to the wall, the potential variation is more sensitive to the position and the values of potential are higher but the effects on the partition function are less important.

The numerical technique used for solving the steady state Schrödinger equations describing the adsorbate motion inside the cavity and at the window plane was the public software SLEDGE [Pruess, 1991]. From the output of SLEDGE both eigenvalues and eigenfunctions can be obtained. In practical calculation we set the stop conditions based on the ratio \( \exp(-\varepsilon_i/kT)/\max[\exp(-\varepsilon_i/kT)] < 10^{-9} \) in order to obtain the accurate translational kinetic energy distribution function for the window.

Table 3.1 shows the calculated results of molecular partition functions for helium, argon, oxygen and nitrogen both in the cavity and at the window plane of 5A zeolite at different temperatures.
Table 3.1 - Partition function values inside the cavity and at the window of 5A zeolite

<table>
<thead>
<tr>
<th>T K</th>
<th>He cav. x10^3</th>
<th>He win. x10^3</th>
<th>Ratio</th>
<th>Ar cav. x10^5</th>
<th>Ar win. x10^5</th>
<th>Ratio</th>
<th>N2 cav. x10^5</th>
<th>N2 win. x10^5</th>
<th>Ratio</th>
<th>O2 cav. x10^5</th>
<th>O2 win. x10^5</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>183.15</td>
<td>73.04</td>
<td>.8527</td>
<td>.0117</td>
<td>232.6</td>
<td>4.319</td>
<td>.0186</td>
<td>848.5</td>
<td>65.42</td>
<td>.0771</td>
<td>226.4</td>
<td>.3136</td>
<td>.0014</td>
</tr>
<tr>
<td>193.15</td>
<td>65.36</td>
<td>.6727</td>
<td>.0106</td>
<td>196.8</td>
<td>2.569</td>
<td>.0131</td>
<td>707.3</td>
<td>32.88</td>
<td>.0465</td>
<td>188.3</td>
<td>.2103</td>
<td>.0011</td>
</tr>
<tr>
<td>203.15</td>
<td>56.02</td>
<td>.5449</td>
<td>.0097</td>
<td>168.7</td>
<td>1.615</td>
<td>.0096</td>
<td>571.4</td>
<td>17.76</td>
<td>.0311</td>
<td>152.6</td>
<td>.1473</td>
<td>.0010</td>
</tr>
<tr>
<td>213.15</td>
<td>50.34</td>
<td>.4516</td>
<td>.0090</td>
<td>130.2</td>
<td>1.064</td>
<td>.0082</td>
<td>417.7</td>
<td>10.20</td>
<td>.0244</td>
<td>123.7</td>
<td>.1071</td>
<td>.0009</td>
</tr>
<tr>
<td>233.15</td>
<td>42.26</td>
<td>.3279</td>
<td>.0076</td>
<td>96.1</td>
<td>.5196</td>
<td>.0054</td>
<td>240.7</td>
<td>3.921</td>
<td>.0162</td>
<td>93.39</td>
<td>.0620</td>
<td>.0007</td>
</tr>
<tr>
<td>253.15</td>
<td>36.96</td>
<td>.2527</td>
<td>.0068</td>
<td>74.63</td>
<td>2.873</td>
<td>.0039</td>
<td>169.3</td>
<td>1.772</td>
<td>.0105</td>
<td>70.44</td>
<td>.0396</td>
<td>.0006</td>
</tr>
<tr>
<td>297.15</td>
<td>30.34</td>
<td>.1648</td>
<td>.0054</td>
<td>37.21</td>
<td>1.064</td>
<td>.0029</td>
<td>92.93</td>
<td>.4636</td>
<td>.0047</td>
<td>33.88</td>
<td>.0188</td>
<td>.0006</td>
</tr>
</tbody>
</table>

The comparison of the interaction potentials in the cavity and at the window plane showed that the interaction potential in the central region of the window is minimum. The transient state theory is unable to explain the diffusional processes on such systems of small molecules in relatively large micropores. The motion of adsorbate molecule at the window plane is restricted to a very small region due to the strong repulsion interaction potential out of that region. Compared to the window, the adsorbate molecule has one more degree of freedom in the cavity. The eigen energy differences between neighboring energy levels at the window plane are much larger than inside the cavity owing to the steeper potential distribution at the window. So the number of terms in the summation when calculating the partition function for satisfying the numerical convergence requirement at the window plane is much smaller than in the cavity. In addition, at the window plane the degeneracy of quantum states with same eigen energy is 1 in our polar coordinate system, while in the cavity it is dependent on another quantum number for the spherical coordinate system. Over all these reasons, the molecular partition function at the window plane is much smaller than that in the cavity. The meaning of molecular partition function stands for the number of microscopic possible states of an adsorbate molecule. So the smaller value at the window plane represents less possibility of finding an adsorbate molecule at the window plane.

The data in Table 3.1 shows that the molecular partition functions of argon, oxygen and nitrogen in both window and cavity are very sensitive to the temperature. While in the case of helium they are less sensitive to temperature. The absolute value of molecular partition functions of helium is much smaller than these for Ar, O2 and N2 due to its weak interaction potential energy with the adsorbent atoms. So the adsorbed amount of helium is negligible compared with the others.

From the eigenfunction at a given quantum state the average properties of an adsorbate molecule at the window plane including position, potential and kinetic energies can be calculated by equations (1.93) to (1.95) and the macroscopic average values of these properties can be evaluated using the Boltzmann weight in equations (1.96) to (1.99). The average position, average kinetic and potential energies of an adsorbate molecule at the window plane are shown in Table 3.2. The potential energies out of the vicinity of window center become greatly repulsive and thus we take the average positions as the critical positions. When the adsorbate molecule inside the cavity hits this area, it will escape the cavity and form the temporary state at the window plane.

The calculated average translational kinetic energies of an adsorbate molecule at the window plane are close to these resulting from thermal motion with two degrees of freedom for He, Ar and O2. For N2 it is lower possibly due to the dimension of N2 molecule which is close to the dimension of the 8 membered ring and thus suffers the action of a stronger repulsion potential. In addition, in the vicinity of the window center
it is acted by strong attractive potential due to the quadrupole moment. These two effects result in a decrease on the range of motion of N₂ molecule at the window plane.

Table 3.2  Average position,  \( \overline{r} \) ( nm ), average kinetic, \( \overline{\mathcal{K}} \) and potential energies, \( \overline{V} \) ( KJ/mol ) at the window plane of 5A zeolite

<table>
<thead>
<tr>
<th>T (K)</th>
<th>He</th>
<th>Ar</th>
<th>N₂</th>
<th>O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \overline{r} )</td>
<td>( \overline{\mathcal{K}} )</td>
<td>( \overline{V} )</td>
<td>( \overline{r} )</td>
</tr>
<tr>
<td>183.15</td>
<td>4.473</td>
<td>1.42</td>
<td>-8.451</td>
<td>2.165</td>
</tr>
<tr>
<td>193.15</td>
<td>4.797</td>
<td>1.50</td>
<td>-8.422</td>
<td>2.211</td>
</tr>
<tr>
<td>203.15</td>
<td>4.848</td>
<td>1.58</td>
<td>-8.394</td>
<td>2.254</td>
</tr>
<tr>
<td>213.15</td>
<td>4.897</td>
<td>1.66</td>
<td>-8.365</td>
<td>2.297</td>
</tr>
<tr>
<td>233.15</td>
<td>4.989</td>
<td>1.81</td>
<td>-8.309</td>
<td>2.377</td>
</tr>
<tr>
<td>253.15</td>
<td>5.075</td>
<td>1.97</td>
<td>-8.253</td>
<td>2.453</td>
</tr>
<tr>
<td>297.15</td>
<td>5.243</td>
<td>2.30</td>
<td>-8.131</td>
<td>2.606</td>
</tr>
</tbody>
</table>

2.3 Stability of the Intermediate State and Rotation of an Adsorbate Molecule at the 5A Window Plane

The stability ratio between the molecule at the window plane and inside the cavity can be expressed by the ratio of the corresponding molecular partition functions \( \varphi_w/\varphi_c \). The partition functions, \( \varphi_w \) and \( \varphi_c \), include all possible motion ways of an adsorbate molecule at the window and inside the cavity. In the adsorption of gases in zeolites the interaction forces between adsorbate molecules and adsorbent atoms are primarily of the van der Waals and electrostatic types that are weaker than the chemical bonding forces; then the internal motion states, such as vibration, electronic and nuclei are practically not affected and so the internal motion ways of the adsorbate molecule can be considered the same in both states and thus the ratio \( \varphi_w/\varphi_c \) only includes the contributions from the translational and rotational motions.

The translational partition functions were already obtained in preceding part. Relatively the dimension of 5A cavity is larger than the molecular sizes of He, Ar, N₂ and O₂ and these adsorbate molecules can move in localized three dimension way inside the cavity. We assume that the rotation of adsorbate molecules is not affected by adsorption and in this condition we calculated the adsorption isotherms and adsorption heats for these adsorbates and the results were in good agreement with published experimental date which was already discussed in Chapter II. This fact shows that the assumption of free rotation of N₂ and O₂ inside the cavity is reasonable. At the window plane the situation is more complicated.

N₂ and O₂ are linear molecules and the molecular dimensions are respectively 3.0 \( \times \) 4.1 and 2.8 \( \times \) 3.9 Å (length \times cross section [Barrer, 1978]). Different orientations of these molecules relative to the window plane imply different interaction potentials. When the molecule and rotation axis are normal to the window plane there is no contribution to the total partition function because this movement does not contribute to new molecule configurations. When the rotation axis is coplanar and the molecule axis is normal to the window plane the potential is minimum whereas when the molecule axis is coplanar this potential becomes maximum for this type of rotational movement. In this case we took
the energy barrier as the difference between an average potential equal to the arithmetic mean between the maximum and minimum potentials when the molecule stays on the window plan and the minimum potential in this case. This energy barrier is much higher than the other case which prevents the molecule to rotate and also to stay on the window plane. So we are going to focus only in the last type of motion. When the rotation axis is normal and the molecule axis is coplanar with the window plane, potential will be minimum when the molecule axis stays between two oxygen atoms, and maximum when it stays colinear with two oxygen atoms. In this case the maximum energy barrier will be the difference of these two potentials.

The rotation kinetic energies associated with different motion quantum states can be expressed by [Atkins, 1986]:

\[ \varepsilon_{rot}^J = J(J + 1) \frac{\hbar^2}{8\pi j} \]

\[ J = 0, 1, 2, \ldots, \infty \]  \hspace{1cm} (3.13)

where \( J \) is the inertia moment and \( J \) is a rotational quantum number. The fraction \( P_{rot} \) of rotation kinetic energies greater than the rotation potential energy barrier, \( \Delta \varepsilon_{rot} \), can be represented by:

\[ P_{rot} = \frac{\sum_{J=J_{\Delta\varepsilon_{rot}}}^{\infty} (2J+1) \exp(-\varepsilon_{rot}^J/kT)}{\sum_{J=0}^{\infty} (2J+1) \exp(-\varepsilon_{rot}^J/kT)} \]  \hspace{1cm} (3.14)

where \( j_{\Delta\varepsilon_{rot}} \) represents the quantum number \( J \) whose energy is greater than the rotational energy barrier. The calculated \( P_{rot} \) values are also listed in Table 3.3. Because of the rotation potential strong energy barrier, the possible rotation fraction is almost negligible.

<table>
<thead>
<tr>
<th>T K</th>
<th>( \Delta E ) KJ/mol</th>
<th>( P_{rot} )</th>
<th>( \varepsilon_{rot} )</th>
<th>( \Delta E ) KJ/mol</th>
<th>( P_{rot} )</th>
<th>( \varepsilon_{rot} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>183.15</td>
<td>30.04</td>
<td>4.75 x 10^{-9}</td>
<td>30.92</td>
<td>23.21</td>
<td>3.27 x 10^{-7}</td>
<td>43.87</td>
</tr>
<tr>
<td>193.15</td>
<td>28.65</td>
<td>4.84 x 10^{-8}</td>
<td>32.60</td>
<td>21.91</td>
<td>1.62 x 10^{-6}</td>
<td>46.27</td>
</tr>
<tr>
<td>203.15</td>
<td>27.36</td>
<td>2.46 x 10^{-7}</td>
<td>34.29</td>
<td>20.67</td>
<td>6.72 x 10^{-6}</td>
<td>48.66</td>
</tr>
<tr>
<td>213.15</td>
<td>26.15</td>
<td>5.19 x 10^{-7}</td>
<td>35.98</td>
<td>19.48</td>
<td>2.39 x 10^{-5}</td>
<td>51.60</td>
</tr>
<tr>
<td>233.15</td>
<td>23.97</td>
<td>9.75 x 10^{-6}</td>
<td>39.36</td>
<td>17.29</td>
<td>2.07 x 10^{-4}</td>
<td>55.85</td>
</tr>
<tr>
<td>253.15</td>
<td>22.07</td>
<td>5.25 x 10^{-5}</td>
<td>42.73</td>
<td>15.30</td>
<td>1.19 x 10^{-3}</td>
<td>60.64</td>
</tr>
<tr>
<td>297.15</td>
<td>18.65</td>
<td>7.99 x 10^{-4}</td>
<td>50.16</td>
<td>11.56</td>
<td>1.73 x 10^{-2}</td>
<td>71.18</td>
</tr>
</tbody>
</table>

Table 3.3 Rotation properties of an adsorbate molecule at the window

The molecular rotation partition function \( \varepsilon_{rot} \) for free rotation of \( N_2 \) and \( O_2 \) can be expressed by [Atkins, 1986]:

134
\[ \psi_{\text{rot}} = \frac{8 \pi \hbar^2 k T}{h^2} \]  

(3.15)

The inertial moments for N$_2$ and O$_2$ are respectively $13.6 \times 10^{-47}$ and $19.2 \times 10^{-47}$ kg.m$^2$ [Hu et al., 1979]. The calculated molecular rotation partition functions of free rotation for N$_2$ and O$_2$ at different temperatures are shown in Table 3.3.

For other motions (axis not coplanar neither orthogonal) the same conclusion should apply. That is, the most probable molecule orientation is with its axis normal to the window plane.

The stability ratios of adsorbate molecule located at the window plane and inside the cavity can be easily obtained by calculating the ratio of the molecular partition functions at the window plane and inside the cavity which are listed in Table 3.1. Most of the stability ratios are less than 0.02 except for nitrogen at low temperature and this means that the intermediate state is very unstable and so the time that adsorbate molecule spends at the window plane compared with the time spent inside the cavity is negligible. So the contribution to the total diffusional resistance from this intermediate state is also negligible. With the increase of temperature, the adsorbate molecules have more translational kinetic energy and thus the intermediate state becomes even less stable.

The energy barriers that an adsorbate molecule must overcome when it diffuses from window to cavity center are listed in Table 3.4.

<table>
<thead>
<tr>
<th>Temperature K</th>
<th>He</th>
<th>Ar</th>
<th>N$_2$</th>
<th>O$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>183.15</td>
<td>9.452</td>
<td>15.39</td>
<td>16.91</td>
<td>13.82</td>
</tr>
<tr>
<td>193.15</td>
<td>9.547</td>
<td>15.45</td>
<td>17.17</td>
<td>13.87</td>
</tr>
<tr>
<td>203.15</td>
<td>9.645</td>
<td>15.52</td>
<td>17.42</td>
<td>14.03</td>
</tr>
<tr>
<td>213.15</td>
<td>9.740</td>
<td>15.58</td>
<td>17.67</td>
<td>14.19</td>
</tr>
<tr>
<td>233.15</td>
<td>9.933</td>
<td>15.72</td>
<td>18.13</td>
<td>14.49</td>
</tr>
<tr>
<td>253.15</td>
<td>10.13</td>
<td>15.86</td>
<td>18.56</td>
<td>14.79</td>
</tr>
<tr>
<td>297.15</td>
<td>10.55</td>
<td>16.17</td>
<td>19.46</td>
<td>15.46</td>
</tr>
</tbody>
</table>

### 2.4 Intracrystalline Diffusivities in 5A Zeolite

The calculated self diffusivities for He, Ar, N$_2$ and O$_2$ in 5A zeolite at different temperatures are shown in Table 3.5. In order to illustrate the importance of the contributions of $D_{cw}$ and $D_{wc}$ to $D_0$, the corresponding calculated $D_{cw}$ and $D_{wc}$ values are also presented. Both $D_{cw}$ and $D_{wc}$ are heavily dependent on the aperture of the window. Because the N$_2$ molecule is larger the probability of escaping the cavity is smaller and thus $D_{cw}$ becomes smaller. Because the diffusional process of N$_2$ molecule from the window to the cavity center must overcome a greater energy barrier, the corresponding $D_{wc}$ is very small. At low temperature the molecular translational kinetic energy is low and the ability to overcome the energy barrier is weak, so $D_0$ is mainly dependent on $D_{wc}$. When the temperature increases $D_{wc}$ increases faster than $D_{cw}$ and thus $D_{cw}$ makes a more
important contribution to the total diffusional resistance. Obviously the diffusion of helium molecule is much faster than Ar, N\textsubscript{2} and O\textsubscript{2} because it is a small molecule, the interaction potential is weak and the energy barrier is small too.

Table 3.5 Zero coverage self - Diffusivities of He, Ar, N\textsubscript{2} and O\textsubscript{2} in 5A zeolite

<table>
<thead>
<tr>
<th>T K</th>
<th>He x 10\textsuperscript{6} cm\textsuperscript{2}/s</th>
<th>Ar x 10\textsuperscript{6} cm\textsuperscript{2}/s</th>
<th>N\textsubscript{2} x 10\textsuperscript{6} cm\textsuperscript{2}/s</th>
<th>O\textsubscript{2} x 10\textsuperscript{6} cm\textsuperscript{2}/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>183.15</td>
<td>.732</td>
<td>.949</td>
<td>.413</td>
<td>.482</td>
</tr>
<tr>
<td>193.15</td>
<td>.768</td>
<td>1.34</td>
<td>.488</td>
<td>.516</td>
</tr>
<tr>
<td>203.15</td>
<td>.805</td>
<td>1.82</td>
<td>.559</td>
<td>.550</td>
</tr>
<tr>
<td>213.15</td>
<td>.841</td>
<td>2.41</td>
<td>.623</td>
<td>.585</td>
</tr>
<tr>
<td>233.15</td>
<td>.913</td>
<td>3.49</td>
<td>.724</td>
<td>.656</td>
</tr>
<tr>
<td>253.15</td>
<td>.985</td>
<td>4.77</td>
<td>.816</td>
<td>.728</td>
</tr>
<tr>
<td>297.15</td>
<td>1.14</td>
<td>9.30</td>
<td>1.02</td>
<td>.889</td>
</tr>
</tbody>
</table>

Usually, the temperature dependency of diffusivity D\textsubscript{o} is regarded as an exponential function, that is, the Arrhenius equation [Ruthven, 1984]:

$$D_{o} = D^{*} \exp\left(\frac{-\varepsilon}{kT}\right)$$  \hspace{1cm} (3.17)

where \(D^{*}\) is the preexponential factor that is independent of temperature and \(\varepsilon\) is the activation energy for diffusion. This equation is borrowed from chemical reaction kinetics theory. In the diffusional process of a small molecule in 5A zeolite, there is no energy barrier to form an intermediate state at the window plane, but there is really a barrier to jump from the intermediate state to the cavity. For comparison, Figure 3.7 shows the temperature dependency of D\textsubscript{o} and some published experimental data [Ruthven, 1991]. The plots of \(\frac{\varepsilon}{kT}\) D\textsubscript{o} against \(1/T\) are close to a straight line and so the Arrhenius equation can usually correlate the experimental data. From the correlation the diffusional activation energy can be extracted and the predicted activation energies are shown in Table 3.6.

Table 3.6 Diffusional activation energies in 5A zeolite

<table>
<thead>
<tr>
<th>source</th>
<th>He</th>
<th>Ar</th>
<th>N\textsubscript{2}</th>
<th>O\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>calculated KJ/mol</td>
<td>3.49</td>
<td>7.44</td>
<td>8.92</td>
<td>4.70</td>
</tr>
<tr>
<td>experimental * KJ/mol</td>
<td></td>
<td></td>
<td>10.74</td>
<td>10.45</td>
</tr>
</tbody>
</table>

* [Ruthven, 1991]
Closed symbols represent the predicted values and the open symbols represent the experimental data [Ruthven, 1991] (D_o is in cm^2/sec)

Figure 3.7 Temperature dependency of diffusivities in 5A zeolite

As a comparison the experimental values of the diffusion activation energies obtained by correlating the data read them from the paper [Ruthven, 1991]. For the smaller adsorbate molecules (He and O_2) even at low temperature, contributions of the diffusion step, cavity to window to total diffusion resistance are important. While the contributions of the diffusion step from the cavity to window for the larger molecules (Ar and O_2) are unimportant at low temperature and the diffusion step from the window to cavity is an activated step. So the correlated activation energies of the larger molecules are larger than for the small molecules. There are discrepancies between our correlated and Ruthven's experimental activation energies specially for the oxygen diffusion system. One reason may be due to the experimental data that only covered a narrow temperature region (for O_2 system temperature is about from 183.15 to 213.15 K and for N_2 system temperature is about from 183.15 to 253.15 K). At low temperature the contribution of the activation diffusion step to the total diffusion resistance is more important than at high temperature and the activation energy is also larger at low temperature than at high temperature. The deviation of the calculated temperature functions of the diffusivities from the linear line shows such effects. Only when the diffusion is a true activated process the Arrhenius equation may be adopted.

2.5 Calculation of the Interaction Potential at the 4A Window and Prediction of Diffusivities

The calculation of the interaction potential of an adsorbate molecule in the 8 membered ring window of 4A zeolite is similar to the calculation carried out for 5A. The Na^+ cation
is fixed at an equidistant place from two adjacent O\(^{0.25}\). This distance is equal to the sum of the radii of Na\(^+\) and O\(^{0.25}\). The free dimension of the 8 membered ring in zeolite A is 4.3 Å. Because of the existence of an exchangeable cation in 4A zeolite, the window size is reduced. Taking into account the strong electrostatic attractive force between the cation and the skeleton O\(^{0.25}\) atoms, we assume that the most probable situation is that this cation combines with two O\(^{0.25}\) in the most tighten packing way. The distance between Na\(^+\) and O\(^{0.25}\) is 2.4 Å [Barrier, 1978]. The free dimension of the window corresponding to this case reduces to about 2.6 Å. Except for very small molecules, most adsorbates will experience a strong repulsive potential at the window.

The calculation was carried out in the region of \(r = 0\) to \(r = r_{\text{win}}\) and \(\eta = 0\) to \(2\pi\). The window area was divided into 100 X 60 elements respectively along the radial and angular directions. The possible cation positions from 0 to \(\pi/2\) were divided into 100 points along the rotation trajectory. The potential at each window network point was taken as the minimum of several possible situations: the cation located at the window plane and the cation taking each one of the remaining 99 positions. The last potential calculations involve mainly the electrostatic interactions between the cation and other cations and oxygen atoms at the window plane and neighboring cavities. The interaction potential energy at a window point is taken as the minimum of two energies: one is the potential energy when the cation is at the window plane and the other is the sum of the potential energy when the cation is deviated from the window plane plus the kinetic energy necessary to deviate it. The average value of the interaction potentials at the four corner points of each element was selected as the potential value in this element. The energy barrier that an adsorbate molecule must overcome when it crosses any window element can be approximately taken as the potential energy at the same window element minus the average interaction potential energy in the cavity. Figures 3.8 to 3.11 show the calculated results of interaction potential distribution at the window plane of 4A zeolite at 297.15 K.

For linear adsorbate molecules like oxygen and nitrogen, when they diffuse through the window they take the orientation such that their axis is normal to the window plane and the interaction for such orientation is much weaker than for other orientations. The interaction potential calculation for the linear molecules was carried out based on such orientation and the atom dimensions were taken as the molecular dimension.

Because the dimension of the eight membered ring window is slightly larger than the dimension of small gas molecules, the existence of a cation at the window plane greatly affects the adsorbate molecule diffusion free path. The structure of the window and the cation position are not rigid. When the adsorbate molecule with a given translational kinetic energy strikes the window, both the structure and the position of atoms will distort in order to increase the window opening aperture. At the window, the bond between oxygen atoms is relatively stable. While the cation at the window plane and the O\(^{0.25}\) atoms are linked by the electrostatic forces which are much less strong than the chemical bonding forces. As long as the adsorbate molecule has enough translational kinetic energy to strike the window plane, the most possible situation is that the position of cation will be changed. The position of this cation can deviate from the window plane so that the free dimension of diffusion path can be increased. Compared with all possible deviation ways, the requirement of the kinetic energy is minimum when the cation rotates around the axis that is the linking line between two adjacent O\(^{0.25}\) atoms of the eight membered ring.

138
Figure 3.8 Potential distribution of helium at the window of 4A zeolite

Figure 3.9 Potential distribution of argon at the window of 4A zeolite
Figure 3.10 Potential distribution of oxygen at the window of 4A zeolite

Figure 3.11 Potential distribution of nitrogen at the window of 4A zeolite
Among the various interaction potentials between two charged particles separated by a couple of angstroms, the electrostatic interaction potential is much stronger than other potentials such as dispersion, induction and quadrupole moment. The distances between the cation and other O$^{0.25}$ atoms except for a pair of O$^{0.25}$ atoms that are the rotation axis for this cation are large so the repulsion interactions are small. When the cation rotates around the axis, the distances between the cation and these two O$^{0.25}$ atoms keep constant. But it deviates the equilibrium position at the window plane and the distances between the cation and other O$^{0.25}$ atoms in the ring and on the cavity shell change. This distance variation results in the change of the interaction potential. The deviation of the cation from the window plane enables the cation to be in an unstable state and the energy of the cation to increase. When the adsorbate molecule minimum kinetic diameter increases, more deviation of the cation position from the window plane is required and this means that more translational kinetic energy is necessary to strike the window. The average values and the distributions of the translational kinetic energy for different size molecules are the same. In addition, the larger molecules will be acted by a stronger repulsion force coming from the O$^{0.25}$ atoms in the eight membered ring. These two effects result in that the probability of an adsorbate molecule crossing the window is sensitive to the minimum kinetic diameter. When O$_2$ and N$_2$ move from the cavity to the window, we assume that they take the orientation of their axis normal to the window plane because in this orientation crossing the energy barriers requires minimum translational kinetic energy.

As the cation position deviates from the window plane the distances between the cation and other six oxygen atoms increase. The interaction potential acting on the cation will increase too. But the contribution of these interactions to the total potential at a given region of the window acting on the adsorbate molecule will decrease.

The contribution of the window to the energy barrier will then be different according to the cation position.

Figures 3.8 to 3.11 show the energy barrier distribution of He, Ar, O$_2$ and N$_2$ at the window of 4A zeolite. In these figures the absence of peaks expresses that the energy barrier contribution already exceeds the coordinate range of the figure. All results are positive. The energy barriers at any position of the window are equal to total contribution minus the average interaction potential inside the cavity. The values of translational kinetic energy of adsorbate molecule inside the cavity are very small when compared with the window contribution to the energy barrier.

The distribution of kinetic energy is narrow and the fraction of kinetic energy levels greater than the energy barrier is very small. The translational kinetic energy distributions of helium, argon, nitrogen and oxygen inside the cavity of 4A zeolite are similar. As an illustration Figure 3.12 shows the translational kinetic energy distributions of a nitrogen molecule inside the cavity at 183.15 and 297.15 K. Most of the kinetic energy levels are located within a narrow lower energy region and are concentrated on the vicinity of the average kinetic energy 3kT/2. Increasing the temperature the distribution moves towards the high energy region. Owing to the degeneracy of each translational energy level, the decreasing rate of translational kinetic energy distribution with increasing energy values is not monotonic and the detailed discussion of this will be held late.

According to the previous discussion on the calculation of the self diffusivity of an adsorbate molecule crossing a blocked eight membered window, the calculated self diffusivities for He, Ar, N$_2$ and O$_2$ in 4A zeolite at different temperatures are shown in Table 3.7.
The larger the adsorbate molecule kinetic diameter the stronger the interaction with the repulsion potential at the window. Because the translational kinetic energy distributions of different adsorbates are almost the same there is smaller probability for the larger molecules to cross the window. The repulsion interaction is a quite short distance force and thus a small variation of the molecular dimension will result in a large variation of the diffusion ability. In order to show this degree of difficulty for different adsorbates to cross the window, two probabilities, $P_{act}$ representing the fraction of translational kinetic energy distribution greater than the energy barrier at the window and $P_{cw}$ representing the random probability of an adsorbate hitting the window area are also shown in the
Except for the smallest molecule, helium, the \( P_{cw} \) are close to each other and the diffusivity differences predominantly result from the differences on \( P_{act} \). Such diffusion is really an activated process. For real activated diffusion the Arrhenius equation is suitable to correlate diffusivities at different temperatures and to extract the activation energy. Figure 3.13 shows the results of calculated diffusivities of helium, argon, nitrogen and oxygen in 4A zeolite at different temperatures. The straight lines of \( \ln(D_o) \) against \( 1/T \) illustrate the correctness of the Arrhenius equation correlating the activated diffusivities. The helium molecule dimension is slightly greater than the free dimension of the blocked eight membered ring window and when it hits some region of the window it interacts a weak repulsion potential. Its self diffusivity is much larger than these of Ar, N\(_2\) and O\(_2\) and the difference of its diffusivities in 4A and 5A zeolite are small. In a macroscopic experimental technique for the determination of the intracrystalline diffusivity such as chromatography, the existence of helium is usually neglected. Our calculated results for the adsorbed amount and self diffusivity of helium show that the effect of the existence of helium on the diffusion of other adsorbate molecules may be negligible due to its small adsorbed amount and large self - diffusivity.

![Figure 3.13 Temperature dependency of diffusivities in 4A](image)

The activation energies obtained by regressing these predicted points of the diffusivities at different temperatures are showed in Table 3.8. Due to the differences on the adsorbents and on the experimental techniques used, there are discrepancies among the experimental results presented in Table 3.8 as high as several times. Our predicted self diffusivities and diffusion activation energies are close the experimental results. The diffusion activation energy of argon is a bit larger than the experimental data and that of oxygen is smaller. The reasons may be that there are many approximations in our models, specially for the calculation of the interaction potential and the experimental data have also errors.
specially due to the finite mass transport rate in the macropores and bulk phase and finite heat release rate.

Table 3.8 Comparison of predicted and experimental diffusivities and activation energies

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Technique</th>
<th>D_0 (cm^2/s)*</th>
<th>E (kcal/mol)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>exp. N_2</td>
<td>frequency response</td>
<td>3.7 x 10^{-10}</td>
<td>5.62</td>
<td>Kärger and Ruthven, 1992</td>
</tr>
<tr>
<td></td>
<td>gravimetric update</td>
<td>4 x 10^{-10}</td>
<td>5.96</td>
<td>Kärger and Ruthven, 1992</td>
</tr>
<tr>
<td></td>
<td>gravimetric update</td>
<td>1.2 x 10^{-10}</td>
<td>4.54</td>
<td>Kärger and Ruthven, 1992</td>
</tr>
<tr>
<td></td>
<td>chromatographic</td>
<td>~ 10^{-10}</td>
<td>5.96</td>
<td>Haq and Ruthven, 1986</td>
</tr>
<tr>
<td></td>
<td>gravimetric update</td>
<td>~ 10^{-10}</td>
<td>5.96</td>
<td>Ruthven and Derrah, 1975</td>
</tr>
<tr>
<td>exp. O_2</td>
<td>frequency response</td>
<td>1.7 x 10^{-8}</td>
<td>4.54</td>
<td>Kärger and Ruthven, 1992</td>
</tr>
<tr>
<td></td>
<td>gravimetric update</td>
<td>1.6 x 10^{-8}</td>
<td>4.54</td>
<td>Ruthven and Derrah, 1975</td>
</tr>
<tr>
<td>exp. Ar</td>
<td>gravimetric update</td>
<td>3 x 10^{-11}</td>
<td>5.74</td>
<td>Ruthven and Derrah, 1975</td>
</tr>
<tr>
<td></td>
<td>chromatographic</td>
<td>3 x 10^{-11}</td>
<td>5.74</td>
<td>Kärger and Ruthven, 1992</td>
</tr>
<tr>
<td>cal. N_2</td>
<td>predicted</td>
<td>4.75 x 10^{-10}</td>
<td>5.74</td>
<td>present work</td>
</tr>
<tr>
<td>cal. O_2</td>
<td>predicted</td>
<td>2.26 x 10^{-8}</td>
<td>3.01</td>
<td>present work</td>
</tr>
<tr>
<td>cal. Ar</td>
<td>predicted</td>
<td>1.8 x 10^{-10}</td>
<td>6.56</td>
<td>present work</td>
</tr>
</tbody>
</table>

* Calculated and experimental D_0 are at 273 K

3 COMPARISON BETWEEN CLASSICAL AND QUANTUM MECHANICS RESULTS: KINETIC ENERGY DISTRIBUTION

In the view of statistical thermodynamics, each molecule has a translational kinetic energy distribution and this distribution can be expressed by the Boltzmann distribution as in equations (1.30) as long as the temperature is not too low. In the equation, the distribution function is expressed as the ratio of summations of the discrete translational energy levels. Traditionally, these summations are replaced by continuous integrals [Ruthven, 1984] and the probability of a molecule having translational kinetic energy greater than a given value (energy barrier Δε) is equal to exp(-Δε/kT) in equation (1.68).

In Chapter I we already shown that the translational energy level spacing is small at low energy and the calculations of partition functions and average properties such as average position and average kinetic energy are almost correct by considering the translational energy as a continuous function and replacing the summations by integrals. When we are interested in the calculation of the translational kinetic energy distribution in the high energy range, the substitution of the summation by the integral will give rise to big errors since the energy level spacing increases at high kinetic energy values. Equation (1.76) shows the relationship between energy level spacing and the quantum state index for a molecule in free motion in a one dimension container. For the case of the motion of a molecule in three dimensions under an interaction potential the equivalent relationship is complex but the trends are similar. In order to show the differences on kinetic energy distributions calculated by summation and by integration, let us avoid the possible numerical errors introduced by the interaction potential calculation while keeping the generality of this analysis. We first discuss the motion of a molecule inside a spherical cavity with radius 7.05 Å at 297.15 K (the cavity dimension of zeolite A). The
calculated average translational kinetic energy distribution using the discrete summation is 3.731 KJ/mole. In this calculation the convergence conditions for the eigenvalues when numerically solving the steady state Schrödinger equation were obtained using \( \exp(-\varepsilon_i/kT)/\text{max}[\exp(-\varepsilon_i/kT)] < 10^{-9} \) and \( (2**\varepsilon+1)\exp(-\varepsilon_i/kT)/\text{max}[(2**\varepsilon+1)\exp(-\varepsilon_i/kT)] < 10^{-9} \) as criteria. We believe the numerical error is negligible. The expected value for the average translational kinetic energy using the equipartition principle is \( 3RT/2 = 3.706 \) KJ/mole. The relative error between them is 0.67%. The good agreement of the two methods shows that the discrete summation is reliable. The kinetic distributions at low kinetic energies calculated using both methods are shown in the Figure 3.14. In this figure, the dashed line represents the classical results (\( \exp(-\Delta\varepsilon/kT) \)) and the solid line was calculated using the summation. There is an obvious difference between these distributions. The results obtained by summation are higher than by integration and this means that this distribution has a longer tail in the higher energy area. Table 3.9 shows the fraction of molecules with translational kinetic energies greater than a given energy barrier. The results obtained using integration gradually deviate relatively to these calculated by summation when energy barrier increases. When the energy barrier is \( 2 \times 10^{-13} \) ergs/molecule, this difference is about 3 times and will be directly reflected in the value of calculated diffusivities.

![Graph showing kinetic energy distribution](image)

Dashed line represents the results calculated by integration and the solid line by summation

Figure 3.14 Kinetic energy distribution without an interaction potential
Table 3.9  Fraction of the kinetic energy distribution greater than an energy barrier without interaction potential

<table>
<thead>
<tr>
<th>Energy Barrier (ergs/molecule x 10^{14})</th>
<th>Fraction Calculated by Classical Mechanics</th>
<th>Fraction Calculated by Quantum Mechanics</th>
<th>Relative Error * %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.7836</td>
<td>0.9284</td>
<td>15.60</td>
</tr>
<tr>
<td>2.0</td>
<td>0.6140</td>
<td>0.8207</td>
<td>25.19</td>
</tr>
<tr>
<td>4.0</td>
<td>0.3770</td>
<td>0.5917</td>
<td>36.29</td>
</tr>
<tr>
<td>6.0</td>
<td>0.2315</td>
<td>0.4149</td>
<td>44.20</td>
</tr>
<tr>
<td>8.0</td>
<td>0.1421</td>
<td>0.2797</td>
<td>49.20</td>
</tr>
<tr>
<td>10.0</td>
<td>8.728 x 10^{-2}</td>
<td>0.1860</td>
<td>53.08</td>
</tr>
<tr>
<td>20.0</td>
<td>7.618 x 10^{-3}</td>
<td>2.159 x 10^{-2}</td>
<td>64.72</td>
</tr>
<tr>
<td>40.0</td>
<td>5.803 x 10^{-5}</td>
<td>2.210 x 10^{-4}</td>
<td>73.74</td>
</tr>
<tr>
<td>60.0</td>
<td>4.421 x 10^{-7}</td>
<td>2.037 x 10^{-6}</td>
<td>78.30</td>
</tr>
</tbody>
</table>

* relative error = (quantum - classical)/quantum

Let us now repeat the calculation for helium when a potential field is present. As a general example, we again take the angular independent potential function used in Chapter II in order to avoid numerical errors associated with the use of a discrete expression for the interaction potential function between adsorbate molecule and wall atoms inside the cavity:

![Graph](image)

Dashed line represents the results calculated by integration and the solid line by summation

Figure 3.15 Kinetic energy distribution with an interaction potential
\[ U(x) = \frac{-2 \times 10^{-14} - 1.73856 \times 10^{-12} x + 2.72205 \times 10^{-12} x^2}{1 - x^2} \]  \tag{2.22}

The system is at 297.15 K and the average translational kinetic energy calculated by quantum mechanics is 3.714 KJ/mol which is very close to the expected value 3.706 KJ/mol and the relative error is 0.22%. Figure 3.15 shows the kinetic energy distributions calculated by both mechanisms.

The curves in Figure 3.15 show that the energy distributions calculated by the two methods are different. The curve calculated by integration is lower than the other. This phenomenon can be explained by looking to the calculation formula. The continuous integral replaces the discrete summation:

\[
\sum_{i=1}^{\infty} g_i \exp(-\epsilon_i / kT) = \frac{\int_{-\infty}^{\infty} \exp(-\epsilon / kT) \, d\epsilon}{\int_{0}^{\infty} \exp(-\epsilon / kT) \, d\epsilon} = \exp\left(-\frac{\Delta \epsilon}{kT}\right) \tag{3.19}\]

Because there is degeneracy of quantum levels, the decreasing rate of the energy distribution of an adsorbate molecule in an interaction potential is not monotonic. The energy and the kinetic energy are dependent on \( \ell \) and \( i \). The increase of both decreases the energy. At the same quantum number \( \ell \), energy distribution decreases monotonically with increasing \( i \). But at the same \( i \), the energy distribution when increasing \( \ell \) first increases and then decreases and has peak values. This phenomenon can not be expressed by classical mechanics. In the classical mechanics the variation of the translational kinetic energy distribution with the value of energy is a monotonic function.

Similarly to the no interaction potential case, Table 3.10 shows the results obtained for the fraction of helium molecules with translational kinetic energy greater than a given energy barrier under an interaction potential field. The difference when using classical or quantum mechanics is large. At low energies the quantum calculation gives larger values whereas for the high energies the opposite is valid. In the very high energy region, the difference is about 7 times.

In above discussion we used two simple cases to illustrate that the classical statistical approach to calculate the translational kinetic energy distribution introduces large errors. The calculation of the intracrystalline activated diffusivities is more complicated because the interaction potential is expressed in a discrete way. The discussion on the differences when using two different mechanisms is more difficult since there are possible numerical errors introduced by potential and average property calculations. The interaction potential field used in the above example is close to the real discrete potential field and thus the conclusions drawn also stand for the real case.
Table 3.10 Fraction of the kinetic energy distribution greater than an energy barrier with interaction potential

<table>
<thead>
<tr>
<th>Energy Barrier (ergs/molecule x 10^{-14})</th>
<th>Fraction Calculated by Classical Mechanics</th>
<th>Fraction Calculated by Quantum Mechanics</th>
<th>Relative Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.7836</td>
<td>0.9532</td>
<td>17.79</td>
</tr>
<tr>
<td>2.0</td>
<td>0.6140</td>
<td>0.8461</td>
<td>27.43</td>
</tr>
<tr>
<td>4.0</td>
<td>0.3770</td>
<td>0.6147</td>
<td>38.67</td>
</tr>
<tr>
<td>6.0</td>
<td>0.2315</td>
<td>0.4208</td>
<td>44.99</td>
</tr>
<tr>
<td>8.0</td>
<td>0.1421</td>
<td>0.2688</td>
<td>47.14</td>
</tr>
<tr>
<td>10.0</td>
<td>8.728 x 10^{-2}</td>
<td>0.1630</td>
<td>46.45</td>
</tr>
<tr>
<td>20.0</td>
<td>7.618 x 10^{-3}</td>
<td>1.207 x 10^{-2}</td>
<td>36.88</td>
</tr>
<tr>
<td>40.0</td>
<td>5.803 x 10^{-5}</td>
<td>3.359 x 10^{-3}</td>
<td>72.76</td>
</tr>
<tr>
<td>60.0</td>
<td>4.421 x 10^{-7}</td>
<td>5.998 x 10^{-8}</td>
<td>637.08</td>
</tr>
</tbody>
</table>

The activated intracrystalline diffusivity is dependent on the fraction of the diffusing molecules with translational kinetic energy greater than a given energy barrier under an interaction potential field and thus the error resulting from the calculation of energy distributions will directly appear in the corresponding diffusivity as shown in Table 3.11. The higher the interaction energy barrier is, the larger the difference between the fractions calculated by classical and quantum mechanics is and thus the larger the difference corresponding diffusivities is. Argon has the most strong interaction energy barrier due to its largest molecule dimension and the errors of diffusivities calculated by two methods are large too. The interaction energy barriers have relatively small temperature dependency. When temperature decreases, the translational kinetic energy distribution moves towards to zero direction and the calculation errors of diffusivities by classical mechanics are more visible. The diffusivities of He, Ar, N2 and O2 calculated by classical mechanics at 183.15 K are almost two orders of magnitude smaller than these calculated by quantum mechanics. This comparison shows that the validity of classical mechanics for the calculation of activated diffusivity is questionable.

Table 3.11 Comparison of Diffusivities of He, Ar, N2 and O2 calculated by classical and quantum mechanics in 4A (cm²/sec)

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Ar (Dₐ (cla.) x 10^{11})</th>
<th>Ar (Dₐ (qun.) x 10^{12})</th>
<th>N₂ (Dₐ (cla.) x 10^{11})</th>
<th>N₂ (Dₐ (qun.) x 10^{11})</th>
<th>O₂ (Dₐ (cla.) x 10^{11})</th>
<th>O₂ (Dₐ (qun.) x 10^{11})</th>
<th>He (Dₐ (cla.) x 10^{6})</th>
<th>He (Dₐ (qun.) x 10^{6})</th>
</tr>
</thead>
<tbody>
<tr>
<td>183.15</td>
<td>.0181</td>
<td>.0028</td>
<td>.2366</td>
<td>.0117</td>
<td>146.7</td>
<td>3.249</td>
<td>.5136</td>
<td>.0028</td>
</tr>
<tr>
<td>193.15</td>
<td>.0461</td>
<td>.0061</td>
<td>.5709</td>
<td>.0468</td>
<td>225.3</td>
<td>7.492</td>
<td>.6182</td>
<td>.0047</td>
</tr>
<tr>
<td>203.15</td>
<td>.1068</td>
<td>.0116</td>
<td>1.375</td>
<td>.0862</td>
<td>332.1</td>
<td>13.68</td>
<td>.7335</td>
<td>.0091</td>
</tr>
<tr>
<td>213.15</td>
<td>.2280</td>
<td>.0240</td>
<td>2.582</td>
<td>.1774</td>
<td>568.8</td>
<td>21.76</td>
<td>.8597</td>
<td>.0167</td>
</tr>
<tr>
<td>233.15</td>
<td>.8637</td>
<td>.0849</td>
<td>9.013</td>
<td>.5360</td>
<td>981.9</td>
<td>53.12</td>
<td>1.144</td>
<td>.0382</td>
</tr>
<tr>
<td>253.15</td>
<td>2.644</td>
<td>.4325</td>
<td>25.88</td>
<td>1.441</td>
<td>1456.0</td>
<td>116.5</td>
<td>1.472</td>
<td>.0835</td>
</tr>
<tr>
<td>273.15</td>
<td>6.865</td>
<td>1.741</td>
<td>47.53</td>
<td>3.282</td>
<td>2259.0</td>
<td>231.8</td>
<td>1.841</td>
<td>.1574</td>
</tr>
<tr>
<td>293.15</td>
<td>18.22</td>
<td>6.817</td>
<td>92.49</td>
<td>7.991</td>
<td>3540.0</td>
<td>487.1</td>
<td>2.337</td>
<td>.2443</td>
</tr>
</tbody>
</table>

148
4 CONCLUSIONS

In this chapter a methodology for the theoretical prediction of the intracrystalline diffusivities of gases in zeolite A series was developed. According to the ratio between the kinetic diameter of the diffusing molecule and the diffusion path in the window, there are two kinds of mechanisms. One is when the dimension of the diffusion window is larger than the molecule size. The interaction potential between diffusing molecule and the adsorbent wall and window atoms shows that in the window central region the interaction potential is lower than inside the cavity. The diffusion process of a molecule from cavity to window is under an attractive force. The free diameter of the eight membered ring window is close to molecular dimensions and thus out of the vicinity of the window central region there is a strong repulsion force acting on the diffusing molecule. This strong repulsion force prevents the molecule from crossing the window. So only when the diffusing molecule strikes the central region it can escape the cavity. The dimension of the central region can be considered as the average position of the molecule at the window plane. The probability of the molecule escaping the cavity and temporally staying at the window can be evaluated by the ratio of the areas of the window central region to the cavity shell.

The window dimension is a bit larger than the molecular kinetic dimension and the molecule can temporally move with two degrees of freedom. The stability of this temporary state can be evaluated by means of the ratio of the molecular partition functions of the diffusing molecule at the window and inside the cavity. Due to the strong repulsion force acting on the diffusing molecule linear molecules like oxygen and nitrogen, take the axis on the window plane. Their rotation is almost negligible. The diffusing molecule at the window can go to the next cavity or return to the original one as long as the molecule has a translational kinetic energy greater than the energy barrier which exists between the window and the cavity. The probability of these jumps should be equal at very low adsorbed amounts.

The whole diffusion process of small molecular gases in relatively large windows can be considered as three steps in series: the molecule diffuses from the cavity to the window and this is a random process; temporally moves at the window plane, overcomes the energy barrier and diffuses to the next window or returns to the original one. The last step is a really activated process. The intermediate state is quite unstable and thus the contribution of this step to the total diffusion resistance can be neglected. The relative importance of the first and last steps to determine the diffusion resistance is dependent on the interaction potential between adsorbate molecule and adsorbent atoms and temperature. For weak interaction molecules, the energy barrier is small, the last step may be less important to the total resistance. Increasing the temperature, the resistances of both steps will reduce but the decrease of importance of the last step is more sensitive to the temperature.

The diffusion process of gases in blocked windows is different. The existence of a cation in the eight membered ring greatly reduces the free diameter. Even for small molecules like helium, the molecule will be interacted by a strong repulsion potential. The forces that keep the cation in the position are mainly electrostatic forces and the cation can deviate from the window plane as long as the diffusing molecule strikes the window with enough translational kinetic energy. The degree of deviation is dependent on the striking energy. Comparing various ways for the cation to deviate from the window plane, the minimum kinetic energy necessary to deviate the cation is when the cation rotates on an axis which links adjacent two $O^{0.25}$ atoms and the cation is in the
most tight packing with these two O\(^{-0.25}\) atoms and at equal distance from them. When the cation deviates from the window plane, it is acted by a force mainly resulting from the anions which exist in the adjacent two cavities and window. The more it deviates from the window plane, more kinetic energy is required and smaller the contribution it makes to the adsorbate molecular interaction potential.

There is a minimum value for the window contribution to the energy barrier for each diffusion system in zeolite 4A. Larger adsorbate molecules require that the cation deviates more from the window plane and thus implies more striking kinetic energy and the corresponding energy barrier is greater. From the kinetic energy distribution, we know that the probability that a molecule with three-dimensional motion has kinetic energy greater than 10\(^{-13}\) ergs/molecule at ambient or low temperature is very small. The rise in the molecular kinetic diameter will rapidly increase the energy barrier and so the corresponding intracrystalline diffusivity quickly decreases. Because the diffusion of gases in the blocked window is a typically activated process, the increase of the temperature will quickly improve the diffusion. The usual way to illustrate the temperature dependency of the intracrystalline diffusivity is the Arrhenius equation.

When dealing with activated diffusion processes, one of the most important issues is the calculation of the translational kinetic energy distribution. We use two simple examples to show the necessity of using quantum mechanics to calculate the Boltzmann distribution instead of using the continuous integral approximation of the classical mechanics. The examples described the case in which a helium molecule moves in a spherical box free of an interaction potential and in the case of the presents of a spherical symmetrical potential field. In these two cases the calculated average kinetic energy values were close to the expected ones by the equipartition principle and this fact confirmed that the calculation procedures were correct. The translational kinetic energy distributions obtained for these two cases were quite different. Specially, the distribution of kinetic energies at high energies is interesting since the activated diffusion processes involve this part of the distribution. The use of the classical approach will introduce great errors resulting from the calculated kinetic energy distribution. The interaction potential does not change the average kinetic energy of an adsorbate molecule, but it will change the distribution function. At low kinetic energies, the interaction potential will make the distribution function move in the direction of higher kinetic energies.

In this methodology, the calculations of the interaction potential and the intracrystalline diffusivities are independent of any adsorption kinetic experimental data and thus the models are truly predictive. In the models the zeolite structure and the adsorbate molecule characteristics are included and thus they should be able to translate to other systems in which the zeolites have similar cavity and window structures. The most similar system may be the diffusion of gases in X and Y zeolites. This methodology is also ready to be used in other zeolite systems by adjusting the calculation of the interaction potential.

The predicted diffusivities and activation energies for permanent gases in 5A and 4A zeolites are in the same order of magnitude published experimental results. Due to the quick diffusion of small molecules like helium, argon, oxygen and nitrogen in relatively large unblocked eight membered ring, the usual macroscopic experimental techniques suffer the same limits [Kärger and Ruthven, 1989]. The simplifying assumptions to real interaction potential field and the uncertainty of the molecular parameters result in some uncertainty of the predicted results.
REFERENCES


Breck, D.W., Zeolite Molecular Sieves, Wiley, 1974


Darken, L.S., Diffusion, Mobility and Their Interrelation through Free Energy in Binary Metallic, Trans. AIME, 174, 184, 1948


Kärger, J. and D.M. Ruthven, On the Comparison between Macroscopic and NMR Measurements of Intracrystalline Diffusion in Zeolites, Zeolite, 9, 267, 1989


Pruess, S. and C. Fulton, SLEDGE/NETLIB Release 2.11, spruess@mines.colorado.edu, 1991


Satterfield C.N., Mass Transfer in Heterogeneous Catalysis, MIT Press, 1970


Theodorou, D. and J. Wei, Diffusion and Reaction in Blocked and High Occupancy Zeolite Catalysts, J. Catalysis, 83, 205 - 224, 1983


152
4 EXPERIMENTAL DETERMINATION OF MASS TRANSPORT PARAMETERS AND MODELS

The effective diffusivities of gases in porous media are some of the most important parameters for describing the dynamic behavior of processes involving gas-solid operations. For many catalytic reaction systems, diffusional mass transport is the rate controlling step. In adsorption separation, the system dynamic properties are usually the main factor for the choice of the operating conditions. The knowledge of the effective diffusivities is limited because of the pore structure complexity. The entire theoretical prediction of effective diffusivities is impractical. Ordinary studies on effective diffusivities are concentrated on two aspects. One is to study the pore network structure to find its approximate description by means of limited experimental information such as the pore size distribution, the pore volume and the specific surface area. The objective of such approximation is to estimate an effective diffusivity by considering the combination of the molecular, Knudsen and surface diffusion and convection mechanisms. Another aspect is the experimental determination of the mass transport rate. The effective diffusivities can be extracted from the experimental mass transport rate data by matching the calculated theoretical values based on a mathematical model that describes the dynamic or steady state mass transport processes to the experimental responses. In the mathematical model the effective diffusivities usually appear as some adjustable parameters. Combination of these two aspects can guide to establish a mathematical model that corresponds to a special pore network structure.

The experimental work plays an important role in the study of effective diffusivities of gases in porous media. The most commonly used macroscopic experimental methods for determining the effective diffusivity include the particle fixed bed and the diffusion cell. By controlling the flow rates in both sides of the cell under isobaric conditions, the effective diffusivity in a single pellet can be determined by the steady state concentration responses of both sides. Biswas et al [1987] used the diffusion cell technique to study the pellet with bidisperse pore structure and developed the corresponding models. Particle fixed bed is another kind of commonly used experimental technique. A pulse or concentration step of the diffusing gas tracer is introduced at the inlet of the bed and the response values are monitored at the outlet. By fitting the theoretical to the experimental response values, the mass transport parameters can be obtained.

The matching techniques ordinarily used include moment analysis and time domain solution. A large number of papers reported the use of the moment matching technique. In spite of its simplicity, the moment method may lead to inaccurate estimation of the effective diffusivity resulting from experimental errors in response measurements. The macro pore effective diffusivity is obtained from the second central moment [Hyun and Danner, 1985]. The micropore diffusional information for a bidispersed structure is extracted from higher experimental moments. The accuracy of various moments decreases when the moment order increases. The results obtained from the moments of order higher than the second are usually unreliable. For diffusional systems with large response tailing, the error will result in inaccurate moments even for the lower order ones. With cheaper computation, the direct time domain fitting of theoretical values to experimental data became a good alternative to moment matching.

Whether we use the moment or direct time domain matching techniques, the fundamental problems are in being able to develop a good mathematical model that can physically and quantitatively describe the mass transport rate processes. From a numerical point of view, the numerical method must also be stable within the interesting range of the
parameters. In this section, gas diffusion in a single pellet, shallow bed and single pellet string fixed bed will be discussed. According to different samples, different experimental techniques were used and thus different mathematical models were developed.

1 DIFFUSION CELL APPARATUS AND MODELS

1.1 Apparatus Description

The simplest case is gas diffusion in homogeneous porous solids with large dimension and slab geometry. The diffusion cell is the ideal experimental technique for the determination of the mass transport parameters in such porous solids. Based on the slab geometry and dimensions, a user-designed diffusion cell holds the sample and the small void between the sample and cell wall must be blocked in order to avoid the leak of tracer gas along both sides of the cell. When the pressures between both sides and the flow rates in both chambers are kept constant the tracer gas mass transfer results from pure diffusion. Theoretically, the condition of isobaricity and equal flow rates can not be approached simultaneously. The diffusion rates of different weight molecules are different and the lighter molecules have faster diffusion rates. When the inlet flow rates at both sides of the cell and the pressures are kept constant, the difference on diffusion rates will result in a difference on the mass transport rates between the tracer and the carrier and thus there is a net flux through the solid. This net flux will change the pressures or the flow rates. If we concentrate our interest in low tracer concentrations and large flow rate, the net flux will be very small. For example, if the tracer concentration is lower than 10%, the flux of tracer through the solid is 10% of the total tracer flow rate in the chambers and the flow rate variation will be smaller than 1%. These approximate conditions of constant pressure and equal flow rates greatly simplify the mathematical treatment of the experimental data.

Figure 4.1 shows the scheme of the experimental apparatus. The inlet flow rates of various streams are accurately controlled by the mass flow controllers. This picture was directly copied from the computer screen. The pressure difference between both sides of the cell is monitored by an accurate differential pressure transducer and adjusted by a self-made pressure difference keeper to less than 1 mmH₂O. The concentration of the outlet streams is measured by two microvolume thermal conductivity detectors and the output signals from these detectors are automatically recorded by the data acquisition system which is composed by a computer and an A/D conversion board. All experimental operating conditions such as temperatures, pressures and flow rates are also recorded.

A data acquisition and treatment software package were developed. The software package for on-line data acquisition, device and experimental curves display was written in ASSEMBLE and QUICK BASIC languages. The ASSEMBLE language has the following advantages: the running speed of ASSEMBLE programs is much higher than for high level language programs; the program can directly and fully utilize computer hardware and software resources. However high level languages, such as QUICK BASIC are easy to use, debug and edit. We combine these two languages to take the advantages of each one. All subroutines which need some system resources not supported by the high level language, like direct hardware control and that are critical in time were written in ASSEMBLE language. Other subroutines including initialization of the system, drawing of the experimental apparatus diagram, managing the whole program, set function keys and input user regulation and verification of experimental
parameters (temperatures, pressures and flow rates) were written in QUICK BASIC language. The package is compatible with all IBM PC family computers. There are a lot of user choices and active function keys when the package is treating different situations, so it is convenient to be used by other people. Using the interrupt facility, the computer can do more jobs when it is processing experimental data without display on line. As user presses DOS shell function key, the software package shrinks program memory and releases all free memory for other programs. This does not affect data acquisition and treatment functions. This software was also used with the other two set-ups.

![Diagram of the pellet or shallow bed diffusion cell experimental set-up](image)

1. carrier gas tank
2. tracer gas tank
3. sample gas tank
4. vacuum pump
5. pressure sensor (absolute)
6. pressure regulators
7. three way ball valves
8. drying units
9. flow control valves
10. two way ball valves
11. mass flow meters
12. pressure sensors (gauge)
13. fine needle valves
14. computer and data acquisition board
15. pressure - difference - keeper
16. conductivity detectors
17. diffusion cell
18. thermocouple
19. oven
20. accurate differential pressure transducer

Figure 4.1 Schematic diagram of the pellet or shallow bed diffusion cell experimental set-up

155
When we adjust the pressure difference through the cell to some desired values and control the flow rates of the inlets and measure the flow rates at the outlets, the total flux resulting from the diffusion and convection through the cell can be obtained. Then the effective convective flow coefficients can be calculated.

1.2. Experimental Procedure

* Activation of porous solids

1. According to the special dimension of the pellet, a corresponding diffusion cell was designed. The pellet was fixed in the cell using epoxy resin and it was carefully verified that there was no any leaking between the cell wall and the pellet.

2. The system was purged by carrier gases (such as helium) at 95 °C for 24 hours in order to remove possible water and other impurity gases.

* Sample gas mixing

The desired composition of the sample gas can be obtained by mixing the pure gases. The sampling cylinder was evacuated, filled with pure tracer gas (such as nitrogen) to a given pressure and then filled with pure carrier gas (such as helium) to the desired pressure. From the partial pressures of tracer gas, total pressure and temperature the composition can be calculated by means of the state equations.

* Calibration and adjustment of carrier and sample gas volumetric flow rates

In order to keep isobaricity and equal flow rates in both sides of the cell, the three volumetric flow rates, top and bottom chamber carrier gas and top chamber sample gas must be exactly equal. The mass flow meter and control units can only control mass flow rate. For different sample gas compositions, the volumetric flow rate was calibrated using a soap bubble meter. Within a certain pressure range including the decrease of the sample gas pressure in the sampling cylinder, the mass flow meter and control units can keep this flow rate constant.

* Dynamic determination of mass transfer parameters

The system should be warmed up at least one hour. The bottom and top chambers were purged by carrier gas. When the baselines of the thermal conductivity detector responses reach constant values, the system is ready for starting the experiment. During the warm up, all parameters such as oven temperature, pressures and flow rates of various streams and baselines were displayed and monitored on the computer screen.

The top chamber gas stream is changed from carrier gas to sample gas by manually changing the sample valve position or sending a trigger signal by computer to the electric actuator. This change should be performed as quickly as possible. The computer automatically records and displays the TCDs (thermal conductivity detectors) response curves. When both response values reach steady state, (it takes about 10 minutes for the nitrogen/helium system.), the top chamber stream was changed again to carrier gas to desorb or regenerate the pellet.

* Repeat previous step four to five times to ensure the reproducibility and averaging
* Measurement of the absolute composition

The calibration curves of TCD responses for various compositions show an almost linear dependency within the experimental composition range. It means that the absolute composition at each point of the response curves can be calculated from the TCD outputs as long as there is one known point of composition and response where temperature, pressure, and flow rate are the same. The sample gas composition is known. This point can be obtained for both TCDs.

First the bottom chamber carrier gas was cut off, the outlet was blocked and the corresponding TCD was switched off. The top chamber gas was changed to sample gas. After it reaches steady state the response value was recorded. This value is independent of the process and only reflects the sample composition. This step was repeated several times. For the calibration of the bottom TCD a similar procedure was used.

* Convection measurement

By introducing pure component sample gas into both cell sides and adjusting the flow resistance at the top chamber outlet, the pressure difference through the cell can be set to any desired value. When the system reaches steady state, the flow rates at both outlets are measured using a soap bubble flow meter. Varying the pressure differences a set of data of flow rates against pressure differences at constant temperature can be obtained. From these flow rates the mass transport flux of the sample gas through the pellet can be calculated.

* Data treatment

From the steady state responses of both detectors an effective diffusivity which does not include the contribution of dead-end pores or a relationship linking the effective diffusivity and the film mass transport coefficient can be obtained. The effective diffusivity which includes the contribution of dead-end pores and/or film mass transport coefficient can be achieved by matching the theoretical response curves of the corresponding mass transport model to the transient response curves of both top and bottom chambers.

1.3 Mass Transfer Model with Macropore Diffusion and Convection for a Single Pellet Diffusion Cell

Figure 4.2 shows the various stream arrangements. We make the following assumptions: chambers of equal volume; perfectly mixing in the top and bottom chambers; negligible adsorbed amount; the input perturbation is a concentration step. In the case of nonisobaric diffusion, the total flux of a gas through a porous solid is expressed in terms of viscous flow. There is a possible film diffusional resistance (on both pellet sides). So the pellet surface can be viewed as a combination of basically two zones: one with convective pore and no film and another with non-convective pore and film. Of course this is a quite simplified model of the reality. The viscous flow through the pellet will destroy the boundary layer on the pellet surface and thus the film. For pure diffusion the film mass transport resistance can be combined with other diffusional resistances in series.

For the combination of the mass transport resistances in series the total resistance is the sum of the individual resistances. Whereas in the parallel combination, the flux is the
sum of various branch fluxes. On the other hand, if the viscous flow is expressed by the
Darcy equation, the total mass flux for the tracer through the pellet can be expressed by
[ Dogu et al, 1989 and Mason and Malinauskas, 1983 ]:

\[ J_{\text{total}} = - D_e \frac{\partial c}{\partial z} - \frac{B_e}{\nu} c \frac{dP}{dz} \]  \hspace{1cm} (4.1)

Where \( c \) is the solute concentration, \( D_e \) is the effective diffusivity, \( B_e \) is the effective
Darcy coefficient, \( \nu \) is the viscosity and \( P \) is the total pressure. Both \( D_e \) and \( B_e \) are
usually dependent on the pore structure. In dilute tracer systems \( D_e \) and \( B_e \) may be
considered as independent of the concentration. Also considering a constant pressure
gradient through the axial direction, the differential mass balance for the diffusing
component (tracer) can be written:

\[ \frac{\partial c}{\partial t} = D_e \frac{\partial c}{\partial z} - \gamma \frac{\partial c}{\partial z} \]  \hspace{1cm} (4.2)

where \( \gamma = \frac{B_e}{\nu} \frac{dP}{dz} \). The validity of equation (4.2) will be discussed in next chapter.

When the pressure gradient is negligible, equation (4.2) can be simplified to:

\[ \frac{\partial c}{\partial t} = D_e \frac{\partial c}{\partial z} \]  \hspace{1cm} (4.3)
If initially the pellet is purged by carrier, the corresponding initial condition is

\[ c(0,z) = 0 \]  \hspace{2cm} (4.4) \]

The boundary conditions are:

\[ c(t,0) = c_o ; \quad c(t,L) = c_L \]  \hspace{2cm} (4.5) \]

where \( c_o \) and \( c_L \) are respectively the concentration at the top and bottom surfaces of the pellet and \( L \) is the thickness of the pellet. \( c_o \) and \( c_L \) can be expressed in terms of the top and bottom chamber concentrations, \( c_t \) and \( c_b \). The difference between them results from the possible existence of a film mass transport resistance around the pellet top and bottom surfaces.

\[ D_e \frac{\partial c}{\partial z} \bigg|_{z=0} = - k_f (c_t - c_o) ; \quad D_e \frac{\partial c}{\partial z} \bigg|_{z=L} = - k_f (c_L - c_b) \] \hspace{2cm} (4.6) \]

where \( k_f \) is the film mass transport coefficient. The mass balance equations in the top and bottom chambers under the conditions of equal and constant inlet and outlet flow rates and equal chamber volumes are:

\[ F c_t = F c_t + V_e \frac{dc_t}{dt} - \omega A D_e \frac{\partial c}{\partial z} \bigg|_{z=0} \] \hspace{2cm} (4.7) \]

\[ F c_b + V_e \frac{dc_b}{dt} + \omega A D_e \frac{\partial c}{\partial z} \bigg|_{z=L} = 0 \] \hspace{2cm} (4.8) \]

where \( F \) is the flow rate, \( A \) is the section area of the pellet, \( V_e \) is the volume of a chamber, \( c_t \) is the sample gas concentration and \( \omega \) is the pellet porosity. Initially, the chambers and pellet are solute free, so the corresponding initial conditions are:

\[ c_o(0) = 0 ; \quad c_t(0) = 0 \] \hspace{2cm} (4.9) \]

The dimensionless forms of equations (4.3) to (4.9) are:

\[ \frac{\partial C}{\partial \theta} = N_e \frac{\partial^2 C}{\partial Z^2} \]  \hspace{2cm} (4.3a) \]

\[ C(0,Z) = 0 \]  \hspace{2cm} (4.4a) \]
\[ \frac{\partial C}{\partial Z} \bigg|_{z=0} = \frac{N_t}{N_e} [C \big|_{z=0} - C_t] ; \quad \frac{\partial C}{\partial Z} \bigg|_{z=1} = \frac{N_t}{N_e} [C_b - C \big|_{z=1}] \]  

\[ \frac{dC_t}{d\theta} = 1 - C_t + N_s N_e \frac{\partial C}{\partial Z} \bigg|_{z=0} \]  

\[ \frac{dC_b}{d\theta} = -C_b - N_s N_e \frac{\partial C}{\partial Z} \bigg|_{z=1} \]  

\[ C_b(0) = 0; \quad C_t(0) = 0; \]  

Dimensionless variables and parameters are defined as:

\[ C = \frac{c}{c_e}, \quad Z = \frac{Z}{L}, \quad v = \frac{V_c}{V_c}, \quad \theta = \frac{t}{v}, \quad N_t = \frac{k_0}{L}, \quad N_e = \frac{D_e}{L^2}, \quad N_s = \frac{L_0 A}{V_c} \]

The solutions of equations (4.3a) to (4.9a) in Laplace domain (the detailed solution procedure will be demonstrated later) are:

\[ \bar{C}_t = \frac{S_4}{s \left[ S_4^2 - (N_t N_s S_2)^2 \right]} \]  

\[ \bar{C}_b = \frac{N_s N_t S_2}{s \left[ S_4^2 - (N_t N_s S_2)^2 \right]} \]  

where \( \bar{C}_t \) and \( \bar{C}_b \) are respectively the Laplace domain solutions for the top and bottom chamber response concentrations, \( s \) is the Laplace variable and \( S_1, S_2, S_3 \) and \( S_4 \) are

\[ S_4 = s + 1 + (1 - S_3)N_t N_s \]

\[ S_3 = \frac{\sqrt{S_1 N_t N_e} \cosh(\sqrt{S_1}) + N_t \sinh(\sqrt{S_1})}{\sinh(\sqrt{S_1})(S_1 N_t^2 + N_t^2) + 2\sqrt{S_1 N_t N_e} \cosh(\sqrt{S_1})} \]

\[ S_2 = \frac{N_s N_e \sqrt{S_1}}{\sinh(\sqrt{S_1})(S_1 N_e^2 + N_t^2) + 2\sqrt{S_1 N_t N_e} \cosh(\sqrt{S_1})} \]

\[ S_1 = \frac{s}{N_e} \]
Equations (4.10) and (4.11) represent the response solutions of the top and bottom chambers for a step input in Laplace domain. Chamber steady state response values (time tends to infinity) can be easily obtained in time domain applying the Laplace transform final value theorem [Seborg et al., 1989].

\[
C_t(\infty) = \lim_{s \to 0} s \overline{C}_t = \frac{N_f + 2N_e N_t N_s}{N_t + 2N_e + 2N_e N_f N_s} \quad (4.12)
\]

\[
C_b(\infty) = \lim_{s \to 0} s \overline{C}_b = \frac{N_e N_t N_s}{N_f + 2N_e + 2N_e N_f N_s} \quad (4.13)
\]

From the Laplace domain solutions of equations (4.10) and (4.11) we can easily calculate the theoretical moments. By comparing these to the experimental ones we are able to obtain the effective diffusivity. Taking into account the drawbacks of the this technique we preferred to use time matching.

The time domain solution of equations (4.10) and (4.11) can be obtained numerically. The fast Fourier transform (FFT) technique is an effective algorithm for numerically inverting Laplace transforms [Hsu and Dranoff, 1987]. Because there is a pole in equations (4.14) and (4.15) at \( s = 0 \), we first drop out the factor \( 1/s \), that is, we invert the impulse input solution and then we integrate the results in the time domain. By using a parameter optimization technique, an effective diffusivity can be obtained when the objective function is minimum. The software package ODRPACK [Boggs et al., 1987] is specially suitable to be used in regressions with the possible presence of experimental errors in both independent and dependent variables. The output of ODRPACK package gives the errors and the parameter (effective diffusivity).

Theoretically, the parameters \( N_e \) and \( N_t \) thus \( D_e \) and \( k_t \) can be obtained by matching the theoretical response values to the experimental measured data. Biswas et al. [1987] deduced mass transport rate equations similar to (4.3a) to (4.9a) for a bidispersed pore distribution and other pore distribution cases and obtained a set of analytical solutions in time domain using the similarity integral transform technique first to achieve the analytical solutions in Laplace domain and then to analytical inversion. In their solutions the response of the bottom chamber was expressed in a complicated infinite series of the time variable. Some parameters in each term of the series must be obtained by solving a nonlinear algebraic equation. The searching of the location of such roots may become a serious task as they are not readily discernible. In general many terms need to be calculated in order to reach enough numerical precision. In order to overcome such convergency difficulties direct numerical inversion was adopted in present work.

The effective diffusivity and the film mass transport coefficient are linked by top and bottom chamber steady state equations (4.12) and (4.13). Here we must emphasize that the effective diffusivity values obtained from the transient data and steady state data are different. The effective diffusivities calculated from the steady state responses do not contain the contribution of dead-end pores.

Some special cases are interesting. The film mass transport resistance contribution to the total resistance is important in practical experimental determination. Qualitatively the
film mass transfer resistance can be neglected when the chamber flow rates are high (film thickness will decrease) and/or when the effective pore diffusivity is much smaller than the molecular diffusivity [Burghardt et al., 1988]. Quantitatively this problem can also be solved [Lu et al., 1992]. Our experimental results showed that the film mass transport resistance even for the case of no convective flow can be neglected if the chamber structure and operating conditions are suitable. A more detailed discussion will be held in next chapter. For the moment let us assume that there is no film mass transport resistance on the pellet surfaces. Mathematically, the optimization process for finding one parameter is much easier than for finding two parameters.

For negligible film mass transport resistance \( N_l \rightarrow \infty \), equations (4.10) to (4.13) are simplified to:

\[
\lim_{N_l \rightarrow \infty} S_1 = \frac{S}{N_e}; \quad \lim_{N_l \rightarrow \infty} S_2 = 0; \quad \lim_{N_l \rightarrow \infty} S_3 = 1; \quad \lim_{N_l \rightarrow \infty} S_4 = s + 1 + N_e N_e \sqrt{S_1 \coth(\sqrt{S_1})} ;
\]

\[
\lim_{N_l \rightarrow \infty} \left[ S_4 - (N_l N_e S_2)^2 \right] = (s+1)^2 + 2(s+1)N_e N_e \sqrt{S_1} \left[ \coth(\sqrt{S_1}) + N_e N_e \sqrt{S_1} \right] ;
\]

\[
\lim_{N_l \rightarrow \infty} N_e N_e S_2 = \frac{N_e N_e \sqrt{S_1}}{\sinh(\sqrt{S_1})}
\]

\[
\lim_{N_l \rightarrow \infty} \overline{C}_t = \frac{s + 1 + N_e N_e \sqrt{S_1 \coth(\sqrt{S_1})}}{(s+1)^2 + 2(s+1)N_e N_e \sqrt{S_1} \left[ \coth(\sqrt{S_1}) + N_e N_e \sqrt{S_1} \right]}
\quad (\text{4.14})
\]

\[
\lim_{N_l \rightarrow \infty} \overline{C}_b = \frac{N_e N_e \sqrt{S_1}}{(s+1)^2 \sinh(\sqrt{S_1}) + 2(s+1)N_e N_e \sqrt{S_1} \left[ \cosh(\sqrt{S_1}) + N_e N_e \sqrt{S_1} \sinh(\sqrt{S_1}) \right]}
\quad (\text{4.15})
\]

\[
C_t(\infty) = \lim_{s \rightarrow 0} s \overline{C}_t = \frac{1 + N_e N_e}{1 + 2N_e N_e}
\quad (\text{4.16})
\]

\[
C_b(\infty) = \lim_{s \rightarrow 0} s \overline{C}_b = \frac{N_e N_e}{1 + 2N_e N_e}
\quad (\text{4.17})
\]

When the system reaches the steady state \( \frac{\partial C}{\partial \theta} = 0 \) and the concentration distribution inside the pellet becomes linear \( \frac{\partial^2 C}{\partial Z^2} = 0 \)

\[
C = (C_t - C_b) Z + C_t
\quad (\text{4.18})
\]

In the steady state we have:
\[ C_t(\infty) - C_b(\infty) = \frac{1}{1 + 2N_eN_s} \]  

(4.19)

1.4 Convective Flux

For the case of a single solute system and the existence of a pressure gradient between both pellet sides, a convective flow through the pellet will develop. For large pore if we neglect the gravitational, initial, wall and creeping flow effects the Darcy law can be directly used to describe the flux with the combination of ideal equation (\( P = \rho RT \), \( r \) is the gas density):

\[ J = -\frac{B_s}{u} \rho \frac{\partial P}{\partial z} \]  

(4.20)

At steady state, the flux, \( J \), and the pressure gradient through the pellet become constant. The flux can be calculated from the flow rates of both chambers and the pressure difference through the pellet can be measured, thus the effective Darcy coefficient, \( B_s \), can be evaluated. By changing the pressure difference through the pellet a set of data relating pressure difference and flux can be experimentally obtained.

It is difficult to obtain the transient response values of the convective mass transport of a binary component system by this experimental apparatus since the net flux through the pellet results in flow rate variations in both chambers and the response signals from the thermal conductivity detectors are dependent not only on the composition but also on the flow rate.

The forced viscous flow through the pellet will destroy the possible static boundary layer on both pellet surfaces. When the pressure gradient through the pellet is very small or \( \rho \) and the pore diameter is very small the convective flux becomes negligible. For single component systems there is no flow through the pellet without a pressure gradient. For multicomponent systems even if there is no pressure gradient, a concentration gradient results in a mass transport flux through the pellet by the diffusional mechanism. For such case the boundary layer on the pellet surfaces will result in a possible film mass transport resistance and this situation reduces to the case discussed in Chapter 1.3.

2 SHALLOW BED APPARATUS AND MODELS

Originally, the diffusion cell technique was limited to be used with single pellets. A modification of the diffusion cell makes it applicable to small particles [Sun et al, 1992], even for the determination of the intraparticle mass transport rates of gases in porous media with bidisperse pore network structure. To obtain reliable experimental data for determining gas molecular and pore diffusivities by this method, the main technical problems derive from being difficult to keep constant the flow rates and pressures of top and bottom chambers. In order to measure and adjust accurately the flow rates, three mass flow meters with automatic adjusting valves and three constant mass flow valves were used. With this equipment the flow rates can be kept constant, even if the up -
stream pressures undergo a large variation. By using a pressure-difference-keeper, the pressure difference between top and bottom chambers can be accurately adjusted for different experimental systems. The experimental apparatus diagram is similar to Figure 4.1 and the experimental procedure is also similar to the single pellet case.

2.1 Evaluation of Linear Adsorption Equilibrium Constants

When the diffusional system has significant adsorption, the adsorption equilibrium effects on the mass transport model must be considered. Specially for the mass transport of gases in zeolites, the adsorption equilibrium is a first importance factor to determine the response values. At low solute partial pressure, the adsorption isotherms are usually linear. Making a tracer gas global mass balance among cell inputs and outputs during an experimental run, the adsorption equilibrium constant at a given bulk phase concentration can be calculated.

The definition of the adsorption equilibrium Henry constant, K is

\[ a_m = K c_a \]  \hspace{1cm} (4.21)

where \( c_a \) is the concentration of tracer gas in macropores (mmol/ml macropore volume) and \( a_m \) is the concentration of tracer gas in the adsorbed phase (mmol/ml microparticle volume).

From the diffusion cell mass balance, we have:

\[ \int_0^{t_e} \mathcal{F} c_e \, dt - \int_0^{t_e} \mathcal{F} c_i \, dt - \int_0^{t_e} \mathcal{F} c_b \, dt = \mathcal{S} + \mathcal{S}' \]  \hspace{1cm} (4.22)

where \( t_e \) is the experimental terminated time, \( \mathcal{S} \) is the total adsorbed amount and \( \mathcal{S}' \) is the residual amount in bulk phase and macropores at steady state.

\[ \mathcal{S}' = c_e V_c + \frac{V_b}{2} c_e (\omega_b + \omega_a - \omega_a \omega_b) \]  \hspace{1cm} (4.23)

Where \( V_b \) and \( V_c \) are the volumes of the empty cell and chambers and \( \omega_a \) and \( \omega_b \) are respectively the macropore and bulk phase porosities. Because the bulk phase concentration distribution along the bed is linear and the concentrations in bulk phase and macropores are equal, we have \( c_b + c_i = c_e \) and \( c_i + c_b = c_e \).

The adsorbed amount is given by:

\[ a_m = \mathcal{S}/[ V_b(1 - \omega_b)(1 - \omega_a) ] \]  \hspace{1cm} (mmol/ml microparticle)
\[
K = \frac{a_m}{\frac{1}{2} c_e} = \frac{2 S}{c_e \left[ V_b \left( 1 - \omega_b \right) \left( 1 - \omega_a \right) \right]}
\]  

(4.24)

\[
S = F c_e t_e - c_e V_e - \frac{1}{2} c_e V_b \left( \omega_b + \omega_a - \omega_b \omega_b \right) - \left( \int_0^{t_e} c_t \, dt \right) + \int_0^{t_e} c_b \, dt \nonumber
\]

(4.25)

The relationship between concentrations, \(c_t\) and \(c_b\), and response signal levels, \(h_t\) and \(h_b\) is

\[
c_t = \frac{c_{t_{\infty}}}{h_t^t}
\]

(4.26)

\[
c_b = \frac{c_{b_{\infty}}}{h_b^t}
\]

(4.27)

Where \(h_t\), \(h_b\), \(h_t^t\) and \(h_b^t\) are respectively the signal levels of top and bottom chambers at time \(t = t\) and \(t = \infty\), \(c_{t_{\infty}}\) and \(c_{b_{\infty}}\) are the concentration on top and bottom chambers and \(c_{t_{\infty}} + c_{b_{\infty}} = c_e\). \(c_{t_{\infty}}\) or \(c_{b_{\infty}}\) can be calculated against \(c_e\) at the same flow rate and other operating conditions. Using the trapezoidal rule with \(\Delta t = t_e/m\)

\[
\int_0^{t_e} c_t \, dt = \frac{c_{t_{\infty}}}{h_t^t} \int_0^{t_e} h_t \, dt = \frac{c_{t_{\infty}} \Delta t}{h_t^t} \left( \frac{1}{2} h_{t1} + \frac{1}{2} h_{t2} + \sum_{k=2}^{n-1} h_{tk} \right)
\]

(4.28)

\[
\int_0^{t_e} c_b \, dt = \frac{c_{b_{\infty}}}{h_b^t} \int_0^{t_e} h_b \, dt = \frac{c_{b_{\infty}} \Delta t}{h_b^t} \left( \frac{1}{2} h_{b1} + \frac{1}{2} h_{b2} + \sum_{k=2}^{n-1} h_{bk} \right)
\]

(4.29)

let \(S_t = \frac{c_{t_{\infty}}}{h_t^t} \left( \frac{1}{2} h_{t1} + \frac{1}{2} h_{t2} + \sum_{k=2}^{n-1} h_{tk} \right)\) and \(S_b = \frac{c_{b_{\infty}}}{h_b^t} \left( \frac{1}{2} h_{b1} + \frac{1}{2} h_{b2} + \sum_{k=2}^{n-1} h_{bk} \right)\)

\[
S = F c_e t_e - c_e V_e - \frac{1}{2} c_e V_b \left( \omega_b + \omega_a - \omega_b \omega_b \right) - F \Delta t \left( S_t + S_b \right)
\]

(4.30)

\[
K = \frac{2 \left[ F \left( t_e - V_e - \frac{1}{2} V_b \left( \omega_b + \omega_a - \omega_b \omega_b \right) - F \Delta t \left( S_t + S_b \right) \right) \right]}{V_b \left( 1 - \omega_b \right) \left( 1 - \omega_a \right)}
\]

(4.31)

165
The adsorption equilibrium constant can be calculated by equation (4.31) from the transient responses of both chambers, the input amount and pellet pore properties. For linear isotherm the adsorption equilibrium constant is independent of the tracer concentration. When the adsorption takes place beyond the Henry region, the adsorption equilibrium constant calculated by equation (4.31) is the value at a given concentration.

2.2. Mass Transport Equations in a Shallow Bed

* Mass Transfer Equations

The necessity of a screening tool that could quickly and easily measure overall effective diffusivities and adsorption equilibrium of a large number of adsorbates and catalysts over a wide range of process conditions prompted the development of a flow through diffusion cell with well mixed chambers that only need minimal analysis. The step input is easy experimentally when compared to the ideal pulse input and the calculated error for the experimental moments resulting from the long - time, tailing region of the pulse input response is reduced [ Gibilaro and Waldram, 1972 and 1973 ].

Assumptions :

* chambers of equal volume
* no convection along axial direction
* perfectly mixing in the top and bottom chambers
* linear adsorption isotherm
* spherical particles
* equal flow rate to and from the chambers
* step input

A shallow bed packed with a bidispersed porous solid is similar to the single pellet cell depicted schematically in Figure 4.2. At time \( t = 0 \), a step input of adsorbable tracer is introduced into the top chamber. The thermal effects can be neglected. The following mass balance equations can be written :

In the microparticle :

\[
\frac{\partial a_m}{\partial t} = D_i \left( \frac{\partial^2 a_m}{\partial r^2} + \frac{2}{r} \frac{\partial a_m}{\partial r} \right) 
\]

(4.32)

IC : \( a_m(r,R,z,0) = 0 \)

(4.33)

BC : \( \frac{\partial a_m}{\partial r} (0,R,z,t) = 0 \), \( a_m(r_0,R,z,0) = Kc_a (R,z,t) \)

(4.34)

In the macropore :

\[
\frac{\partial c_a}{\partial t} = D_a \left( \frac{\partial^2 c_a}{\partial R^2} + \frac{2}{R} \frac{\partial c_a}{\partial R} \right) - \frac{3}{r_o} \frac{1}{\sigma_a} \left. D_i \frac{\partial a_m}{\partial r} \right| _{r=r_o}
\]

(4.35)
\[ \text{IC} : \quad c_a(R,z,0) = 0 \]  \hspace{1cm} (4.36)\\
\[ \text{BC} : \quad \frac{\partial c_a}{\partial R}(0,z,t) = 0, \quad c_a(R_0,z,t) = c(z,t) \]  \hspace{1cm} (4.37)\\

In the bulk phase:

\[ \frac{\partial c}{\partial t} = D_{me} \frac{\partial^2 c}{\partial z^2} - \frac{3}{R_0} \rho_b D_s \frac{\partial c_a}{\partial R} \bigg|_{R=R_0} \]  \hspace{1cm} (4.38)\\
\[ \text{IC} : \quad c(z,0) = 0 \]  \hspace{1cm} (4.39)\\
\[ \text{BC} : \quad \frac{\partial c}{\partial z}(0,t) = \frac{k_r}{D_{me}} [c(0,t) - c_i(t)], \quad \frac{\partial c}{\partial z}(L,t) = \frac{k_r}{D_{me}} [c_b(t) - c(L,t)] \]  \hspace{1cm} (4.40)\\

In the top chamber:

\[ \mathcal{F}_{c_e} = \mathcal{F}_{c_i} + V_c \frac{dc_i}{dt} - \rho_b AD_{me} \frac{\partial c}{\partial z} \bigg|_{z=0} \]  \hspace{1cm} (4.41)\\
\[ \text{IC} : \quad c_i(0) = 0 \]  \hspace{1cm} (4.42)\\

In the bottom chamber:

\[ \mathcal{F}_{c_b} + V_c \frac{dc_b}{dt} + \rho_b AD_{me} \frac{\partial c}{\partial z} \bigg|_{z=L} = 0 \]  \hspace{1cm} (4.43)\\
\[ \text{IC} : \quad c_b(0) = 0 \]  \hspace{1cm} (4.44)\\

Where \( r_0 \) and \( R_0 \) are respectively the microparticle and pellet radii; \( r, R \) and \( z \) are the radial and axial variables, respectively. The following dimensionless transformations were taken by letting:

\[ C = c/c_e, \quad \mathcal{A} = \alpha_m/c_e, \quad X = r/r_0, \quad Y = R/R_0, \quad Z = z/L, \]

\[ v = V_c/\mathcal{F}, \quad \theta = u/v, \quad \phi_a = \frac{1 - \omega_a}{\omega_a}, \quad \phi_b = \frac{1 - \omega_b}{\omega_b}, \]

167
\[ N_s = \frac{D_{me} \nu}{R_0^2}, \quad N_i = \frac{D_i \nu}{r_0^2}, \quad N_f = \frac{k_f \nu}{L}, \quad N_b = \frac{D_{me} \nu}{L^2}, \quad N_s = \frac{L \phi_b A}{V_c} \]

The corresponding dimensionless equations are:

**Microparticle equation** :

\[ \frac{\partial \mathcal{A}}{\partial \theta} = N_i \left( \frac{\partial^2 \mathcal{A}}{\partial X^2} + \frac{2}{X} \frac{\partial \mathcal{A}}{\partial X} \right) \quad (4.45) \]

**IC** :

\[ C_i(X,Y,Z,0) = 0 \]

**BC** :

\[ \frac{\partial \mathcal{A}}{\partial X} (0,Y,Z,\theta) = 0, \quad \mathcal{A}(1,Y,Z,\theta) = KC_d(Y,Z,\theta) \quad (4.46) \]

**Macropore equation** :

\[ \frac{\partial C_a}{\partial \theta} = N_a \left( \frac{\partial^2 C_a}{\partial Y^2} + \frac{2}{Y} \frac{\partial C_a}{\partial Y} \right) - 3 \phi_a N_i \frac{\partial \mathcal{A}}{\partial X} \bigg|_{X=1} \quad (4.47) \]

**IC** :

\[ C_a(Y,0) = 0 \quad (4.48) \]

**BC** :

\[ \frac{\partial C_a}{\partial Y} (0,\theta) = 0, \quad C_a(1,\theta) = C(Z,\theta) \quad (4.49) \]

**Bulk phase equation** :

\[ \frac{\partial C}{\partial \theta} = N_b \frac{\partial^2 C}{\partial Z^2} - 3 \phi_b \mathcal{A} N_a \frac{\partial C_a}{\partial Y} \bigg|_{Y=1} \quad (4.50) \]

**IC** :

\[ C(Z,0) = 0 \quad (4.51) \]

**BC** :

\[ \frac{\partial C}{\partial Z} (0,\theta) = \frac{N_i}{N_b} [C(0,\theta) - C_i(\theta)]; \quad \frac{\partial C}{\partial Z} (1,\theta) = \frac{N_i}{N_b} [C_b(\theta) - C(1,\theta)] \quad (4.52) \]

**Top chamber equation** :
\[
\frac{\partial C_i}{\partial \theta} = 1 - C_i + N_s N_b \frac{\partial C}{\partial Z} \bigg|_{Z=0} \quad (4.53)
\]

**IC :** \[ C_i(0) = 0 \] \quad (4.54)

**Bottom chamber equation :**

\[
\frac{\partial C_b}{\partial t} = - C_b - N_s N_b \frac{\partial C}{\partial Z} \bigg|_{Z=1} = 0 \quad (4.55)
\]

**IC :** \[ C_b(0) = 0 \] \quad (4.56)

All these equations and the boundary conditions are linear. For linear partial differential equations, the Laplace transform is a powerful tool for obtaining the analytical solutions in Laplace domain and then the original solutions in real domain can be calculated by means of a numerical inversion technique. As a comparison, the orthogonal collocation method is also applied to solve these equations.

For the special case where the velocities of gas in chambers are high enough and thus the film mass transport resistance is negligible ( \( k_f \) and \( N_f \) tend to infinity ), equation (4.52) is simplified to

**BC :** \[ C_i(\theta) = C(0,\theta); \quad C(1,\theta) = C_b(\theta) \] \quad (4.52a)

Other equations and the solution procedure are the same. In order to keep the generality of the solutions in the following part we concentrate our attention on using the equation (4.52) instead of the equation (4.52a).

### 2.3 Numerical Solution Techniques

#### I. Analytical Solutions in Laplace Domain and Numerical Inversion

The Laplace transform definition and properties can be found in engineering mathematics standard text - books, such as [Kreyszig, 1988]. The linear and constant coefficient ordinary differential equations in real time domain can be converted into linear algebraic equations in Laplace domain. While linear partial differential equations containing the time variable can be converted into ordinary differential equations in Laplace domain. Solving ordinary differential equations is usually much easier than solving partial differential equations.

Let us take the Laplace transform to the variable \( \theta \) in equations (4.32) to (4.56)

**Microparticle :**
\[ s \mathbf{A} = N_i \left( \frac{d^2 \mathbf{A}}{dX^2} + \frac{2}{X} \frac{d \mathbf{A}}{dX} \right) \]  
(4.57)

\[ X = 0, \quad \frac{d \mathbf{A}}{dX} = 0; \quad \quad X = 1, \quad \mathbf{A} = K \mathbf{C}_a \]  
(4.58)

**Macropore:***

\[ s \mathbf{C}_a = N_a \left( \frac{d^2 \mathbf{C}_a}{dY^2} + \frac{2}{Y} \frac{d \mathbf{C}_a}{dY} \right) - 3 \phi_a N_i \frac{d \mathbf{A}}{dX} \bigg|_{X=1} \]  
(4.59)

\[ Y = 0, \quad \frac{d \mathbf{C}_a}{dY} = 0; \quad \quad Y = 1, \quad \mathbf{C}_a = \mathbf{C} \]  
(4.60)

**Bulk phase:***

\[ s \mathbf{C} = N_b \frac{d^2 \mathbf{C}}{dZ^2} - 3 \phi_b \mathbf{C}_a N_a \frac{d \mathbf{C}_a}{dY} \bigg|_{Y=1} \]  
(4.61)

\[ Z = 0, \quad \frac{d \mathbf{C}}{dZ} = \frac{N_t}{N_b} [\mathbf{C} - \mathbf{C}_i], \quad \quad Z = 1, \quad \frac{d \mathbf{C}}{dZ} = \frac{N_t}{N_b} [\mathbf{C}_b - \mathbf{C}] \]  
(4.62)

**Top chamber:***

\[ s \mathbf{C}_i = 1/s - \mathbf{C}_i + N_a N_b \frac{d \mathbf{C}}{dZ} \bigg|_{Z=0} \]  
(4.63)

**Bottom chamber:***

\[ s \mathbf{C}_b = - \mathbf{C}_b - N_x N_b \frac{d \mathbf{C}}{dZ} \bigg|_{Z=1} \]  
(4.64)

**Solution of the microparticle equation***

\[ \mathbf{C}_i = \frac{\mathbf{C}_a \sinh(\sqrt{S_i}X)}{X \sinh(\sqrt{S_i})} \]  
(4.65)

\[ \frac{d \mathbf{C}_i}{dX} \bigg|_{X=1} = \mathbf{C}_a [\sqrt{S_i} \coth(\sqrt{S_i}) - 1] = S_2 \mathbf{C}_a \]  
(4.66)

170
Where \( S_1 = \frac{s}{N_1} \) and \( S_2 = K \left( \sqrt{S_1} \coth(\sqrt{S_1}) - 1 \right) \)

Solution of the macropore equation

\[ \overline{C}_a = \frac{C \sinh(\sqrt{S_3}Y)}{Y \sinh(\sqrt{S_3})} \]  \hspace{1cm} (4.67)

\[ \frac{d\overline{C}_a}{dY} \bigg|_{Y=1} = \overline{C} \left[ \sqrt{S_3} \coth(\sqrt{S_3}) - 1 \right] = S_4 \overline{C} \]  \hspace{1cm} (4.68)

Where \( S_3 = \frac{s + 3 \phi_b N_1 S_2}{N_a} \) and \( S_4 = \sqrt{S_3} \coth(\sqrt{S_3}) - 1 \)

Solution of the bulk phase equation

\[ \overline{C} = \alpha_1 \exp(\sqrt{S_5}Z) + \alpha_2 \exp(-\sqrt{S_5}Z) \]  \hspace{1cm} (4.69)

Where \( S_5 = \frac{s + 3 \phi_b \sigma_a N_a S_4}{N_b} \)

At the points \( Z = 0 \) and \( Z = 1 \) we have:

\[ \overline{C} \big|_{Z=0} = \alpha_1 + \alpha_2 \hspace{1cm} \overline{C} \big|_{Z=1} = \alpha_1 \exp(\sqrt{S_5}) + \alpha_2 \exp(-\sqrt{S_5}) \]

From the boundary condition (4.52) the derivatives of \( \overline{C} \) at \( Z = 0 \) and \( Z = 1 \) are:

\[ \frac{d\overline{C}}{dZ} \bigg|_{Z=0} = \alpha_1 \sqrt{S_5} - \alpha_2 \sqrt{S_5} \hspace{1cm} \frac{d\overline{C}}{dZ} \bigg|_{Z=1} = \alpha_1 \sqrt{S_5} \exp(\sqrt{S_5}) - \alpha_2 \sqrt{S_5} \exp(-\sqrt{S_5}) \]

The combination of these two sets of equations gives the integration constants \( \alpha_1 \) and \( \alpha_2 \)

\[ \alpha_1 = \frac{\sqrt{S_3} N_b N_f (\overline{C}_b + \overline{C}_e \exp(-\sqrt{S_5})) + N_f (\overline{C}_b - \overline{C}_e \exp(-\sqrt{S_5}))}{2 \sinh(\sqrt{S_3})(S_2 N_f^2 + N_f^2) + 4 \sqrt{S_3} N_b N_f \cosh(\sqrt{S_5})} \]  \hspace{1cm} (4.70)

171
\[
\alpha_2 = \frac{\sqrt{S_5}N_bN_t \overline{C}_b + \overline{C}_c \exp(\sqrt{S_5}) - N_t \overline{C}_b - \overline{C}_c \exp(\sqrt{S_5})}{2 \sinh(\sqrt{S_5}) (S_5 N_b^2 + N_t^2) + 4 \sqrt{S_5} N_b \sinh(\sqrt{S_5}))} \quad (4.71)
\]

And then the solutions of \( C \) at \( Z = 0 \) and \( Z = 1 \) are

\[
\overline{C} \bigg|_{Z=0} = \frac{\sqrt{S_5}N_bN_t \overline{C}_b + \left[ \sqrt{S_5}N_bN_c \cosh(\sqrt{S_5}) + N_t^2 \sinh(\sqrt{S_5}) \right] \overline{C}_c}{\sinh(\sqrt{S_5}) (S_5 N_b^2 + N_t^2) + 2 \sqrt{S_5} N_b \cosh(\sqrt{S_5})} \quad (4.72)
\]

\[
\overline{C} \bigg|_{Z=1} = \frac{\sqrt{S_5}N_bN_t \overline{C}_b + \left[ \sqrt{S_5}N_bN_c \cosh(\sqrt{S_5}) + N_t^2 \sinh(\sqrt{S_5}) \right] \overline{C}_c}{\sinh(\sqrt{S_5}) (S_5 N_b^2 + N_t^2) + 2 \sqrt{S_5} N_b \cosh(\sqrt{S_5})} \quad (4.73)
\]

Let \( S_6 = \frac{N_bN_t \sqrt{S_5}}{\sinh(\sqrt{S_5}) (S_5 N_b^2 + N_t^2) + 2 \sqrt{S_5} N_b \cosh(\sqrt{S_5})} \)

\[
S_7 = \frac{\sqrt{S_5}N_bN_c \cosh(\sqrt{S_5}) + N_t^2 \sinh(\sqrt{S_5})}{\sinh(\sqrt{S_5}) (S_5 N_b^2 + N_t^2) + 2 \sqrt{S_5} N_b \cosh(\sqrt{S_5})}
\]

\[
\overline{C} \bigg|_{Z=0} = S_6 \overline{C}_b + S_7 \overline{C}_c \quad \overline{C} \bigg|_{Z=1} = S_7 \overline{C}_b + S_6 \overline{C}_c
\]

The derivatives of \( C \) at \( Z = 0 \) and \( Z = 1 \) are

\[
\frac{d\overline{C}}{dZ} \bigg|_{Z=0} = \frac{N_t}{N_b} [(S_7 - 1) \overline{C}_c + S_6 \overline{C}_b] \quad \frac{d\overline{C}}{dZ} \bigg|_{Z=1} = \frac{N_t}{N_b} [(1 - S_7) \overline{C}_c - S_6 \overline{C}_c]
\]

**Top and bottom equations become**:

\[
[s + 1 + (1 - S_7) N_t N_s] \overline{C}_c = 1/s + N_t N_s S_6 \overline{C}_b \quad (4.74)
\]

\[
[s + 1 + (1 - S_7) N_t N_s] \overline{C}_b = N_t N_s S_6 \overline{C}_c \quad (4.75)
\]

Let \( S_8 = s + 1 + (1 - S_7) N_t N_s \)

172
The solutions of equations (4.74) and (4.75) are:

$$\bar{C}_t = \frac{S_\infty}{s \left[ S_\infty^2 - (N_fN_bS_\infty)^2 \right]} \quad (4.76)$$

$$\bar{C}_b = \frac{N_fN_bS_\infty}{s \left[ S_\infty^2 - (N_fN_bS_\infty)^2 \right]} \quad (4.77)$$

Equations (4.76) and (4.77) represent the Laplace domain responses of top and bottom chambers for a step input. The steady state solutions corresponding to these equations in real time domain are:

$$C_t(\infty) = \lim_{s \to 0} s \bar{C}_t = \frac{N_f + 2N_b + N_bN_fN_s}{N_f + 2N_b + 2N_bN_fN_s} \quad (4.78)$$

$$C_b(\infty) = \lim_{s \to 0} s \bar{C}_b = \frac{N_bN_fN_s}{N_f + 2N_b + 2N_bN_fN_s} \quad (4.79)$$

Combining equations (4.78) and (4.79) gives a relationship that links $N_f$ and $N_b$:

$$N_f = \frac{2N_bC_b}{N_bN_s \left( C_t - C_b \right) - C_b} \quad (4.80)$$

The fast Fourier transform technique was used to obtain the real time solution. Equations (4.76) and (4.77) can be numerically inverted by taking off 1/s, that is, the step input is changed to a Dirac input. The time functions, $C_t$ and $C_b$, can be obtained by numerical integration of the time domain Dirac input results. For comparison the numerical solution by orthogonal collocation will be focused next.

When the film mass transport resistance is negligible equations (4.76) and (4.77) can be simplified to:

$$\bar{C}_t = \frac{S_\infty}{s \left[ S_\infty^2 - (S_\infty)^2 \right]} \quad (4.76a)$$

$$\bar{C}_b = \frac{S_\infty}{s \left[ S_\infty^2 - (S_\infty)^2 \right]} \quad (4.77a)$$

173
Where $S_{6s} = \frac{N_b N_s \sqrt{S_s}}{\sinh(\sqrt{S_s})}$ and $S_{8s} = s + 1 + \frac{N_b N_s \sqrt{S_s} \cosh(\sqrt{S_s})}{\sinh(\sqrt{S_s})}$. Similarly the steady state concentration responses of both top and bottom chambers are

$$C_t(\infty) = \lim_{s \to 0} s \overline{C}_t = \frac{1 + N_b N_s}{1 + 2N_b N_s} \quad (4.78a)$$

$$C_b(\infty) = \lim_{s \to 0} s \overline{C}_b = \frac{N_b N_s}{1 + 2N_b N_s} \quad (4.79a)$$

Under this simplification the effective diffusivity can be calculated by just using the steady state responses.

II. Solution by Orthogonal Collocation

The orthogonal collocation method for solving partial differential equations has been well discussed in the books by Villadsen and Michelsen [1978] and Finlayson [1980]. This numerical technique belongs to the method of weighted residuals. The main principles of the method of weighted residuals are that the unknown functions in partial differential equations and boundary conditions are expanded in a series of known functions of spatial variables with unknown coefficients that are functions of the time variable. These coefficients are determined to satisfy the equations and boundary conditions in some best senses. The criteria used to choose these best senses determine the methods. The orthogonal collocation method has several advantages over other collocations. First, the collocation points are taken as the roots of an orthogonal polynomial, thus avoiding the arbitrary choice (usually a poorer one) by the user and the error decreases much faster as the number of terms increases. Second, the dependent variables are the solution values at the collocation points rather than the coefficients in the expansion.

The basic ideas of the orthogonal collocation method are to approximate the solution functions by a series of orthogonal polynomials that only contain the spatial variables and the unknown coefficients that are time dependent.

$$C(Z, \theta) = \sum_{j=1}^{N} P_{j}^{(\alpha, \beta)}(Z)C_j(\theta) \quad (4.81)$$

The first and second order derivatives of $C$ relative to the spatial variables can be related to $P_{j}^{(\alpha, \beta)}(Z)$. When the collocation points are chosen, the first and second order derivatives at the collocation points can be evaluated by means of a relationship between orthogonal polynomials and Lagrange interpolation polynomials [Villadsen and Michelsen, 1978]. The results are two matrices $A$ and $B$ with elements that are the derivatives and are independent of time. The partial differential equations can be converted into a set of ordinary differential equations of initial value type by such method.

The concentration distributions inside microparticles and particles are symmetric. For such system, the variable substitutions $v = X^2$ and $w = Y^2$ should be introduced so that a more accurate collocation can be reached [Villadsen and Michelsen, 1978]. After preparing
these variable substitutions, the boundary conditions \( \frac{\partial C_i}{\partial x} \big|_{x=0} = 0 \) and \( \frac{\partial C_a}{\partial y} \big|_{y=0} = 0 \) are automatically satisfied.

\[
v = X^2 ; \quad \frac{\partial C_i}{\partial X} = 2\sqrt{v} \frac{\partial C_i}{\partial v} ; \quad \frac{\partial^2 C_i}{\partial X^2} + \frac{2}{X} \frac{\partial C_i}{\partial X} = 6\frac{\partial C_i}{\partial v} + 4v \frac{\partial^2 C_i}{\partial v^2}
\]

and

\[
w = Y^2 ; \quad \frac{\partial C_a}{\partial Y} = 2\sqrt{w} \frac{\partial C_a}{\partial w} ; \quad \frac{\partial^2 C_a}{\partial Y^2} + \frac{2}{Y} \frac{\partial C_a}{\partial Y} = 6\frac{\partial C_a}{\partial w} + 4w \frac{\partial^2 C_a}{\partial w^2}
\]

* Microparticle \( n \)th internal collocation point

\[
\frac{\partial C_{in}}{\partial \theta} = N_i \left( \sum_{j=1}^{N} A_{n_j} C_{ij} + 4v \sum_{j=1}^{N} B_{n_j} C_{ij} + 6KA_{n,N+1} C_{am} + 4Kv_n B_{n,N+1} C_{am} \right)
\]

\[n = 1, 2, \ldots, N \quad (4.82)\]

In short form

\[
\frac{\partial C_i}{\partial \theta} = N_i \left( [BMv] C_i + C_{am} [BVv] \right) \quad (4.82a)
\]

\[
[BMv] = \begin{bmatrix}
6A_{11}^y + 4v_1 B_{11}^y & 6A_{12}^y + 4v_1 B_{12}^y & \ldots & 6A_{1N}^y + 4v_1 B_{1N}^y \\
6A_{21}^y + 4v_2 B_{21}^y & 6A_{22}^y + 4v_2 B_{22}^y & \ldots & 6A_{2N}^y + 4v_2 B_{2N}^y \\
\vdots & \vdots & \ddots & \vdots \\
6A_{N1}^y + 4v_N B_{N1}^y & 6A_{N2}^y + 4v_N B_{N2}^y & \ldots & 6A_{NN}^y + 4v_N B_{NN}^y
\end{bmatrix}
\]

\[
C_i = (C_{1i}, C_{2i}, C_{3i}, \ldots, C_{Ni})^T
\]

\[
[BVv] = (K(6A_{1,N+1}^y + 4v_1 B_{1,N+1}^y), K(6A_{2,N+1}^y + 4v_2 B_{2,N+1}^y), \ldots, K(6A_{N,N+1}^y + 4v_N B_{N,N+1}^y))^T
\]

where the boundary condition \( C_{1,N+1} = C_{am} \) has been used.
* Macropore $m$th internal collocation point:

$$\frac{\partial \mathbf{C}_a}{\partial \theta} = N_a \left[ 6 \sum_{j=1}^{M} A_{m,j} w C_{a,j} + 4 w_m \sum_{j=1}^{M} B_{m,j} w C_{a,j} + (6A_{m,M+1} + 4w_m B_{w,M+1} w C_{e}) \right] - 6\phi_a N_i \left( \sum_{j=1}^{N} A_{N+1,j} N_i C_{ij} + A_{N+1,N+1} C_{a,m} \right) \quad m = 1, 2, \ldots, M \quad (4.83)$$

In short form

$$\frac{\partial \mathbf{C}_a}{\partial \theta} = N_a \left[ \mathbf{BM}_w \left[ \mathbf{C}_a \right] + C_e \left[ \mathbf{BV}_w \right] \right] + C_i \quad (4.83a)$$

$$\mathbf{BM}_w = \begin{bmatrix}
6A_{11} w + 4w_1 B_{11} w - \alpha & 6A_{12} w + 4w_1 B_{12} w & \cdots & 6A_{1M} w + 4w_1 B_{1M} w \\
6A_{21} w + 4w_2 B_{21} w & 6A_{22} w + 4w_2 B_{22} w - \alpha & \cdots & 6A_{2M} w + 4w_2 B_{2M} w \\
\vdots & \vdots & \ddots & \vdots \\
6A_{M1} w + 4w_M B_{M1} w & 6A_{M2} w + 4w_M B_{M2} w & \cdots & 6A_{MM} w + 4w_M B_{MM} w - \alpha
\end{bmatrix}$$

Where $\alpha = 6\phi_a N_i A_{N+1,N+1}$

$$\mathbf{C}_a = (C_{a1}, C_{a2}, \ldots, C_{aM})^T$$

$$\mathbf{BV}_w = \left( (6A_{1,M+1} w + 4w_1 B_{1,M+1} w ), (6A_{2,M+1} w + 4w_2 B_{2,M+1} w ), \ldots, (6A_{M,M+1} w + 4w_M B_{M,M+1} w ) \right)^T$$

$$\mathbf{C}_i = \left( -6\phi_a N_i \sum_{j=1}^{N} A_{N+1,j} C_{ij} \Big|_{m=1}, -6\phi_a N_i \sum_{j=1}^{N} A_{N+1,j} C_{ij} \Big|_{m=2}, \ldots, -6\phi_a N_i \sum_{j=1}^{N} A_{N+1,j} C_{ij} \Big|_{m=M} \right)$$

where the boundary condition $\mathbf{C}_{a,M+1} = C_e$ has been used.

* Bulk phase $\ell$th internal collocation point:

$$\frac{d\mathbf{C}_\ell}{d\theta} = N_b \sum_{j=1}^{L} B_{\ell,j} C_j + N_b (B_{\ell,a} C_a + B_{\ell,L+1} C_{L+1}) - 6\phi_b c_a N_a \sum_{j=1}^{M} A_{M+1,j} C_{aj} + A_{M+1,M+1} C_{e} \quad (4.84)$$

from the boundary conditions
\[
\sum_{j=0}^{L+1} A_{ij}^z C_j = \frac{N_t}{N_b} (C_0 - C_1) \quad \text{and} \quad \sum_{j=0}^{L+1} A_{L+1,j}^z C_j = \frac{N_t}{N_b} (C_b - C_{L+1})
\]
we have:

\[
C_0 = \frac{N_t C_b (N_t + A_{0,1}^z N_{b,1}) - A_{0,1}^z N_{b,1} N_r C_1 + \sum_{j=1}^{L+1} [N_b (N_r + A_{0,1}^z N_{b,1}) A_{0,j}^z - A_{0,j}^z A_{0,1}^z N_{b,1} A_{L+1,j}^z] C_j}{(N_t - A_{0,0}^z N_{b,1}) (N_t + A_{0,1}^z N_{b,1}) - A_{0,1}^z A_{L+1,0}^z N_{b,1}^2}
\]  
\[
(4.85)
\]

\[
C_{L+1} = \frac{N_t C_b (N_t - A_{0,0}^z N_{b,1}) - A_{L+1,0}^z N_{b,1} N_r C_1 - \sum_{j=1}^{L+1} [N_b (N_r - A_{0,0}^z N_{b,1}) A_{L+1,j}^z + A_{0,1}^z N_{b,1} A_{L+1,j}^z] C_j}{(N_t - A_{0,0}^z N_{b,1}) (N_t + A_{L+1,0}^z N_{b,1}) + A_{0,1}^z A_{L+1,0}^z N_{b,1}^2}
\]  
\[
(4.86)
\]

In short form

\[
\frac{dC_\ell}{d\theta} = N_b ([BMz] C_\ell + C_0 [BVz_0] + C_{L+1} [BVz_{L1}]) + C_a
\]  
\[
(4.87)
\]

\[
[BMz] = \begin{bmatrix}
B_{\ell 1}^z - \beta & B_{\ell 2}^z & \cdots & B_{\ell \ell}^z \\
6A_{21}^z + 4z_1 B_{21}^z & B_{22}^z - \beta & \cdots & B_{2\ell}^z \\
\vdots & \vdots & \ddots & \vdots \\
B_{\ell 1}^z & B_{\ell 2}^z & \cdots & B_{\ell \ell}^z - \beta
\end{bmatrix}
\]

Where \( \beta = 6\phi_r \varepsilon_a N_a A_{M+1,M+1}^w \)

\[
C_\ell = (C_1, C_2, C_3, \ldots, C_\ell)^T
\]

\[
[BVz_0] = (B_{0,0}^z, B_{2,0}^z, \ldots, B_{L,0}^z)^T
\]

\[
[BVz_{L1}] = (B_{L+1,0}^z, B_{2,L+1}^z, \ldots, B_{L,L+1})^T
\]

\[
C_a = (-6\phi_r \varepsilon_a N_a \sum_{j=1}^{M+1,j} A_{M+1,j}^w C_{aj}|_{\ell=1}, -6\phi_r \varepsilon_a N_a \sum_{j=1}^{M+1,j} A_{M+1,j}^w C_{aj}|_{\ell=2}, \ldots, -6\phi_r \varepsilon_a N_a \sum_{j=1}^{M+1,j} A_{M+1,j}^w C_{aj}|_{\ell=L})
\]

* Top chamber collocation:

177
\[
\frac{dC_i}{d\theta} = 1 - C_i + N_b N_s \sum_{j=1}^{L} A_{0,j}^z C_j + N_b N_s (A_{0,0}^z C_0 + A_{0,1}^z C_{L+1}) \quad (4.88)
\]

Substituting equations (4.85) and (4.86) into (4.88), we have:

\[
\frac{dC_i}{d\theta} = N_b N_s \sum_{j=1}^{L} A_{0,j}^z C_j + \frac{N_b N_s N_c \left[ A_{0,0}^z (N_f + A_{L+1,1}^z N_b) - A_{0,1}^z A_{L+1,0}^z N_b \right]}{(N_f - A_{0,0}^z N_b) (N_f + A_{L+1,1}^z N_b)} + A_{0,1}^z A_{L+1,0}^z N_b^2 - C_i +
\]

\[
N_b N_s \sum_{j=1}^{L} \left\{ A_{0,0}^z [(N_f + A_{j+1,1}^z N_s) A_{j,0}^z - A_{j,1}^z N_b A_{j+1,0}^z] - A_{0,1}^z [(N_f - A_{0,0}^z N_b) A_{j+1,1}^z + A_{j,1}^z N_b A_{j,0}^z] \right\} C_j
\]

\[
\frac{1}{(N_f - A_{0,0}^z N_b) (N_f + A_{j+1,1}^z N_s) + A_{0,1}^z A_{j+1,0}^z N_b^2} + 1 \quad (4.89)
\]

**Bottom chamber collocation:**

\[
\frac{dC_b}{d\theta} = -C_b - N_b N_s \sum_{j=1}^{L} A_{L+1,j}^z C_j - N_b N_s (A_{L+1,0}^z C_0 + A_{L+1,1}^z C_{L+1}) \quad (4.90)
\]

Substituting equations (4.85) and (4.86) into (4.90), we have:

\[
\frac{dC_b}{d\theta} = -N_b N_s \sum_{j=1}^{L} A_{L+1,j}^z C_j - \frac{N_b N_s N_c \left[ A_{L+1,0}^z (N_f - A_{0,0}^z N_b) + A_{L+1,1}^z A_{L+1,0}^z N_b \right]}{(N_f - A_{0,0}^z N_b) (N_f + A_{L+1,1}^z N_b)} + A_{0,1}^z A_{L+1,0}^z N_b^2 - C_b -
\]

\[
N_b N_s \sum_{j=1}^{L} \left\{ A_{L+1,0}^z [(N_f + A_{L+1,1}^z N_s) A_{0,0}^z - A_{0,1}^z N_b A_{L+1,0}^z] - A_{L+1,1}^z [(N_f - A_{0,0}^z N_b) A_{L+1,1}^z + A_{0,1}^z N_b A_{L+1,0}^z] \right\} C_j
\]

\[
\frac{1}{(N_f - A_{0,0}^z N_b) (N_f + A_{L+1,1}^z N_s) + A_{0,1}^z A_{L+1,0}^z N_b^2} \quad (4.91)
\]

Where $A_{n,j}^z$, $A_{m,j}^z$, $B_{n,j}^z$, $B_{m,j}^z$, and $B_{j,i}$ are the collocation coefficients for the first and second derivatives in microparticle, macropore and axial directions which can be calculated by means of the Lagrange polynomials [Villadsen and Michelsen, 1978]. These ordinary differential equations are ready to be solved by Gear’s backwards difference
approximations [Davis, 1984]. The software package LSODE can be used to deal with such problems [Hindmarsh, 1980].

III. Parameter Regression

Above we discussed the solution techniques for the shallow bed mass transport equations. Among the variables and parameters, the geometric parameter, $N_g$, particle and bed porosity parameters, $\sigma_p$ and $\sigma_b$, are available before experiment. $C_t$ and $C_b$ are measured from the transient response curves. $F$ should be adjusted to estimate the mass transfer parameters $N_a, N_b, N_f$ and $N_i$. The input concentration of the adsorbable component should be low so that model assumptions are valid. The three parameter optimizing procedure is a difficulty task. In order to reduce the difficulty of the optimization procedure, the effective bulk phase diffusivity, $D_{me}$ was approximately estimated by the following equation [Gangwal et al, 1979]:

$$D_{me} = \sigma_b D_m / \tau_{bulk} \quad (4.92)$$

where $\tau_{bulk}$ is the bulk phase tortuosity. Schneider an Smith [1968] presented the above equation as a parallel pore model of the bed and thus $\tau_{bulk}$ should be independent of the solute and of the temperature. A few experimental values of $\tau_{bulk}$ for silica gel are 1.45 - 1.59 [Gangwal et al, 1979]. The theoretical prediction of $\tau_{bulk}$ for a bed randomly packed with uniform spherical particles is $\sqrt{2}$ [Wheeler, 1955]. Our effective bulk phase diffusivities determined by three parameter regression of the experimental responses for a variety of systems show that the error using the approximate estimation (4.92) is within the range of the uncertainty of the regressed $D_{me}$. The simplification of the regression from three to two parameters will significantly reduce the computing task. If the effective bulk phase diffusivity can be estimated the film mass transport coefficient can be calculated from the steady state responses by equations (4.78) and (4.79).

In the previous discussion, the form of the particles was assumed as spherical. This assumption is mathematically convenient. For the non-spherical particle, Greco Jr. et al [1975] developed a set of equivalence equations for processing experimental results of effective diffusivities measured in one geometry with the mathematics of a second geometry. From the transient behavior of each geometry a set of so-called geometric factors, $f_g$, were defined and for the sphere and cylinder they are respectively equal to

$$f_{g\, sphere} = 1/6 \quad (4.93)$$

$$f_{g\, cylinder} = \frac{64}{\pi} \sum_{m=1}^{\infty} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2 J_m^2 [J_m^2 + (2n+1)^2 \rho^2 \pi^2]} \quad (4.94)$$

where $\rho$ is the ratio of the cylinder radius to the cylinder length and $J_m$ is the $m$th root of the zeroth order Bessel function. With the aid of the geometric factors we can convert the
effective diffusivity extracted using mathematical models with spherical geometry to real cylindrical geometry.

\[
D_{\text{cylinder}} = D_{\text{sphere}} \times \frac{f_{g \text{ sphere}}}{f_{g \text{ cylinder}}} \times \frac{V_{\text{cylinder}}}{V_{\text{sphere}}}
\]  

(4.95)

where \(V_{\text{cylinder}}\) and \(V_{\text{sphere}}\) are the volumes of cylinder and sphere, respectively.

3 FIXED BED APPARATUS AND MODELS

The chromatographic technique is another useful experimental method for the determination of effective diffusivities of porous media. A pulse or step input of tracer gas is introduced at the inlet and the eluting stream is monitored. From the system response and dynamic information can be obtained. In experimental practice the chromatographic column is packed with particles obtained by crushing the industrial catalyst or adsorbent pellets of regular shape (cylinder, sphere etc.). If the particle dimension is small enough in comparison with the column diameter, axial dispersion contribution to the response curve shape can be expressed by the existing correlations for a packed bed [Langer et al. 1978]. However, the crushing process will destroy some pore network structure and the effective diffusivity and convective flow coefficient obtained may not reflect the real ones. For important industrial porous solids the typical particle dimension is several millimeters and if the traditional chromatographic column is used the column diameter for satisfying the requirement of no wall effects is unreasonably large. Thus the corresponding flow rate of carrier gas for reaching the necessary interstitial linear velocity is unsuitably high and the injection of tracer and analysis of the exit stream from the column are impractically difficult.

As an alternative of using a wide body column, the single particle string column technique was proposed by Scott et al [1974]. In this technique, the particle size is slightly smaller than the column diameter (the ratio of the column diameter to the particle diameter is 1.1 - 1.4). Because of the narrow space between the particle and the column interior wall higher carrier gas linear velocities can be reached under small pressure drops through the column. High carrier gas velocity results in a small external film mass transport resistance. If the sample is well arranged inside the column to form an infinite cylinder, a theoretical analysis of the axial dispersion for the coaxial cylinder is possible and thus no adjustable axial dispersion parameters need to be determined from the experimental data.

3.1 Apparatus Description and Experimental Procedures

I. Experimental Apparatus

Figure 4.3 shows the fixed-bed experimental apparatus used for the determination of the effective diffusivity of gases in the porous media. Flow rates of the pure carrier gas and sample gas are accurately controlled by the mass flow controllers. The desired composition of the sample can be achieved by adjusting the flow rates of the pure carrier and pure diffusing gases. In order to keep a stable concentration, one of the streams
must be vented through the sampling valve and a circuit with the same pressure drop as the column assembly.

II. Experimental Procedures

* Packing the column

1. Sieved and previously activated porous solids (the activation conditions for zeolite are 24 hours at 400 °C and for alumina are 24 hours at 300 °C) are carefully put inside the column. The packing amount is accounted. The columns were activated by purging pure carrier gas 24 hours at 150 °C.

* Calibration and adjustment of volumetric flow rates of carrier and sample gases

The mass flow controller read out should be calibrated with different composition and gas types. The flow rates through two thermal conductivity detectors must be accurately measured by a soap bubble flow meter. The amount into the column can be obtained by the difference between the amount through the mass flow controller and the amount through the detector. The flow rate through the detectors should be as high as possible within their best sensitivity range in order to reduce the velocity effects on the detector response.

* Mass transfer dynamic determination

The system should be warm up at least for one hour. When the baselines of both detectors are stable, the sample valve position is manually changed to change the gas stream. The responses from both detectors are automatically recorded and displayed by the computer data acquisition system. When the outputs of both detectors are unchanged during minutes the column is saturated by the sample gas. The regeneration is performed by changing the sample valve to the original position.

* Repeat the above step four to five times to ensure reproducibility and averaging

* Repeat the experiment at different velocities and temperatures

The experiment is repeated for various flow rates at constant temperature to examine the external mass transport resistance and axial dispersion effects. In order to compare the experimental data to the data obtained by the diffusion cell technique, the experiments were carried out at the same three temperatures (40, 70 and 95 °C).

* Data treatment

The dead volume contribution to delay the responses of both detectors must be subtracted from the corresponding response values to obtain the real response results. The dead volume among various streams can be calculated from the tubing dimensions.
3.2. Mass Transport Model

The whole mass transport process of the tracer gas from the bulk phase to the micropores of a porous solid with a bidispersed pore structure includes bulk flow, molecular diffusion and eddy mixing that transports solute molecules from the fixed bed inlet to the particle vicinity; then film diffusion to cross the boundary layer around the particles; once inside the particles the molecules diffuse towards the center through the macropore and simultaneously to the microparticle center. All these transport mechanisms are included in the following model.
I. Mass Balance Equations.

The dimensionless mass balance for the bulk phase with the condition of spherical particles, constant velocity, constant mass transport coefficients, isothermicity and no heat loss are

\[
\frac{\partial C}{\partial \theta} + \frac{\partial C}{\partial Z} - \frac{P_e}{P_e} \frac{\partial^2 C}{\partial Z^2} + 3 \phi_b \omega_a \frac{\partial C_a}{\partial Y} \bigg|_{Y=1} = 0
\]

(4.96)

**IC:** \(C(Z,0) = 0\) \hspace{1cm} (4.97)

**BC:** \(\frac{1}{P_e} \frac{\partial C}{\partial Z} \bigg|_{Z=0} = C(0,\theta) - 1 \quad ; \quad \frac{\partial C}{\partial Z} \bigg|_{Z=1} = 0\) \hspace{1cm} (4.98)

For the macropores:

\[
\frac{\partial C_a}{\partial \theta} = N_a \left( \frac{\partial^2 C_a}{\partial Y^2} + \frac{2}{Y} \frac{\partial C_a}{\partial Y} \right) - 3 \phi_a N_i \frac{\partial C_i}{\partial X} \bigg|_{X=1}
\]

(4.99)

**IC:** \(C_a(Z,Y,0) = 0\) \hspace{1cm} (4.100)

**BC:** \(\frac{\partial C_a}{\partial Y} \bigg|_{Y=0} = 0 \quad ; \quad C_a(Z,1,\theta) = C(Z,\theta) - \frac{N_a}{N_i} \frac{\partial C_a}{\partial Y} \bigg|_{Y=1}\) \hspace{1cm} (4.101)

For the microparticle:

\[
\omega_a \frac{\partial \omega}{\partial \theta} = N_i \left( \frac{\partial^2 \omega}{\partial X^2} + \frac{2}{X} \frac{\partial \omega}{\partial X} \right)
\]

(4.102)

**IC:** \(\omega(X,Y,Z,0) = 0\) \hspace{1cm} (4.103)

**BC:** \(\frac{\partial \omega}{\partial X} \bigg|_{X=0} = 0 \quad ; \quad \omega(1,Y,Z,\theta) = KC_a(Y,Z,\theta)\) \hspace{1cm} (4.104)

The dimensionless variables and parameters in equations (4.96) to (4.104) are:
\[ C = \frac{c}{c_e}, \quad C_a = \frac{c_a}{c_e}, \quad \alpha = a_m/c_e, \quad Z = z/L, \quad Y = \frac{R}{R_o}, \quad X = \frac{r}{r_o}, \quad \nu = L/u, \quad \theta = t/\nu \]

\[ \phi_b = \frac{1 - \alpha_b}{\alpha_b}, \quad \phi_a = \frac{1 - \alpha_a}{\alpha_a}, \quad N_a = \frac{D_a \nu}{R_o}, \quad N_f = \frac{k_f \nu}{r_o}, \quad N_i = \frac{D_i \nu}{r_o}, \quad P_e = \frac{uL}{D_{ax}} \]

where \( D_{ax} \) is the axial dispersion coefficient and \( u \) is the interstitial velocity.

The solution of equations (4.96) to (4.104) in Laplace domain for a step input is

\[ \bar{C} \bigg|_{Z=1} = \frac{\exp(P_e) (\gamma_2 - \gamma_1)}{s \left[ \gamma_1 \exp(\gamma_1) (\gamma_2/P_e - 1) - \gamma_2 \exp(\gamma_2) (\gamma_1/P_e - 1) \right]} \tag{4.105} \]

where

\[ \gamma_{1,2} = \frac{1}{2} \left[ P_e \pm \sqrt{P_e^2 + 4P_e \left( s + 3 \phi_b \frac{N_a}{S_5} \right)} \right] \]

\[ S_5 = \frac{N_f S_4}{N_f + \frac{S_4}{S_5}; \quad S_4 = \sqrt{S_3 \coth(\sqrt{S_3}) - 1}; \quad S_3 = \frac{s + 3 \phi_p N_i S_2}{N_a} \]

\[ S_2 = K \left[ \sqrt{S_1 \coth(\sqrt{S_1}) - 1} \right]; \quad S_1 = \frac{s}{N_i} \]

It is difficult to find the original function of equation (4.105) analytically due to its complexity and so FFT will be used to obtain numerically the time domain solution. For this purpose the behavior of equation (4.105) can be improved by removing the singular point

\[ \bar{C} \bigg|_{Z=1} = \frac{\exp(P_e) (\gamma_2 - \gamma_1)}{s \left[ \gamma_1 \exp(\gamma_1) (\gamma_2/P_e - 1) - \gamma_2 \exp(\gamma_2) (\gamma_1/P_e - 1) \right]} \]

\[ + \frac{1}{s} \tag{4.106} \]

The original function of the second term is 1 and FFT can be applied to the first term. Similarly, the mass transport parameters can be extracted by matching the theoretical response values to the experimental results. Before doing the optimization process we should analyze the effects of the film mass transport resistance and axial dispersion on the theoretical responses because sometimes these two effects can be neglected. The reduction of the optimization parameters will greatly improve the optimization results. These discussions will be held in the next chapter.
REFERENCES


Davis, M.E., Numerical Methods and Modeling for Chemical Engineers, John Wiley & Sons, 1984


Schneider, P. and J.M. Smith, Adsorption Rate Constants from Chromatography, AIChE J, 14, 762, 1968


V. RESULTS AND DISCUSSION OF MASS TRANSFER PARAMETERS

In the previous chapters we have discussed the mass transport models and experimental techniques for the estimation of gas transport parameters in porous media. In this section the experimental results and the theoretically calculated values for the diffusion of gases in single pellets and small particles will be presented. According to the experimental techniques and porous solid types they are arranged in three parts, 1. single pellet diffusion cell; 2. shallow bed diffusion cell and 3. fixed bed.

1 DIFFUSION CELL PACKED WITH A SINGLE PELLET

For some fast gas-solid catalytic reactions, the mass transport resistance in the catalyst pore network is the rate controlling step. In order to improve the process rate, the reduction of the mass transport resistance inside the pores is very important. The change of the operating conditions is limited by reaction factors. The increase of the number of convective pores is a useful way to achieve that objective.

The determination of the mass transport rate of gases in porous solids is an important criterion to evaluate the characteristics of mass transport. For industrial large pellets, the diffusion cell is an efficient tool. We used this technique and determined the data for gas systems Ar - He, O₂ - He and N₂ - He in five solid samples at 40, 70 and 95 °C. The experimental results were used to regress the effective diffusivities and effective convective flow coefficients. The results obtained were used to simulate the theoretical response values. The good agreement between the experimental and theoretical response values confirmed the reliability of the mathematical models.

1.1 Pellet Pore Structural Properties

The experiments for the determination of effective diffusivities and convective flow coefficients in porous solids were performed over five samples. All five samples are catalyst supports and made of aluminum oxide. These samples can be divided into two types: one has convective pores and another does not have such pores. Table 5.1 illustrates the geometrical dimensions and pore physical properties. Samples 4# and 6# are cylindrical rings and all the others are cylinders.

In Table 5.1, the apparent (gram of particle / ml of particle) and skeletal (gram of particle / ml of solid) densities and macropore structural properties were determined using the "PoreSizer 9320" of Micromeritics. The principle of this experiment is based on the mercury porosimetry technique. Mercury is a non-wetting liquid for most solid surfaces and in the case of cylindrical pores the pore diameter through which the mercury can penetrate is dependent on the applied pressure. In the PoreSizer 9320, the volume of mercury penetrating into the pores is directly measured as a function of the applied pressure. By changing the applied pressure a curve relating volume and pressure can be obtained. This pressure and volume information serves for the characterization of the pore structure. Because the pores are rarely cylindrical, such theoretical relation is just an approximate expression of the real situation.
Table 5.1 Pellet properties

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>4 #</th>
<th>6 #</th>
<th>8 #</th>
<th>9 #</th>
<th>10 #</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter mm (outside)</td>
<td>8.0</td>
<td>8.0</td>
<td>16.5</td>
<td>13.0</td>
<td>13.0</td>
</tr>
<tr>
<td>Diameter mm (inside)</td>
<td>2.4</td>
<td>2.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Length mm</td>
<td>13.0</td>
<td>9.0</td>
<td>17.0</td>
<td>13.5</td>
<td>16.0</td>
</tr>
<tr>
<td>Apparent density g/ml</td>
<td>1.24</td>
<td>1.50</td>
<td>2.01</td>
<td>2.85</td>
<td>0.94</td>
</tr>
<tr>
<td>Skeletal density g/ml</td>
<td>3.77</td>
<td>3.84</td>
<td>3.08</td>
<td>3.77</td>
<td>2.17</td>
</tr>
<tr>
<td>Pore volume ml/g (^a)</td>
<td>0.54</td>
<td>0.17</td>
<td>0.41</td>
<td>0.086</td>
<td>0.605</td>
</tr>
<tr>
<td>Specific area, A, m(^2)/g (^a)</td>
<td>6.07</td>
<td>7.11</td>
<td>17.88</td>
<td>8.74</td>
<td>10.59</td>
</tr>
<tr>
<td>Average pore diameter (4V/A) (^a) (\mu m)</td>
<td>0.36</td>
<td>0.23</td>
<td>0.039</td>
<td>0.039</td>
<td>0.228</td>
</tr>
<tr>
<td>Pore volume ml/g (^b)</td>
<td>0.006</td>
<td>0.011</td>
<td>0.102</td>
<td>0.021</td>
<td>0.024</td>
</tr>
<tr>
<td>Specific area, A, m(^2)/g (^b)</td>
<td>0.783</td>
<td>3.115</td>
<td>18.64</td>
<td>7.109</td>
<td>4.218</td>
</tr>
<tr>
<td>Average pore diameter (4V/A) (^b) (\mu m)</td>
<td>0.031</td>
<td>0.014</td>
<td>0.022</td>
<td>0.012</td>
<td>0.022</td>
</tr>
<tr>
<td>Convective pores</td>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
</tr>
</tbody>
</table>

\(V\) is the total pore volume  
\(A\) is the specific area  
Apparent density is defined as particle mass / particle volume  
Skeletal density is defined as particle mass / solid volume  
Specific area is defined as total surface area / particle mass  
\(^a\) data obtained by the mercury porosimetry (> 60 Å)  
\(^b\) data obtained from BET adsorption experiments

The pellet volume is measured when the pressure is close to zero and the skeletal volume of the solid is the difference between the pellet and pore volumes measured by mercury porosimetry. The corresponding apparent and skeletal densities are easily obtained from the pellet weight and these volumes. The pore wall surface area computed on the basis of the work required to immerse a surface in mercury is calculated assuming that the pores are cylinders using the following geometrical relationship [Micrometics, 1990]:

\[
\sum \Delta A = \frac{\sum PAV}{\kappa \cos \eta}
\]

(5.1)

where \(P\) is the applied pressure, \(\Delta A\) is the increment of the surface area at the pressure \(P\), \(\Delta V\) is the increment of the penetrated volume at the pressure \(P\), \(\kappa\) is the mercury surface tension and \(\eta\) is the wetting angle between mercury and pore surface. The recommended values for \(\kappa\) and \(\eta\) are respectively 485 dynes/cm and 130°. The maximum pressure of this instrument is about 30000 psi and the corresponding minimum pore dimension that can be measured is about 60 Å. The results in Table 5.1 show the pore structure properties measured by mercury porosimetry. For samples 4#, 9# and 10# there are visible large pores and we roughly say that these samples have convective pores. The total pore volume for samples 4# and 10# is large and this means that except for convective pores they have abundant diffusional pores. Although sample 9# has visible convective pores the total volume is small.

In the last chapter we developed mathematical models for mass transport based on monodisperse pore size distributions and negligible adsorption effects. In order to
confirm the pore structure and adsorption characteristics of these samples in the micropore region (specially for pore diameters less than 60 Å), we used a BET experimental apparatus (ASAP 2000 of Micromeritics) to measure these properties. The desorption branch of an isotherm can be used to relate the amount of adsorbate lost in a desorption step to the average size of the pore emptied in that step. A pore loses its condensed liquid by the Kelvin equation (Chapter 1). After the core has evaporated, a layer of adsorbate remains on the wall of the pore. The thickness of this layer can be calculated for a particular relative pressure. The layer becomes thinner with decreasing pressure, so that the measured quantity of gas desorbed in a step is composed of a quantity equivalent to the liquid cores evaporated in that step plus the quantity desorbed from the pore walls for the pores whose cores have been evaporated in that and previous steps. The results from the BET experiments are also shown in Table 5.1.

The specific area for all these samples is very small and thus the micropore volume is negligible. Because the specific areas are so low then the absorbed amount measured by this method has large errors and this may result in wrong results for the specific area that is smaller than by mercury porosimetry. A qualitative conclusion from the BET results is that for these samples the assumptions of negligible adsorption effects and monodisperse pore structure are reasonable and thus the mathematical model developed in last chapter is suitable.

Figures 5.1 to 5.5 show the pore size distributions. In these figures V is the pore volume (ml/g) and d is the pore diameter (Å). These curves show that all five samples look like to have continuous pore size distributions and the average pore dimensions are in the range of 300 - 4000 Å. We adopted the ratio of the differential volume to the log differential pore size instead of the usual ratio of the differential volume to the differential pore size, in order to weight the distribution in the large pore region. Pore size distributions of Samples 4#, 9# and 10# have peaks in the pore size range of 10 to 100 µm. Such pores will play an important role for the convective flow. While samples 6# and 8# have macropore distribution peaks in the range of less than 1 µm. The convective flow contribution from these pores is not so important as in the former case.

The pore structure information given by mercury penetration measurements provides useful but not sufficient information to study mass transport mechanisms in porous solids from a fundamental point of view. The structural data obtained by the mercury penetration technique have significant shortcomings in the correct interpretation of the experimentally determined mass transport rate results. Mercury porosimetry is usually used to determine the pore size distribution and the results are model dependent. The pore size distribution inferred by this technique is subject to significant errors since the highly simplified parallel bundle model used to interpret the mercury penetration curves is largely unrealistic [Dullien, 1975]. Nevertheless the actual pore size distribution and the way in which the pores are interconnected to each other play a crucial role in the mass transport rates. The frequency of the dead ends strongly affects the mass transport through the pore space. Furthermore since porous solids exhibit a range of pore sizes where both Knudsen and molecular diffusion processes (may also include activated diffusion in micropores whose pore diameter is in the order of molecule size) may be significant, the connectivity of the structure substantially influences the mass transport rate. In particular, the existence of narrow pore necks may be a key factor. These effects are certainly even more pronounced in porous solids exhibiting bidisperse pore size distributions where the mass transport mechanism in the micropores is most likely of Knudsen and activated types, while a bulk diffusion regime dominates in the macropores. Finally neither dead ends, narrow necks nor general interconnectivity features of the pore space can be evaluated by mercury penetration technique using the analytical tools we
described. Other analytical models were developed that enable to take more information from mercury porosimetry experiments [Mann and Thomson, 1989].

The knowledge of pore network structure obtained by nitrogen condensation experiments is also model dependent and insufficient. The assumption considering the pore structure as parallel cylindrical capillaries enables the calculation of the pore size distribution and specific surface area from the condensation or/and vaporization curves of nitrogen at the temperature of the nitrogen boiling point (77 K). But this assumption is so rough that the real structural properties such as narrow necks and interconnectivities are not included. The difference between the adsorption and desorption branches of an isotherm confirms the weakness of this measurement. For the determination of the micropores whose diameters are in the same order of magnitude as nitrogen molecule the information obtained is only considered as a qualitative description of the pore structure since the adsorbate molecular state in such small pores is difficult to define. One of the assumptions of the nitrogen condensation technique is that the behavior of the nitrogen molecule in the adsorbed phase is like a liquid and the nitrogen molecular section area is used to calculate the adsorbed layer area.

Nevertheless the information on pore network structure obtained by conventional techniques is indispensable to distinguish the pore types and help to establish the corresponding mass transport models.

![Differential pore size distribution of sample 4#](image)

Figure 5.1 Differential pore size distribution of sample 4#
Figure 5.2 Differential pore size distribution of sample 6#

Figure 5.3 Differential pore size distribution of sample 8#
Figure 5.4 Differential pore size distribution of sample 9#

Figure 5.5 Differential pore size distribution of sample 10#
1.2 Effective Diffusivities and Simulation of the Response Values.

The diffusion cell dimensions were designed according to pellet dimensions. The pellets were fixed in the cell with epoxy resin. The voids between pellet and cell wall and pellet central part were blocked and no leaking was left. By carefully adjusting the pressures at both sides of cell to zero pressure difference we performed the experiments for determining the effective diffusivities at different temperatures.

Table 5.3 shows the experimental conditions and results for the diffusion cell packed with a single pellet. The molecular diffusivities, \( D_m \), can be determined from the steady state responses of both chambers with an empty cell using equations (4.16) and (4.17). Because there may be eddy effects such determination is rough. We compared the diffusivities determined by empty cell with these calculated by the Chapman - Enskog equation (1.113) for several systems including argon - helium, nitrogen - helium and oxygen - helium at 40 °C. Our experimental values are close to the calculated ones and the relative errors are around 10%. Because the calculation is more convenient than the experimental determination, in the following we use the Chapman - Enskog equation to calculate the molecular diffusivities.

The flow rate conditions in both sides were kept the same in order to eliminate the pressure difference.

The effective diffusivities were obtained by two ways. Theoretically dynamic responses calculated by the model developed in Chapter IV were fitted to the experimental ones until a minimum difference between these two curves was achieved by adjusting the mass transport parameter, \( D_e \). From the steady state responses of both sides of the diffusion cell the effective diffusivity can be evaluated by equations (4.16) or (4.17). The effective diffusivities obtained from the dynamic responses are always greater than these obtained from the steady state and this difference confirms the existence of dead end pores which do not make any contribution to the mass transport at steady state.

The assumption of perfectly mixing in both chambers was implied in the calculation of the effective diffusivities. In order to confirm the validity of this assumption we determined a "blank" chamber response to a concentration step with the cell bed blocked with epoxy resin. For perfectly mixing the chamber responses should satisfy the following mass balance equations:

\[
\mathcal{I}_c = \mathcal{I}_t + V_e \frac{dc_i}{dt} \quad \text{or} \quad \mathcal{I}_c = \mathcal{I}_b + V_e \frac{dc_b}{dt} \quad (5.2)
\]

the corresponding dimensionless form is

\[
\frac{dC_i}{d\theta} = 1 - C_i \quad \text{or} \quad \frac{dC_b}{d\theta} = 1 - C_b \quad (5.2a)
\]

The solutions of equations (5.2a) are
\[ C_i = 1 - \exp(-\theta) \quad \text{or} \quad C_b = 1 - \exp(-\theta) \quad (5.3) \]

The initial condition \( t = 0, C_i = 0 \) (or \( \theta = 0, C_i = 0 \)) has been used. The chamber volume including the dead volume of the tubing and connectors between chambers and thermal conductivity detectors can be calculated from the blank chamber experimental responses and it should be equal to the product of the experimental stoichiometric time of the blank chamber response curves and the flow rate. Figure 5.6 illustrates the experimental and calculated blank chamber response curves for argon - helium at 40 °C and the corresponding dead volume is 0.252 cm³. The experimental and calculated curves are almost coincident. For higher temperatures the perfectly mixing effect should be better due to the increase of molecular random motion. In the chamber design we set the gas flow inlet normal to the pellet surface so that the perfectly mixing can be improved. The experimental results of blank chamber responses guarantee the assumption of perfectly mixing in the chambers.

![Graph showing concentration over time](image)

**Figure 5.6** Experimental (Dashed line) and calculated (solid line) "blank" chamber responses for the system argon - helium at 40 °C

The experimental runs for each system and operating conditions were carried out at least 3 times. If all three response curves were coincident within the detection range of the thermal conductivity detectors and data acquisition board, any one can be used as the experimental response curve for parameter regression. Otherwise the experimental set-up was warmed up and other three experimental runs were carried. The standard deviation of the three run response curves is so small that the experimental errors were considered negligible.
Importance of Film Diffusion

In our models for the single pellet diffusion cell there are three dimensionless parameters, \( N_t \), \( N_e \) and \( N_p \), that respectively represent the effect on the responses of the film mass transport resistances between pellet surfaces and chambers, the diffusional resistance inside the pellet and the chamber geometry. The responses have different sensitivities for different parameter ranges. We are interested in the analysis of the calculation where film diffusion can be neglected. One way to deal with this problem is to look for the range of \( N_e \) and \( N_p \) where the cell response curves are close to these obtained when \( N_t = \infty \), i.e., when film diffusion is negligible. So we want to compare \( C_b(N_t, \theta) \) with \( C_b(\infty, \theta) \) and \( C_t(N_t, \theta) \) with \( C_t(\infty, \theta) \) and calculate for every \( N_e \) and \( N_p \) the minimum \( N_t \) that makes the time domain responses almost equal to those obtained with \( N_t = \infty \).

The system transfer function, \( G(s) \) for the single pellet diffusion cell can be considered as the ratio of Laplace domain concentration responses of bottom and top chambers, that is:

\[
G(s) = \frac{C_b(s)}{C_t(s)} \tag{5.4}
\]

The transfer function is a moment generating function that uniquely describes the time domain distribution, if it exists. Sometimes the time domain distribution is a known distribution like normal, gamma, etc., that is characterized by two parameters that are the mean and the variance or related with these. In this case the comparison between the transfer functions with and without film diffusion can be carried out by just comparing these moments that fully characterize the time domain solution. When this is not the case the generating functions

\[
G(s) = \mu_o \cdot s \mu'_1 + \frac{s^2}{2!} \mu'_2 \cdot \ldots \tag{5.5}
\]

must be compared, that is, all the non central moments. In equation (5.5) \( \mu_o \) is the system gain, \( \mu'_1 \) is the mean and \( \mu'_2 \) is related with the dispersion of the distribution.

In our case we did not try to find a theoretical distribution that can fit the time domain solutions and so we must use the comparison between the generating functions. In practice we are going to restrict the comparison to the first and second moments thus assuming that the series is rapidly convergent or that the higher moments are negligible.

The comparison criterion was set as

\[
\sqrt{\left( G(N_t, s) - G(\infty, s) \right)^2} = \sqrt{(\mu_o(N_t) - \mu_o(\infty))^2 + s^2 (\mu'_1(N_t) - \mu'_1(\infty))^2 + \frac{s^4}{4} (\mu'_2(N_t) - \mu'_2(\infty))^2} \leq E \tag{5.6}
\]
where $E$ is the global error in Laplace domain. If we look to this equation we see that for the steady state the error is controlled by the difference between the zeroth order moments and that for initial times it is controlled by the higher order moments. Of course in this case the error must go to zero when $s$ tends infinity. One problem is how to distribute $E$ among the three moment errors. Possibly the best solution is to weight the moment error according to their importance that is dependent on the value of $s$. To simplify this problem we just assumed a constant and equal error, $err$, for all the moments, that is

$$err \sqrt{1 + s^2 + \frac{s^4}{4}} \leq E \quad (5.7)$$

From the Laplace domain solutions (4.10) and (4.11) of top and bottom chamber responses, the zeroth absolute moment and the first and the second normalized moments are:

$$\mu_o = \frac{N_c N_s N_f}{(1 + N_c N_s) N_f + 2 N_c} \quad (5.8)$$

$$\frac{\mu_1}{\mu_o} = \frac{(1 + 6 N_c + 3 N_c N_s) N_f^2 + (6 N_c N_f + 12 N_c^2 + 6 N_c^2 N_s) N_f + 6 N_c^2}{6 N_c N_f ((1 + N_c N_s) N_f + 2 N_c)} \quad (5.9)$$

$$\frac{\mu_2}{\mu_o} = \left[ (75 N_c^2 N_s^2 + 300 N_c^2 N_s + 7 + 42 N_c N_s + 60 N_c + 360 N_c^3) N_f^4 + (360 N_c^2 N_s + 300 N_c^2 N_s + 480 N_c^2 + 84 N_c + 1440 N_c^3 + 1080 N_c^3 N_s) N_f^3 + (360 N_c^2 + 1440 N_c^2 + 1080 N_c^3 + 360 N_c^2 N_s + 900 N_c^2 N_s + 1080 N_c^2 N_s) N_f^2 + (360 N_c^2 + 720 N_c^2 N_s + 720 N_c^2 N_s) N_f + 360 N_c^2 \right] / [180 (N_c^2 N_f^2 (1 + N_c N_s) N_f + 2 N_c) ^2] \quad (5.10)$$

The second central moment ($\sigma^2 = \frac{\mu_2}{\mu_o} - \left[ \frac{\mu_1}{\mu_o} \right]^2$) is given by

$$\sigma^2 = \left[ (90 N_c^2 + 60 N_c^2 N_s + 15 N_c^2 N_s + 6 N_c N_s + 1) N_f^2 + (180 N_c^2 N_s + 360 N_c^3 + 12 N_c + 60 N_c^2 N_s + 60 N_c^2 N_s) N_f^3 + (90 N_c^2 N_s + 60 N_c^2 + 180 N_c^2 N_s + 180 N_c^2 N_s + 360 N_c^4) N_f^2 + (180 N_c^2 N_s + 120 N_c^2) N_f + 90 N_c^2 \right] / [180 (N_c^2 N_f^2 (1 + N_c N_s) N_f + 2 N_c) ^2] \quad (5.11)$$
Equations (5.8) to (5.11) show that all moments are dependent on all three parameters.

Let us begin the comparison by the zeroth moment

\[
\sqrt{\left( \mu_0(N_{f}) - \mu_0(\infty) \right)^2} \leq err
\]  
(5.12)

This equation can be solved analytically and gives

\[
N_f \geq \frac{2N_c\left[ N_cN_s - err \left( 1 + N_cN_s \right) \right]}{err \left( 1+2N_cN_sN_s + N_s^2N_s^2 \right)}
\]  
(5.12a)

Figures 5.7 and 5.8 show the results for \( err = 1\% \) and \( err = 5\% \), respectively using \( N_c \) and \( N_s \) in the range that is interesting for our systems and experiments. The surface in these plots shows the minimum \( N_f \) that satisfies equation (5.12a) for fixed error. When the surface goes to negative \( N_f \) it means that the criterion is satisfied for any \( N_f \geq 0 \)

Figure 5.7 Region where \( N_f \) can be neglected using the zeroth moment criterion with 1% error
Let us assume know that the zeroth moment criterion is satisfied and thus that we can consider $\mu_o(N_f) = \mu_o(\infty)$. In these conditions equation (5.6) can be written

$$
\begin{vmatrix}
G(N_f,0) - G(\infty,0) \\
\mu_o(N_f) - \mu_\infty
\end{vmatrix}
= \sqrt{s^2 \left[ \frac{\mu_1(N_f)}{\mu_o(N_f)} - \frac{\mu_1(\infty)}{\mu_o(\infty)} \right]^2 + \frac{s^4}{4} \left[ \frac{\mu_2(N_f)}{\mu_o(N_f)} - \frac{\mu_2(\infty)}{\mu_o(\infty)} \right]^2}
$$

(5.6a)

So instead of comparing the raw moments we can compare the normalized ones. This possibility is interesting because it increases the convergency of the optimization calculations.

When $N_f$ tends to infinity, the first and second normalized moments are given by

$$
\frac{\mu_1}{\mu_o} \bigg|_{N_f \rightarrow \infty} = \frac{1 + 6N_e + 3N_eN_s}{6N_e(1 + N_eN_s)}
$$

(5.13)
\[
\begin{align*}
\frac{\mu}{\mu_o} \bigg|_{N_r=\infty} &= \frac{75N_c^2N_s^2 + 300N_c^2N_eN_s + 7 + 42N_cN_eN_s + 60N_e + 360N_s^2}{180N_c^2(1 + N_cN_s)^2} \\
\sigma^2 \bigg|_{N_r=\infty} &= \frac{1 + 15N_c^2N_s^2 + 90N_c^2 + 90N_cN_eN_s + 60N_eN_s}{90N_s^2(1 + N_cN_s)^2}
\end{align*}
\] (5.14) (5.15)

Now the error conditions for the first and second moments can be written

\[
F_1(N_r) = \frac{\mu'(N_r)}{\mu_o(N_r)} \cdot \frac{\mu'(\infty)}{\mu_o(\infty)} - err \leq 0
\] (5.16)

\[
F_2(N_r) = \frac{\mu''(N_r)}{\mu_o(N_r)} \cdot \frac{\mu''(\infty)}{\mu_o(\infty)} - err \leq 0
\] (5.17)

We can calculate the partial derivatives of $F_1$ and $F_2$ relative to $N_r$. These derivatives are always positive for any positive $N_c$, $N_e$ and $N_s$ and thus there is only one $N_r$ that satisfies each one of the equations (5.16) or (5.17) given $N_s$ and $N_e$. So for any $N_r$ greater than the solution and for fixed $N_s$, $N_e$ and $err$, the film diffusion can be neglected. Figures 5.9 and 5.10 show the results obtained when $err = 5\%$.

Comparing the results shown in Figures 5.8 and 5.9 we see that the first moment condition is much more restrictive than the zeroth moment condition and looking for Figure 5.10 we see that the second moment criterion is even more restrictive. This is physically acceptable because the dispersion should be more affected by the presence of the film diffusion than the center of gravity of the time domain solution.

As an illustration, Figure 5.11 shows the results obtained for the variance (the second central moment).

The fundamental mechanism for film mass transport is the existence of a laminar fluid boundary layer. Out of the boundary layer the fluid properties such as, temperature and composition, are considered uniform. The concentration difference between the bulk phase and the surface of the solid through the boundary layer results in a mass transport driving force. The mass transport mechanism within the boundary layer is mainly molecular diffusion and thus the minimum limit for the film mass transport resistance is molecular diffusion [Hines and Maddox, 1985]. Furthermore the limit for the film mass transport coefficient can be considered as:

\[
k_r = \frac{D_m}{\delta}
\] (5.18)
Figure 5.9 Region to neglect $N_f$ by the first moment criterion when $err = 5\%$

Figure 5.10 Region to neglect $N_f$ by the second moment criterion when $err = 5\%$
Figure 5.11 Region to neglect \( N_f \) by the variance criterion when \( err = 5\% \)

where \( \delta \) is the thickness of the boundary layer. In our system, the maximum distance between the pellet surface and the opposite chamber wall is less than 0.1 cm. As a very conservative estimation, the minimum value of the film mass transport coefficient can be calculated by equation (5.18) using \( \delta = 0.1 \) cm and thus \( N_f \).

In order to compare our experimental results with the criteria already shown, \( N_e \) was predicted assuming that \( D_e \approx 0.2 D_m \). Table 5.2 shows these results.

If we took \( err = 5\% \) we see that the zeroth order moment criterion is fulfilled for all experiments.

To make easier the verification with the first and second moments we draw the plots represented in Figures 5.12, 5.13 and 5.14 that show \( N_f = f(N_e) \) for the \( N_e \) values valid in our experiments.

Using the parameter values in Table 5.2 and the plots in Figures 5.12 and 5.13 we can see that \( N_f \) can not be neglected in all experiments according with the second moment criterion. Although the first moment is a less restrictive criterion we see that except for sample 6#, it is also not fulfilled. Nevertheless in this case all other samples (4#, 8#, 9# and 10#) have \( N_f \) close to the required minimum values. Real experimental \( N_f \) should be higher than those used to verify these criteria.
Table 5.2 Validity of the assuming $N_f = \infty$ in the experiments

<table>
<thead>
<tr>
<th>gas</th>
<th>T</th>
<th>Parameters</th>
<th>Sample No.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>4 #</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N_e$</td>
<td>0.176</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N_s$</td>
<td>1.583</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$S$</td>
<td>0.00271</td>
</tr>
<tr>
<td></td>
<td>70 °C</td>
<td>$N_f$</td>
<td>12.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N_e$</td>
<td>0.187</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N_s$</td>
<td>1.583</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$S$</td>
<td>0.00272</td>
</tr>
<tr>
<td></td>
<td>95 °C</td>
<td>$N_f$</td>
<td>12.71</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N_e$</td>
<td>0.196</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N_s$</td>
<td>1.583</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$S$</td>
<td>0.00273</td>
</tr>
<tr>
<td></td>
<td>40 °C</td>
<td>$N_f$</td>
<td>10.96</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N_e$</td>
<td>0.169</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N_s$</td>
<td>1.583</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$S$</td>
<td>0.00269</td>
</tr>
<tr>
<td></td>
<td>70 °C</td>
<td>$N_f$</td>
<td>11.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N_e$</td>
<td>0.179</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N_s$</td>
<td>1.583</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$S$</td>
<td>0.00271</td>
</tr>
<tr>
<td></td>
<td>95 °C</td>
<td>$N_f$</td>
<td>12.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N_e$</td>
<td>0.188</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N_s$</td>
<td>1.583</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$S$</td>
<td>0.00272</td>
</tr>
<tr>
<td></td>
<td>40 °C</td>
<td>$N_f$</td>
<td>11.71</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N_e$</td>
<td>0.180</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N_s$</td>
<td>1.583</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$S$</td>
<td>0.00271</td>
</tr>
<tr>
<td></td>
<td>70 °C</td>
<td>$N_f$</td>
<td>12.44</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N_e$</td>
<td>0.192</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N_s$</td>
<td>1.583</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$S$</td>
<td>0.00273</td>
</tr>
<tr>
<td></td>
<td>95 °C</td>
<td>$N_f$</td>
<td>13.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N_e$</td>
<td>0.201</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N_s$</td>
<td>1.583</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$S$</td>
<td>0.00274</td>
</tr>
</tbody>
</table>

In Table 5.2 the standard deviation, $S$, associated to the time domain response curves when $N_f = N_f$ predicted and $N_f = \infty$ are also shown and were defined as

$$S = \sqrt{\frac{\sum_{i=1}^{n} [C_i(N_f) - C_i(\infty)]^2 + \sum_{i=1}^{n} [C_h(N_f) - C_h(\infty)]^2}{2(n-1)}} \quad (5.19)$$

202
Figure 5.12 Region to neglect $N_r$ using the first moment criterion with $err = 5\%$ and fixed $N_s$.

Figure 5.13 Region to neglect $N_r$ using the second moment criterion with $err = 5\%$ and fixed $N_s$. 
where n is the number of points used for top or bottom chamber responses. Figure 5.15 illustrates one of these cases showing that the two curves are not distinguishable.

As is shown in Table 5.2 these errors are smaller than 0.004 and such small concentration error is already within the range of the experimental concentration measurement error. In addition, these errors are much smaller than these used when calculating the criteria on Laplace domain. That, of course, supports a damping effect when passing from Laplace to time domain solution.

So it seems that the correct way to develop those criteria implies the following:

— define the error in time domain according with the experimental error;

— develop a relationship between time domain and Laplace domain errors;

— then develop the criteria as done before.

Using this time domain criterion we see that $S$ is smaller or of the same size as the experimental standard error that we estimated around 0.01 ~ 0.02.
The matching process of the theoretical response values to the experimental ones was carried out by the weighted orthogonal distance regression algorithm [Boggs et al., 1987a and b]. As discussed previously, the experimental response curves of both chambers were taken when the results of three experimental runs were coincident. The experimental response values from both chambers were collected in an unequal time series. For small time we set a large weight, that is, we took more points and when the curve tends asymptotically to the steady state values fewer points were adopted. By comparing the regressed results we found that setting the experimental points in a way of a power of 2 time series was good to keep reasonable the number of the experimental points and response curve shapes. The theoretical response values were calculated by the model developed in Chapter IV. By adjusting the effective diffusivity we varied the theoretical response curve shapes until the sum of the squares of the differences between experimental and theoretical response values at a given time was minimum. In the parameter estimation, the objective functions included both top and bottom chamber responses.

The software package, ODRPACK [Boggs et al., 1987a and b], is designed for such parameter optimization. Specially this software can handle the cases when the independent and the dependent variables have significant errors by solving the weighted orthogonal distance regression problem, that is, minimizing the sum of the squares of the weighted orthogonal distance between each data point and the curve described by the model equations. The number of adjustable parameters to be estimated, experimental independent and dependent variable values, the possible observation errors of the experimental independent variable, the initial guess of the adjustable parameters and the precision requirements for the estimation of the adjustable parameters are inputted to the ODRPACK package. A user defined subroutine is required to provide the theoretical
model values of the dependent variables at given values of the independent variable. User is allowed to decide whether the current estimated values of the adjustable parameters are acceptable according to their physical meaning. In our case we restricted the effective diffusivity to be larger than that obtained from the steady state responses. In the output of the package, we have the final values of the adjustable parameters which satisfied the precision requirements, the estimated errors of the independent variable and the theoretical dependent variable values. In the application of this software package the initial guess of the adjustable parameters is important to ensure the convergency of the regression. In our practice, we set the initial guess for the effective diffusivity, $D_{m}$ as $0.2D_{m}$ and this initial guess is usually successful. In addition, the precision requirements of the adjustable parameters must be reasonable otherwise requiring too high precision will also result in convergency problems. We specified two effective digit precision for the effective diffusivity.

If a good result from the parameter regression technique is desired the response curves must have enough sensitivity to the parameters to be estimated. Figure 5.16 shows the theoretical response curves with different effective diffusivities in the interesting range for Ar in sample 4# at 40 °C. When the effective diffusivity varies from 0.005 to 0.20 cm$^2$/sec the curves are quite different and this ensures that the parameters obtained by regression are reasonably reliable. The same sensitivity was found for all other cases studied in this research.

The simulated results for the diffusivities of argon, oxygen and nitrogen in the 5 samples at three temperatures are shown in Table 5.3. Some examples of simulated and experimental responses are shown in Figures 5.17 to 5.21. All dashed lines in these figures are the simulated values and the solid lines are the experimental ones and the corresponding operating conditions are listed in Table 5.3. The upper curves represent the response of the top chamber which undergoes a step concentration variation during an experimental run and the lower curves represent the response of the bottom chamber.

The effective diffusivities of all these three gases in the same porous solid sample and at the same temperature are close to each other. This regularity is expected since the difference between molecular and Knudsen diffusivities for these gases is small. The calculated effective diffusivities are very sensitive to the pore size distributions of the solid samples. Samples 4#, 9# and 10# have a lot of pores whose sizes are greater than 10 μm. In such large pores the molecular diffusion mechanism should be the main contribution to total mass transport rate. For samples 6# and 8# the pore sizes are principally concentrated in the range less than 1 μm. When the pore size decreases the Knudsen diffusion mechanism makes a larger contribution to the total mass transport rate and the effective diffusivities become the combination of molecular and Knudsen diffusivities. Because the Knudsen diffusivity is much smaller than the molecular diffusivity, when the contribution of Knudsen diffusion increases, the effective diffusivity decreases.

The standard deviation between simulated and experimental responses is also shown in the table and was defined as

$$
S = \sqrt{\frac{\sum_{i=1}^{n} [C_i(\text{sim.}) - C_i(\text{expt.})]^2 + \sum_{i=1}^{n} [C_b(\text{sim.}) - C_b(\text{expt.})]^2}{2(n-1)}}
$$

(5.20)
<table>
<thead>
<tr>
<th>gas</th>
<th>T</th>
<th>Sample No.</th>
<th>4 #</th>
<th>6 #</th>
<th>8 #</th>
<th>9 #</th>
<th>10 #</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40  °C</td>
<td>flow rate ml/s</td>
<td>0.126</td>
<td>0.126</td>
<td>0.126</td>
<td>0.126</td>
<td>0.126</td>
<td>0.126</td>
</tr>
<tr>
<td></td>
<td>$D_m$ cm$^2$/s</td>
<td>0.7542</td>
<td>0.7542</td>
<td>0.7542</td>
<td>0.7542</td>
<td>0.7542</td>
<td>0.7542</td>
</tr>
<tr>
<td></td>
<td>$D_e$ cm$^2$/s</td>
<td>0.1304</td>
<td>0.0489</td>
<td>0.0321</td>
<td>0.0822</td>
<td>0.1011</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$S$</td>
<td>0.028</td>
<td>0.032</td>
<td>0.035</td>
<td>0.031</td>
<td>0.027</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$D_e$ cm$^2$/s b</td>
<td>0.1203</td>
<td>0.0447</td>
<td>0.0296</td>
<td>0.0754</td>
<td>0.0937</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$D_e$ b /$D_e$ a</td>
<td>0.923</td>
<td>0.915</td>
<td>0.921</td>
<td>0.918</td>
<td>0.926</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$C_i$</td>
<td>0.8360</td>
<td>0.9044</td>
<td>0.9170</td>
<td>0.8807</td>
<td>0.7848</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a_e$</td>
<td>0.6708</td>
<td>0.6095</td>
<td>0.3478</td>
<td>0.2443</td>
<td>0.5677</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\tau_e$</td>
<td>4.04</td>
<td>9.79</td>
<td>8.51</td>
<td>2.337</td>
<td>4.41</td>
<td></td>
</tr>
<tr>
<td>Ar  70  °C</td>
<td>flow rate ml/s</td>
<td>0.138</td>
<td>0.138</td>
<td>0.138</td>
<td>0.138</td>
<td>0.138</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$D_m$ cm$^2$/s</td>
<td>0.8780</td>
<td>0.8780</td>
<td>0.8780</td>
<td>0.8780</td>
<td>0.8780</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$D_e$ cm$^2$/s a</td>
<td>0.1575</td>
<td>0.0571</td>
<td>0.0362</td>
<td>0.0903</td>
<td>0.1156</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$S$</td>
<td>0.027</td>
<td>0.032</td>
<td>0.035</td>
<td>0.031</td>
<td>0.026</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$D_e$ cm$^2$/s b</td>
<td>0.1453</td>
<td>0.0515</td>
<td>0.0324</td>
<td>0.0901</td>
<td>0.1024</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$D_e$ b /$D_e$ a</td>
<td>0.922</td>
<td>0.903</td>
<td>0.895</td>
<td>0.887</td>
<td>0.886</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$C_i$</td>
<td>0.8250</td>
<td>0.8995</td>
<td>0.9151</td>
<td>0.8805</td>
<td>0.7796</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a_e$</td>
<td>0.6708</td>
<td>0.6095</td>
<td>0.3478</td>
<td>0.2443</td>
<td>0.5677</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\tau_e$</td>
<td>3.90</td>
<td>9.78</td>
<td>8.80</td>
<td>2.48</td>
<td>4.49</td>
<td></td>
</tr>
<tr>
<td>95  °C</td>
<td>flow rate ml/s</td>
<td>0.148</td>
<td>0.148</td>
<td>0.148</td>
<td>0.148</td>
<td>0.148</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$D_m$ cm$^2$/s</td>
<td>0.9866</td>
<td>0.9866</td>
<td>0.9866</td>
<td>0.9866</td>
<td>0.9866</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$D_e$ cm$^2$/s a</td>
<td>0.1797</td>
<td>0.0649</td>
<td>0.0407</td>
<td>0.1036</td>
<td>0.1346</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$S$</td>
<td>0.027</td>
<td>0.031</td>
<td>0.034</td>
<td>0.031</td>
<td>0.026</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$D_e$ cm$^2$/s b</td>
<td>0.1679</td>
<td>0.0586</td>
<td>0.0364</td>
<td>0.0953</td>
<td>0.1263</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$D_e$ b /$D_e$ a</td>
<td>0.934</td>
<td>0.903</td>
<td>0.896</td>
<td>0.920</td>
<td>0.939</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$C_i$</td>
<td>0.8180</td>
<td>0.8948</td>
<td>0.9118</td>
<td>0.8743</td>
<td>0.7695</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a_e$</td>
<td>0.6708</td>
<td>0.6095</td>
<td>0.3478</td>
<td>0.2443</td>
<td>0.5677</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\tau_e$</td>
<td>3.84</td>
<td>9.66</td>
<td>8.80</td>
<td>2.43</td>
<td>4.34</td>
<td></td>
</tr>
<tr>
<td>N2  40  °C</td>
<td>flow rate ml/s</td>
<td>0.126</td>
<td>0.126</td>
<td>0.126</td>
<td>0.126</td>
<td>0.126</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$D_m$ cm$^2$/s</td>
<td>0.7858</td>
<td>0.7858</td>
<td>0.7858</td>
<td>0.7858</td>
<td>0.7858</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$D_e$ cm$^2$/s a</td>
<td>0.1365</td>
<td>0.0461</td>
<td>0.0288</td>
<td>0.0763</td>
<td>0.0896</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$S$</td>
<td>0.028</td>
<td>0.032</td>
<td>0.035</td>
<td>0.032</td>
<td>0.027</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$D_e$ cm$^2$/s b</td>
<td>0.1231</td>
<td>0.0422</td>
<td>0.0257</td>
<td>0.0702</td>
<td>0.0828</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$D_e$ b /$D_e$ a</td>
<td>0.902</td>
<td>0.914</td>
<td>0.892</td>
<td>0.920</td>
<td>0.924</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$C_i$</td>
<td>0.8309</td>
<td>0.9089</td>
<td>0.9244</td>
<td>0.8873</td>
<td>0.7995</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a_e$</td>
<td>0.6708</td>
<td>0.6095</td>
<td>0.3478</td>
<td>0.2443</td>
<td>0.5677</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\tau_e$</td>
<td>3.71</td>
<td>9.97</td>
<td>9.12</td>
<td>2.42</td>
<td>4.77</td>
<td></td>
</tr>
<tr>
<td>N2  70  °C</td>
<td>flow rate ml/s</td>
<td>0.138</td>
<td>0.138</td>
<td>0.138</td>
<td>0.138</td>
<td>0.138</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$D_m$ cm$^2$/s</td>
<td>0.9150</td>
<td>0.9150</td>
<td>0.9150</td>
<td>0.9150</td>
<td>0.9150</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$D_e$ cm$^2$/s a</td>
<td>0.1532</td>
<td>0.0504</td>
<td>0.0359</td>
<td>0.0888</td>
<td>0.1072</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$S$</td>
<td>0.028</td>
<td>0.032</td>
<td>0.035</td>
<td>0.031</td>
<td>0.027</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$D_e$ cm$^2$/s b</td>
<td>0.1418</td>
<td>0.0458</td>
<td>0.0336</td>
<td>0.0810</td>
<td>0.0965</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$D_e$ b /$D_e$ a</td>
<td>0.925</td>
<td>0.908</td>
<td>0.936</td>
<td>0.912</td>
<td>0.900</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$C_i$</td>
<td>0.8281</td>
<td>0.9091</td>
<td>0.9156</td>
<td>0.8820</td>
<td>0.7888</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a_e$</td>
<td>0.6708</td>
<td>0.6095</td>
<td>0.3478</td>
<td>0.2443</td>
<td>0.5677</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\tau_e$</td>
<td>3.84</td>
<td>10.62</td>
<td>8.50</td>
<td>2.42</td>
<td>4.65</td>
<td></td>
</tr>
<tr>
<td>N2  95  °C</td>
<td>flow rate ml/s</td>
<td>0.148</td>
<td>0.148</td>
<td>0.148</td>
<td>0.148</td>
<td>0.148</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$D_m$ cm$^2$/s</td>
<td>1.0284</td>
<td>1.0284</td>
<td>1.0284</td>
<td>1.0284</td>
<td>1.0284</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$D_e$ cm$^2$/s a</td>
<td>0.1725</td>
<td>0.0582</td>
<td>0.0403</td>
<td>0.1022</td>
<td>0.1172</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$S$</td>
<td>0.027</td>
<td>0.032</td>
<td>0.034</td>
<td>0.031</td>
<td>0.027</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$D_e$ cm$^2$/s b</td>
<td>0.1608</td>
<td>0.0544</td>
<td>0.0374</td>
<td>0.0933</td>
<td>0.1044</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$D_e$ b /$D_e$ a</td>
<td>0.932</td>
<td>0.934</td>
<td>0.928</td>
<td>0.913</td>
<td>0.891</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$C_i$</td>
<td>0.8226</td>
<td>0.9035</td>
<td>0.9123</td>
<td>0.8756</td>
<td>0.7865</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a_e$</td>
<td>0.6708</td>
<td>0.6095</td>
<td>0.3478</td>
<td>0.2443</td>
<td>0.5677</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\tau_e$</td>
<td>3.84</td>
<td>10.33</td>
<td>8.51</td>
<td>2.36</td>
<td>4.78</td>
<td></td>
</tr>
</tbody>
</table>
Table 5.3 Experimental conditions and results (continuation)

<table>
<thead>
<tr>
<th>gas</th>
<th>T</th>
<th>4 #</th>
<th>6 #</th>
<th>8 #</th>
<th>9 #</th>
<th>10 #</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>flow rate ml/s</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.126</td>
<td>0.126</td>
<td>0.126</td>
<td>0.126</td>
<td>0.126</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.8057</td>
<td>0.8057</td>
<td>0.8057</td>
<td>0.8057</td>
<td>0.8057</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1325</td>
<td>0.0464</td>
<td>0.0335</td>
<td>0.0784</td>
<td>0.1025</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.028</td>
<td>0.032</td>
<td>0.035</td>
<td>0.031</td>
<td>0.026</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1245</td>
<td>0.0410</td>
<td>0.0299</td>
<td>0.0707</td>
<td>0.0949</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.940</td>
<td>0.884</td>
<td>0.894</td>
<td>0.902</td>
<td>0.926</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.8342</td>
<td>0.9084</td>
<td>0.9140</td>
<td>0.8850</td>
<td>0.7832</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.6708</td>
<td>0.6095</td>
<td>0.3478</td>
<td>0.2443</td>
<td>0.5677</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.08</td>
<td>10.58</td>
<td>8.37</td>
<td>2.51</td>
<td>4.46</td>
</tr>
</tbody>
</table>

|     |      | flow rate ml/s |       |         |         |         |         |
|     |      | 0.138   | 0.138   | 0.138   | 0.138   | 0.138   |
|     |      | 0.9385  | 0.9385  | 0.9385  | 0.9385  | 0.9385  |
|     |      | 0.1571  | 0.0586  | 0.0361  | 0.0914  | 0.1201  |
|     |      | 0.0627  | 0.031   | 0.035   | 0.031   | 0.026   |
|     |      | 0.1441  | 0.0532  | 0.0337  | 0.0850  | 0.1094  |
|     |      | 0.918   | 0.908   | 0.936   | 0.930   | 0.910   |
|     |      | 0.8253  | 0.8973  | 0.9153  | 0.8793  | 0.7748  |
|     |      | 0.6708  | 0.6095  | 0.3478  | 0.2443  | 0.5677  |
|     |      | 4.01    | 9.76    | 9.06    | 2.51    | 4.43    |

|     |      | flow rate ml/s |       |         |         |         |         |
|     |      | 0.148   | 0.148   | 0.148   | 0.148   | 0.148   |
|     |      | 1.055   | 1.055   | 1.055   | 1.055   | 1.055   |
|     |      | 0.1833  | 0.0618  | 0.0429  | 0.1003  | 0.1274  |
|     |      | 0.026   | 0.031   | 0.034   | 0.030   | 0.026   |
|     |      | 0.1664  | 0.0573  | 0.0384  | 0.0917  | 0.1155  |
|     |      | 0.908   | 0.927   | 0.894   | 0.915   | 0.907   |
|     |      | 0.8157  | 0.8987  | 0.9078  | 0.8773  | 0.7763  |
|     |      | 0.6708  | 0.6095  | 0.3478  | 0.2443  | 0.5677  |
|     |      | 3.86    | 10.40   | 8.55    | 2.57    | 4.47    |

\( \alpha \) obtained from dynamic responses; \( \beta \) obtained from steady state responses
\( \alpha \) is the porosity, \( \tau \) is the tortuosity

In our model for the mass transport process of gases in single pellets there is only one adjustable parameter, the effective diffusivity (negligible film resistance). This parameter not only affects the response curve shape but also the steady state response values. In order to achieve the minimum value of the sum of the squares of the differences between experimental and theoretical response values in the parameter estimation both the transient and the steady state responses are important to construct the objective function. The dead end pores only make contribution to the transient responses. The theoretical model must balance these two parts of the responses. This means that the effect of dead end pore contribution is reduced in the theoretical model. The percentage of dead end pores can be expressed by means of the ratio between both effective diffusivities obtained from the transient and steady states and the results are also listed in Table 5.2. The differences between the simulated and experimental responses shown in figures 5.17 to 5.21 result partially from this factor. In the transient state the response curves of both top and bottom chambers rise a little slower than the theoretical curves due to the dead pore contribution.

The standard deviations are shown in Table 5.3 and are of the same order of magnitude as the experimental errors (\( \pm 0.03 \)) which means that the model fits quite well the experimental results.
Figure 5.16 Comparison of response curves with different $D_e$ in sample 4# at 40 °C using Ar - He

Figure 5.17 Theoretical (dashed lines) and experimental (solid lines) response curves for $N_2$ in sample 4# at 70 °C
Figure 5.18 Theoretical (dashed lines) and experimental (solid lines) response curves for Ar in sample 8 at 40 °C

Figure 5.19 Theoretical (dashed lines) and experimental (solid lines) response curves for O₂ in sample 8 at 95 °C
Figure 5.20 Theoretical (dashed lines) and experimental (solid lines) response curves for Ar in sample 9# at 40 °C

Figure 5.21 Theoretical (dashed lines) and experimental (solid lines) response curves for O₂ in sample 10# at 70 °C
1.3 Convective Flow Coefficients

The determination of the convective flow coefficients in single pellets is straightforward. When there is a pressure difference between both sides of the pellet, a net mass flux through the pellet is produced and this flux mainly results from the convective flow for monocomponent systems in relatively large pores [Mason et al, 1967]. The Darcy law is usually used to describe the flux. For the application of Darcy law to our cases we need discuss its limits.

Bird et al [1960] gave the following equation that considers the contributions of gravity and wall effects on the convective velocity

\[ J = - \frac{B_e}{\nu} \frac{dP}{dZ} + B_e \rho \frac{d^2 \nu_o}{dZ^2} + \frac{B_e}{\nu} \rho g \]  \hspace{1cm} (5.21)

where \( \rho \) is the gas density and \( \nu_o \) is the velocity of gas inside pores. Normally gravity effects are negligible for gases because of their low density.

At steady state the flux through the pellet is constant and the pressure profile is linear. In these conditions the contributions of the first term in equation (5.21), Darcy contribution, and of the second term, wall effects, to the total flux can be compared using the following equation

\[ \frac{J_{\text{Darcy}}}{J_{\text{wall}}} = \frac{1}{2} \left( \frac{P_o - Z \Delta P}{RT J \Delta P} \right)^3 \]  \hspace{1cm} (5.22)

where \( P_o \) is the pressure at \( Z = 0 \) and \( \Delta P \) is the pressure difference between pellet top and bottom surfaces. In the conditions of our experiments the ratio of fluxes in equation (5.22) is of the order of \( 10^{12} \) and thus the wall effects can be safely neglected. Turbulent flow contribution to the total flux can also be neglected in our case because intrapore velocities are quite small (in the order of 0.3 cm/sec). So, Darcy law as defined by equation (4.20) can be used in this work.

The viscosities for argon, oxygen and nitrogen at three temperatures were calculated by following formula [Reid et al, 1988]:

\[ \nu = \frac{26.69 \sqrt{MT}}{\sigma^2 \Omega_c} \]  \hspace{1cm} (5.23)

where \( \sigma \) is the molecular (hard-sphere) diameter in Å and \( \Omega_c \) is the collision integral that can be calculated by:
\[ \Omega_v = A(T^*)^3 + C \exp(-DT^*) + E \exp(-FT^*) \quad (5.24) \]

Constants, A to F are respectively 1.16145, 0.14874, 0.52487, 0.77320, 2.16178 and 2.43787. \( T^* \) is defined as

\[ T^* = kT/\varepsilon \quad (5.25) \]

where \( \varepsilon \) is the Lennard-Jones constant. \( \sigma \) and \( \varepsilon/k \) for argon, oxygen and nitrogen are respectively 3.542, 3.467, 3.798, 93.3, 106.7 and 71.4. The calculated viscosities for these gases are shown in Table 5.4.

Table 5.4 Calculated viscosities (\( \mu \text{P} \)) [Reid et al, 1988]

<table>
<thead>
<tr>
<th></th>
<th>40 °C</th>
<th>70 °C</th>
<th>95 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>235.8</td>
<td>252.2</td>
<td>265.6</td>
</tr>
<tr>
<td>O(_2)</td>
<td>212.6</td>
<td>228.0</td>
<td>240.3</td>
</tr>
<tr>
<td>N(_2)</td>
<td>182.4</td>
<td>194.5</td>
<td>204.2</td>
</tr>
</tbody>
</table>

As it was already demonstrated in the case of no convection, film mass transport resistance can be neglected. The presence of convection across the pellet guarantees that for all convective pores there is no boundary layer and thus no film. The film mass transport resistance will also be neglected in these measurements.

The flow rates at the inlets of both chambers are accurately controlled and the outlet flow rates are measured with a soap bubble flow meter. From the differences of the flow rates between inlets and outlets and pellet section area the flux can be calculated. The pressure difference can also be directly measured. Figures 5.22 to 5.36 show the experimental results of \( J \) against \( \Delta P^2 \) for argon, nitrogen and oxygen in all five samples at different temperatures. The symbols in these figures represent the experimental data and the lines represent the calculated results using the regressed effective convective coefficients.

Samples 4#, 9# and 10# have visible convective pores. When the pressure difference across the pellet is about 0.1 to 1 mbar there are observable fluxes while the pressure difference must attain hundred mbar so that samples 6# and 8# achieve the same fluxes.

In order to access the possible dependence of \( B_v \) on pressure we also plotted this effective coefficient as a function of the average pressure, \( \bar{P} \). This is shown in Figures 5.37 to 5.41 for some cases. Looking to these plots we see that for samples 6# and 8# there is a clear dependence of \( B_v \) on \( \bar{P} \) whereas for all other samples this dependence is not so clear. To overcome the difficulty in distinguishing that dependence we used a \( t \)-student test to verify if the assumption of null slope (that is, independence) is valid.
Figure 5.22 Flux of argon as a function of pressure difference in sample 4#

Figure 5.23 Flux of nitrogen as a function of pressure difference in sample 4#
Figure 5.24 Flux of oxygen as a function of pressure difference in sample 4#

Figure 5.25 Flux of argon as a function of pressure difference in sample 6#
Figure 5.26 Flux of nitrogen as a function of pressure difference in sample 6#

Figure 5.27 Flux of oxygen as a function of pressure difference in sample 6#
Figure 5.28 Flux of argon as a function of pressure difference in sample 8#

Figure 5.29 Flux of nitrogen as a function of pressure difference in sample 8#
Lines represent calculated values.

Figure 5.30 Flux of oxygen as a function of pressure difference in sample 8#

Lines represent calculated values.

Figure 5.31 Flux of argon as a function of pressure difference in sample 9#
Figure 5.32 Flux of nitrogen as a function of pressure difference in sample 9#

Figure 5.33 Flux of oxygen as a function of pressure difference in sample 9#
Figure 5.34 Flux of argon as a function of pressure difference in sample 10#

Figure 5.35 Flux of nitrogen as a function of pressure difference in sample 10#
Figure 5.36 Flux of nitrogen as a function of pressure difference in sample 10#

Figure 5.37 Apparent convective coefficient variation with average pressure for oxygen in sample 4#
Figure 5.38 Apparent convective coefficient variation with average pressure for argon in sample 6#

Figure 5.39 Apparent convective coefficient variation with average pressure for nitrogen in sample 8#
Figure 5.40 Apparent convective coefficient variation with average pressure for argon in sample 9#

Figure 5.41 Apparent convective coefficient variation with average pressure for nitrogen in sample 10#
These calculations shown that at a 5% significance level the assumption is true for all experiments with samples 4#, 9# and 10# and not true for samples 6# and 8#. Then the conclusion is that for samples 4#, 9# and 10# with visible convective pores the permeability is approximately constant with average pressure whereas for samples 6# and 8# with a pore size distribution centered in a region of smaller pores, the apparent permeability is pressure dependent.

According with other authors (Mason and Malinauskas 1983) this dependence can be expressed assuming that we are in a region where more than one flow regime is important. As it is known three fundamental flow regimes are usually considered (Bird et al, 1960) and approximately classified according with the pore radius, $r_e$ and the molecular mean free path $\lambda$:

- Knudsen flow: $\lambda \geq 0.65 r_e$
- Slip flow: $0.10 \leq \lambda < 0.65 r_e$
- Ordinary flow: $\lambda \leq 0.10 r_e$

In samples #6 and #8 we think that slip and Knudsen diffusional flow regimes may have a nonnegligible contribution to total flux. In these conditions we can write a phenomenological expression for the apparent permeability [Mason and Malinauskas, 1983] where we lumped the Knudsen and slip coefficients in $D_K$

$$\mathbb{R}_e = D_K + \frac{B_s}{\nu} \overline{P}$$  \hspace{1cm} (5.26)

Table 5.5 shows the values obtained for $B_e$ in all experiments including those for samples 6# and 8# where the equation (5.26) was used.

This table also shows the effective pore radius, $r_e = \sqrt{8B_e}$ (for cylindrical pores), the fitting standard deviation, $S$, and the values of $r$ for 10 experimental points.

For samples 6# and 8# there are no visible convective pores and the pore size distribution peaks are mainly in the range of less than 1 μm. In such small pores the convective flow contribution to the total flux will significantly decrease. Although our experimental range of pressure differences is not enough wide to cover the variation of convective flux from the negligible to the dominant region, the conclusion about the important region for convective flow is reliable. There are some errors between the experimental points of the flux against the pressure at different temperatures and the regressed curves due to the flow rate experimental measurements. The tendency of the flux variation with temperature is reasonable. When temperature increases the flux at a fixed pressure difference decreases.
Table 5.5 Effective convective coefficients, $B_e \ (cm^2 \times 10^{10})$ for samples 4# 9# and 10# and $(cm^2 \times 10^{10})$ for samples 6# and 8# and the effective convective pore radii

<table>
<thead>
<tr>
<th>Sample</th>
<th>$B_e$</th>
<th>$r_e \ \mu m$</th>
<th>$S$</th>
<th>$t$</th>
<th>$4 #$</th>
<th>$6 #$</th>
<th>$8 #$</th>
<th>$9 #$</th>
<th>$10 #$</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 °C Ar</td>
<td>608.6</td>
<td>6.98</td>
<td>$4.55 \times 10^{-7}$</td>
<td>-0.7488</td>
<td>0.3691</td>
<td>0.0202</td>
<td>12.25</td>
<td>372.7</td>
<td></td>
</tr>
<tr>
<td>70 °C Ar</td>
<td>739.6</td>
<td>7.69</td>
<td>$4.04 \times 10^{-7}$</td>
<td>-0.2864</td>
<td>0.3488</td>
<td>0.0193</td>
<td>9.26</td>
<td>35.50</td>
<td></td>
</tr>
<tr>
<td>95 °C Ar</td>
<td>777.7</td>
<td>7.89</td>
<td>$3.99 \times 10^{-7}$</td>
<td>-0.3339</td>
<td>0.4300</td>
<td>0.0191</td>
<td>93.8</td>
<td>303.7</td>
<td></td>
</tr>
<tr>
<td>40 °C N₂</td>
<td>679.0</td>
<td>7.37</td>
<td>$5.36 \times 10^{-7}$</td>
<td>1.489</td>
<td>0.3774</td>
<td>0.0204</td>
<td>102.2</td>
<td>338.9</td>
<td></td>
</tr>
<tr>
<td>70 °C N₂</td>
<td>644.6</td>
<td>7.18</td>
<td>$6.32 \times 10^{-7}$</td>
<td>-1.758</td>
<td>0.3686</td>
<td>0.0161</td>
<td>117.1</td>
<td>356.0</td>
<td></td>
</tr>
<tr>
<td>95 °C N₂</td>
<td>705.4</td>
<td>7.51</td>
<td>$4.94 \times 10^{-7}$</td>
<td>-3.653</td>
<td>0.4173</td>
<td>0.0159</td>
<td>119.2</td>
<td>373.6</td>
<td></td>
</tr>
<tr>
<td>40 °C O₂</td>
<td>620.9</td>
<td>7.05</td>
<td>$5.18 \times 10^{-7}$</td>
<td>0.1199</td>
<td>0.4181</td>
<td>0.0201</td>
<td>99.7</td>
<td>322.3</td>
<td></td>
</tr>
<tr>
<td>70 °C O₂</td>
<td>707.8</td>
<td>7.85</td>
<td>$5.42 \times 10^{-7}$</td>
<td>-0.2540</td>
<td>0.4580</td>
<td>0.0210</td>
<td>104.1</td>
<td>339.0</td>
<td></td>
</tr>
<tr>
<td>95 °C O₂</td>
<td>579.2</td>
<td>6.81</td>
<td>$3.25 \times 10^{-7}$</td>
<td>-1.131</td>
<td>0.4506</td>
<td>0.0193</td>
<td>97.6</td>
<td>351.9</td>
<td></td>
</tr>
</tbody>
</table>

We did not calculate $D_K$ for two reasons:

— $D_K$ is obtained in the limit of zero pressure and our experiments are far away thus giving a very large error in the estimation.

— $D_K$ at very low pressure is no longer constant with pressure as demonstrated by other authors [Mason and Malinauskas 1983].
2 SHALLOW BED DIFFUSION CELL

Traditionally, the diffusion cell experimental technique was essentially applied for single pellets with slab geometry. When the pellet dimensions are small experimental measurements and cell design are limited by the system dead volume accurate calibration and by the observability of the response signals. For very small pellets the quantity of gas inside the pellets is small when compared with the dead volumes and the errors due to dead volume calibration and the possible deviation of flow patterns from the ideal plug flow will heavily affect the calculation of the mass transport rate parameters from the experimental response curves. Many chemical processes involving gas - solid mass transport use non slab small particles to achieve good mechanical properties and to reduce the particle mass transport time constant.

In order to take the advantage of the diffusion cell technique, we adjusted the diffusion cell dimensions and controlled the pressure difference in both sides of the cell to zero. We were able to combine the shallow bed principles with the diffusional cell technique and to measure the responses in both sides. From these response curves the mass transport rate parameters can be extracted by using the models developed in Chapter IV. Experiments were carried out by applying positive and negative concentration steps at the inlet of the top chamber. Inlet tracer concentrations are from 3.5 to 20% in volume. In each experimental run the same carrier (helium) flow rate is maintained in both chambers. Argon, oxygen and nitrogen were used as solutes.

2.1 Effective Diffusivity Determination

A. Solid Sample Properties

We use the diffusion cell shallow bed technique to determine the effective bulk phase, macropore and micropore diffusivities of argon, nitrogen and oxygen at 40, 70 and 95 °C in Laporte 4A and 5A (Lap 4A and Lap 5A), Rhône Poulenc 4A and 5A (RP 4A and RP 5A), Rhône Poulenc alumina (RP Al) and LaRoche alumina (La Al). The pore network information for these samples is shown in Table 5.6. Rhône Poulenc 4A and 5A are cylindrical pellets and all others are spheres. The pore network structure of zeolite particles shows the typical bidispersed pore distribution. The micropore dimensions are completely determined by the crystal structure and have uniform size. The macropores are composed by the voids between crystals and the sizes are also more regular than alumina because the crystal size distribution is usually narrow. The pore size distribution of alumina has an almost continuous distribution. There is not a clear distinction between macro and micropores and thus the micropore dimensions are difficult to be set. We roughly set the volume determined by mercury porosimetry as the macropore volume. The bulk phase void volume can be calculated using the cell geometry, apparent pellet density and the packing amount. As a reference for the bulk phase diffusivities determined by this technique we also measured the bulk phase diffusivities for a non porous solid, glass beads, with similar dimensions. The dimensions of zeolite microparticles in Table 5.6 were measured from scanning electronic microscope photographs.
### Table 5.6 Pore structure and particle properties

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>glass bed</th>
<th>Lap 4A</th>
<th>Lap 5A</th>
<th>RP 4A</th>
<th>RP 5A</th>
<th>RP Al</th>
<th>La Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter mm</td>
<td>1.79</td>
<td>1.84</td>
<td>1.84</td>
<td>1.6</td>
<td>1.6</td>
<td>3.2</td>
<td>3.8</td>
</tr>
<tr>
<td>Length mm</td>
<td>1.38</td>
<td>1.38</td>
<td>1.84</td>
<td>1.84</td>
<td>3.5</td>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Microparticle diameter μm</td>
<td>1.853</td>
<td>0.714</td>
<td>0.714</td>
<td>0.720</td>
<td>0.720</td>
<td>0.564</td>
<td>0.734</td>
</tr>
<tr>
<td>Bulk density g/ml</td>
<td>2.950</td>
<td>1.16</td>
<td>1.16</td>
<td>1.13</td>
<td>1.13</td>
<td>0.9705</td>
<td>1.2591</td>
</tr>
<tr>
<td>Apparent density g/ml</td>
<td>1.68</td>
<td>1.68</td>
<td>1.86</td>
<td>0.351</td>
<td>0.351</td>
<td>0.7294</td>
<td>0.1922</td>
</tr>
<tr>
<td>Skeletal density g/ml</td>
<td>0.267</td>
<td>0.267</td>
<td>0.351</td>
<td>48.0</td>
<td>147.25</td>
<td>22.532</td>
<td></td>
</tr>
<tr>
<td>Pore volume ml/g</td>
<td>31.0</td>
<td>31.0</td>
<td>48.0</td>
<td>0.0046</td>
<td>0.0046</td>
<td>0.0258</td>
<td>0.0258</td>
</tr>
<tr>
<td>Specific area, A, m²/g</td>
<td>0.372</td>
<td>0.384</td>
<td>0.384</td>
<td>0.363</td>
<td>0.363</td>
<td>0.419</td>
<td>0.417</td>
</tr>
<tr>
<td>Average pore diameter (4V/A) μm</td>
<td>0.0100</td>
<td>0.0096</td>
<td>0.0258</td>
<td>0.0258</td>
<td>0.0258</td>
<td>0.0194</td>
<td>0.0341</td>
</tr>
<tr>
<td>a</td>
<td>calculated by ( \bar{b} = \frac{1}{\text{Bulk density}} / \text{Apparent density} )</td>
<td>( \bar{b} = \frac{1}{\text{Apparent density}} / \text{Skeletal density} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

V is the total pore volume
Bulk density is defined as particle mass / particle packing volume
Apparent density is defined as particle mass / particle volume
Skeletal density is defined as particle mass / solid volume
Specific area is defined as total surface area / particle mass

a this value was measured from scanning electronic microscope photographs
b calculated by \( \bar{b} = \frac{1}{\text{Bulk density}} / \text{Apparent density} \)
c calculated by \( \bar{a} = \frac{1}{\text{Apparent density}} / \text{Skeletal density} \)

1 data provided by Laporte corporation
2 data provided by Rhône Poulenc corporation (Reference No. 1164 for 5A and 1163 for 4A)
3 Rhône Poulenc corporation (Reference No. A 6) and data were measured by mercury porosimetry
4 LaRoche corporation (Reference No. A 201) and data were measured by mercury porosimetry

* 4A macropore structure properties were borrowed from the corresponding 5A Samples

Figures 5.42 to 5.45 show the detailed differential pore diameter distributions of Laporte 5A, Rhône Poulenc 5A, Rhône Poulenc alumina and LaRoche alumina. Because the 5A zeolites were usually obtained by ion exchange from the corresponding 4A zeolites, the pore structure characteristics measured by the mercury porosimetry are the same for 5A and 4A zeolites of the same source. The characteristics of the macropore size distribution of both Laporte and Rhône Poulenc 5A look very similar. In the range of 0.1 to 1 μm there is an observable distribution peak. These peaks are expected since the zeolite macropores are composed by the voids among crystals and binding material. The crystal size and the binding material particle dimension are of the order of 1 μm and thus the void dimensions should be close to that number. The Rhône Poulenc alumina pore structures are completely different. There is a pore size distribution peak in the range of 0.01 to 0.03 μm for Rhône Poulenc alumina. The LaRoche alumina pore size distribution seems continuous and possibly there is a distribution peak in the limit of mercury porosimetry detection. The main use of this alumina is as a desiccant and thus it must contain abundant micropores to achieve high adsorption capacity. In our models for the mass transport in the shallow bed diffusion cell one of the interesting pore structure parameters is the macropore porosity which can be directly obtained from the mercury porosimetry measurements. The micropore structure characteristics are less important since in our mass transport models there are no variables or parameters explicitly linked to the micropore structure properties and the effective micropore diffusivities and adsorption equilibrium constants were expressed in microparticle dimension basis.
Figure 5.42 Differential pore size distribution of Laporte 5A obtained by mercury porosimetry

Figure 5.43 Differential pore size distribution of Rhône Poulenc 5A obtained by mercury porosimetry
Figure 5.44 Differential pore size distribution of Rhône Poulenc alumina obtained by mercury porosimetry

Figure 5.45 Differential pore size distribution of LaRoche alumina obtained by mercury porosimetry
B. Effective Bulk Phase Diffusivities

Similar to the single pellet diffusion cell the chamber dead volumes including the tubing and connectors between the chamber and the thermal conductivity detector were measured by blocking the shallow bed. The mixing degree in the chamber was tested and perfectly mixing was obtained. All experiments were conducted at ambient total pressure and desired temperatures. Three runs for each set of experimental conditions were performed and repeated if the responses were not coincident. This coincidence ensures that the confidence of the experimental data is enough high for the parameter regression. In order to test the effect of the pressure difference between the top and bottom chambers on the response curves, pressure differences were varied from -20 mmHg to +20 mmHg. The response curves are coincident for pressure differences within ±5 mmHg. The cell dimension is 2.8 × 2.0 cm (diameter × thickness) and the corresponding geometric parameters, \( N_r \), are 18.92, 18.92, 17.88, 17.88, 20.64 and 20.54 for Laporte 4A and 5A, Rhône Poulenc 4A and 5A, Rhône Poulenc, and LaRoche alumina, respectively.

In our mass transport model developed in last chapter for the shallow bed diffusion cell all variables or parameters can be measured except the effective bulk phase diffusivity, \( D_{\text{me}} \), macropore diffusivity, \( D_m \), microparticle diffusivity \( D_i \) and film mass transport coefficient, \( k_f \). Comparing with the single pellet diffusion cell where the effective diffusivities are small and the film mass transport resistances could be neglected, both diffusional and film resistances may be important in shallow bed diffusion cell due to the small bulk phase mass transport resistance. Among these four mass transport parameters \( D_m \) and \( k_f \) are linked by equation (4.80) and one of them can be calculated from the other using the steady state responses. \( D_b \), \( D_a \) and \( D_{\text{me}} \) (or \( k_f \)) can be obtained by parameter regression. Three parameter regression is much more difficult than two parameter regression. If we manage to estimate one of the parameters, \( D_b \), \( D_a \) and \( D_{\text{me}} \) (or \( k_f \)) before the optimization the decrease on the number of parameters will significantly reduce the computing task.

The molecular diffusion should be the only contribution to the bulk phase mass transfer without the existence of a pressure difference across the cell. Due to the increase of the diffusional path length and the variation of the path geometry the effective bulk phase diffusivity, \( D_{\text{me}} \), must be smaller than the corresponding molecular diffusivity, \( D_m \), and the relationship between them can be expressed as [Gangwal et al., 1979]:

\[
D_b = D_{\text{me}}/\tau_{\text{bulk}}
\]

(5.27)

where \( \tau_{\text{bulk}} \) is the bulk phase tortuosity. Schneider and Smith [1968] presented the above equation as a parallel pore model of the bed and thus \( \tau_{\text{bulk}} \) should be independent of the solute and of the temperature. Because the responses at steady state are independent of the pore network structure the bulk phase tortuosity should be also independent of the solid pore structure and only dependent on the packing way and particle geometry. A few experimental values of \( \tau_{\text{bulk}} \) for silica gel are 1.45 - 1.59 [Gangwal et al., 1979]. The theoretical prediction of \( \tau_{\text{bulk}} \) for a bed randomly packed with uniform spherical particles is \( \sqrt{2} \) [Wheeler, 1955]. The error when using Chapman - Enskog formula (1.113) in the estimation of binary molecular diffusivities were reported as less than 5% for a variety of systems [Reid et al., 1986] and we used this correlation to calculate the binary molecular diffusivities. In order to confirm such estimation we calculated the diffusivities using
three parameter regression from the dynamic responses of both chambers for nitrogen in Rhône Poulenc and Laporte 5A particles at 40 and 95 °C. This two solid samples have different geometries. The results regressed and estimated by equation (5.27) with $\tau_{\text{bulk}} = \sqrt{2}$ are shown in Table 5.7.

Table 5.7 Comparison of the effective bulk phase diffusivities (cm$^2$/s) for nitrogen obtained by regression and estimation

<table>
<thead>
<tr>
<th></th>
<th>Lap 5A</th>
<th></th>
<th>RP 5A</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>regressed value</td>
<td>estimated value</td>
<td>regressed value</td>
<td>estimated value</td>
</tr>
<tr>
<td>40 °C</td>
<td>0.5380</td>
<td>0.5556</td>
<td>0.5337</td>
<td>0.5556</td>
</tr>
<tr>
<td>95 °C</td>
<td>0.6734</td>
<td>0.7269</td>
<td>0.6767</td>
<td>0.7269</td>
</tr>
</tbody>
</table>

The data in Table 5.7 show that the regressed results are slightly smaller than the estimated values and the difference between them is less than 5%. Such small error is in the uncertainty range of the experimental determination and parameter regression. So we adopted this theoretical estimation method for the calculation of the effective bulk phase diffusivities. When the effective bulk phase diffusivities can be evaluated, the film mass transport coefficients can be calculated using the steady state responses of both chambers and this calculation is independent of the dynamic responses. Table 5.8 shows the experimental flow conditions, molecular diffusivities calculated by Chapman - Enskog equation (1.113), effective bulk phase diffusivities calculated with $\tau_{\text{bulk}} = \sqrt{2}$ and mass transport coefficients obtained from the steady state response of both chambers.

C. Adsorption Equilibrium Constants

Zeolites A have a large quantity of micropores and large specific areas. The adsorption amount at the experimental partial pressure range may not be negligible. Usually the adsorption equilibrium behavior will severely affect the response values. A global mass balance of adsorbable component over a step input experiment can be used to evaluate the adsorption equilibrium constant, $K$, from the experimental transient response curves by using equation (4.31). Table 5.9 shows the average adsorption equilibrium constants of nitrogen, oxygen and argon in all samples over several tracer concentrations.

Because the adsorbed amount of gases in alumina is small, specially in the case of Rhône Poulenc alumina, the experimental global mass balance has relatively large errors. For zeolites the adsorbed amount is non-negligible specially in the case of nitrogen in 5A zeolite. As a comparison of equilibrium constants of nitrogen and oxygen in Rhône Poulenc 5A we listed the experimental results from Garcin [1991] obtained by gravimetric and chromatographic techniques and our work in Figures 5.46 and 5.47. The conversion between the adsorption constant, $K$ (volume of macropore/volume of microparticle), used by us and the adsorption amount, $a_m$ (g/g adsorbent), used by Garcin [1991] is:

$$a_m = \frac{\varnothing_b (1 - \varnothing_a) MK c}{\rho_s \varnothing_a (1 - \varnothing_b)} \quad (5.28)$$
<table>
<thead>
<tr>
<th>Sample</th>
<th>glass bond</th>
<th>Lap 4A</th>
<th>Lap 5A</th>
<th>RP 4A</th>
<th>RP 5A</th>
<th>RP Al</th>
<th>La Al</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>flow rate ml/s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 °C</td>
<td>0.126</td>
<td>0.126</td>
<td>0.126</td>
<td>0.126</td>
<td>0.126</td>
<td>0.126</td>
<td>0.126</td>
</tr>
<tr>
<td></td>
<td>0.7542</td>
<td>0.7542</td>
<td>0.7542</td>
<td>0.7542</td>
<td>0.7542</td>
<td>0.7542</td>
<td>0.7542</td>
</tr>
<tr>
<td></td>
<td>0.5337</td>
<td>0.5337</td>
<td>0.5337</td>
<td>0.5337</td>
<td>0.5337</td>
<td>0.5337</td>
<td>0.5337</td>
</tr>
<tr>
<td></td>
<td>0.5743</td>
<td>0.5866</td>
<td>0.5869</td>
<td>0.5907</td>
<td>0.5910</td>
<td>0.5890</td>
<td>0.5809</td>
</tr>
<tr>
<td></td>
<td>10.63</td>
<td>11.46</td>
<td>10.60</td>
<td>11.52</td>
<td>10.69</td>
<td>10.41</td>
<td>11.45</td>
</tr>
<tr>
<td></td>
<td>3.620</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.698</td>
<td>1.595</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>flow rate ml/s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70 °C</td>
<td>0.138</td>
<td>0.138</td>
<td>0.138</td>
<td>0.138</td>
<td>0.138</td>
<td>0.138</td>
<td>0.138</td>
</tr>
<tr>
<td></td>
<td>0.8780</td>
<td>0.8780</td>
<td>0.8780</td>
<td>0.8780</td>
<td>0.8780</td>
<td>0.8780</td>
<td>0.8780</td>
</tr>
<tr>
<td></td>
<td>0.6208</td>
<td>0.6208</td>
<td>0.6208</td>
<td>0.6208</td>
<td>0.6208</td>
<td>0.6208</td>
<td>0.6208</td>
</tr>
<tr>
<td></td>
<td>0.5707</td>
<td>0.5824</td>
<td>0.5825</td>
<td>0.5863</td>
<td>0.5863</td>
<td>0.5766</td>
<td>0.5770</td>
</tr>
<tr>
<td></td>
<td>11.76</td>
<td>13.09</td>
<td>12.66</td>
<td>13.21</td>
<td>13.30</td>
<td>13.19</td>
<td>12.78</td>
</tr>
<tr>
<td></td>
<td>3.253</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.584</td>
<td>1.461</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>95 °C</td>
<td>flow rate ml/s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.148</td>
<td>0.148</td>
<td>0.148</td>
<td>0.148</td>
<td>0.148</td>
<td>0.148</td>
<td>0.148</td>
</tr>
<tr>
<td></td>
<td>0.9866</td>
<td>0.9866</td>
<td>0.9866</td>
<td>0.9866</td>
<td>0.9866</td>
<td>0.9866</td>
<td>0.9866</td>
</tr>
<tr>
<td></td>
<td>0.6976</td>
<td>0.6976</td>
<td>0.6976</td>
<td>0.6976</td>
<td>0.6976</td>
<td>0.6976</td>
<td>0.6976</td>
</tr>
<tr>
<td></td>
<td>0.5675</td>
<td>0.5794</td>
<td>0.5794</td>
<td>0.5832</td>
<td>0.5834</td>
<td>0.5740</td>
<td>0.5740</td>
</tr>
<tr>
<td></td>
<td>3.573</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.446</td>
<td>1.306</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>flow rate ml/s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70 °C</td>
<td>0.126</td>
<td>0.126</td>
<td>0.126</td>
<td>0.126</td>
<td>0.126</td>
<td>0.126</td>
<td>0.126</td>
</tr>
<tr>
<td></td>
<td>0.7858</td>
<td>0.7858</td>
<td>0.7858</td>
<td>0.7858</td>
<td>0.7858</td>
<td>0.7858</td>
<td>0.7858</td>
</tr>
<tr>
<td></td>
<td>0.5556</td>
<td>0.5556</td>
<td>0.5556</td>
<td>0.5556</td>
<td>0.5556</td>
<td>0.5556</td>
<td>0.5556</td>
</tr>
<tr>
<td></td>
<td>0.5764</td>
<td>0.5894</td>
<td>0.5895</td>
<td>0.5937</td>
<td>0.5937</td>
<td>0.5835</td>
<td>0.5835</td>
</tr>
<tr>
<td></td>
<td>11.91</td>
<td>11.56</td>
<td>11.42</td>
<td>11.27</td>
<td>11.26</td>
<td>11.65</td>
<td>11.79</td>
</tr>
<tr>
<td></td>
<td>4.852</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.253</td>
<td>2.068</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>95 °C</td>
<td>flow rate ml/s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.138</td>
<td>0.138</td>
<td>0.138</td>
<td>0.138</td>
<td>0.138</td>
<td>0.138</td>
<td>0.138</td>
</tr>
<tr>
<td></td>
<td>0.9150</td>
<td>0.9150</td>
<td>0.9150</td>
<td>0.9150</td>
<td>0.9150</td>
<td>0.9150</td>
<td>0.9150</td>
</tr>
<tr>
<td></td>
<td>0.6470</td>
<td>0.6470</td>
<td>0.6470</td>
<td>0.6470</td>
<td>0.6470</td>
<td>0.6470</td>
<td>0.6470</td>
</tr>
<tr>
<td></td>
<td>0.5729</td>
<td>0.5851</td>
<td>0.5850</td>
<td>0.5895</td>
<td>0.5892</td>
<td>0.5793</td>
<td>0.5795</td>
</tr>
<tr>
<td></td>
<td>4.660</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.192</td>
<td>1.952</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>flow rate ml/s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70 °C</td>
<td>0.126</td>
<td>0.126</td>
<td>0.126</td>
<td>0.126</td>
<td>0.126</td>
<td>0.126</td>
<td>0.126</td>
</tr>
<tr>
<td></td>
<td>0.8058</td>
<td>0.8058</td>
<td>0.8058</td>
<td>0.8058</td>
<td>0.8058</td>
<td>0.8058</td>
<td>0.8058</td>
</tr>
<tr>
<td></td>
<td>0.5698</td>
<td>0.5698</td>
<td>0.5698</td>
<td>0.5698</td>
<td>0.5698</td>
<td>0.5698</td>
<td>0.5698</td>
</tr>
<tr>
<td></td>
<td>0.5724</td>
<td>0.5849</td>
<td>0.5846</td>
<td>0.5855</td>
<td>0.5857</td>
<td>0.5786</td>
<td>0.5790</td>
</tr>
<tr>
<td></td>
<td>12.21</td>
<td>11.62</td>
<td>12.56</td>
<td>13.04</td>
<td>12.29</td>
<td>12.77</td>
<td>12.59</td>
</tr>
<tr>
<td></td>
<td>4.202</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.195</td>
<td>2.024</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>95 °C</td>
<td>flow rate ml/s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.138</td>
<td>0.138</td>
<td>0.138</td>
<td>0.138</td>
<td>0.138</td>
<td>0.138</td>
<td>0.138</td>
</tr>
<tr>
<td></td>
<td>0.9385</td>
<td>0.9385</td>
<td>0.9385</td>
<td>0.9385</td>
<td>0.9385</td>
<td>0.9385</td>
<td>0.9385</td>
</tr>
<tr>
<td></td>
<td>0.6636</td>
<td>0.6636</td>
<td>0.6636</td>
<td>0.6636</td>
<td>0.6636</td>
<td>0.6636</td>
<td>0.6636</td>
</tr>
<tr>
<td></td>
<td>0.5688</td>
<td>0.5807</td>
<td>0.5805</td>
<td>0.5847</td>
<td>0.5845</td>
<td>0.5750</td>
<td>0.5753</td>
</tr>
<tr>
<td></td>
<td>3.876</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.972</td>
<td>1.742</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

232
Table 5.9 Average adsorption equilibrium constants

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lap 4A</th>
<th>Lap 5A</th>
<th>RP 4A</th>
<th>RP 5A</th>
<th>RP Al</th>
<th>La Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>2.534</td>
<td>2.800</td>
<td>2.657</td>
<td>2.648</td>
<td>1.435</td>
<td>1.815</td>
</tr>
<tr>
<td>40 °C</td>
<td>1.964</td>
<td>1.761</td>
<td>1.981</td>
<td>2.084</td>
<td>negligible</td>
<td>1.566</td>
</tr>
<tr>
<td>70 °C</td>
<td>1.429</td>
<td>1.431</td>
<td>1.467</td>
<td>1.472</td>
<td>1.273</td>
<td>1.446</td>
</tr>
<tr>
<td>95 °C</td>
<td>5.544</td>
<td>11.79</td>
<td>5.271</td>
<td>10.47</td>
<td>1.238</td>
<td>1.338</td>
</tr>
<tr>
<td>N2</td>
<td>40 °C</td>
<td>3.786</td>
<td>6.512</td>
<td>3.285</td>
<td>6.944</td>
<td>1.146</td>
</tr>
<tr>
<td>70 °C</td>
<td>2.600</td>
<td>4.673</td>
<td>2.669</td>
<td>4.369</td>
<td>1.258</td>
<td></td>
</tr>
<tr>
<td>95 °C</td>
<td>2.817</td>
<td>3.561</td>
<td>3.125</td>
<td>3.593</td>
<td>1.146</td>
<td></td>
</tr>
<tr>
<td>O2</td>
<td>40 °C</td>
<td>2.373</td>
<td>2.274</td>
<td>2.108</td>
<td>2.533</td>
<td>1.258</td>
</tr>
<tr>
<td>70 °C</td>
<td>1.875</td>
<td>1.879</td>
<td>1.938</td>
<td>1.837</td>
<td>1.070</td>
<td></td>
</tr>
<tr>
<td>95 °C</td>
<td>5.544</td>
<td>11.79</td>
<td>5.271</td>
<td>10.47</td>
<td>1.273</td>
<td>1.446</td>
</tr>
</tbody>
</table>

where \( M \) is the adsorbate molecular weight, \( \rho_a \) is the adsorbent particle density and \( c \) is the adsorbate concentration in bulk phase. The experimental values are close to each other. The adsorption equilibrium constants in Laporte 5A are smaller than in Rhône Poulenc 5A. Because the adsorption equilibrium constants expressed in volume of macropore / volume of microparticle include the factor macropore porosity, the porosity factor \((1 - \Omega_m) / \Omega_m\) of Laporte 5A is larger than that of Rhône Poulenc 5A and thus the equilibrium adsorbed amount expressed in weight of adsorbate/weight of adsorbent is close. This is expected since the adsorption equilibrium characteristics of zeolite crystals should be independent of the synthesis process and if we neglect the difference on the amount of binding material used by Laporte and Rhône Poulenc the weight of zeolite crystals per unit weight of particles should be approximately the same for these two samples.

In the range of the tracer gas concentrations used for the determination of the mass transport rate parameters, the adsorption isotherms are linear which confirms the validity of the assumption of a linear equilibrium relationship. It should be explained that the determination of the adsorption equilibria is not limited to the linear equilibrium case because the adsorbed amount of gases in the solid is calculated by a global mass balance that is independent of the mass transport rate model. When the adsorption isotherms are nonlinear the mass transport rate model developed in last chapter is not applicable.

In Chapter II we developed a methodology for predicting the adsorption equilibria of permanent gases in 5A and 4A zeolites at low coverage. The Henry adsorption equilibrium constants at different temperatures can be related to the isosteric adsorption heats by following equation [Ruthven, 1984]:

\[
K = K_0 \exp\left(-\frac{\Delta H}{RT}\right)
\]

(5.29)
Figure 5.46 Comparison of nitrogen adsorption isotherms in Rhône Poulenc 5A at various temperatures. (open symbols: Garcin work [1991]; closed symbols: present work)

Figure 5.47 Comparison of oxygen adsorption isotherms in Rhône Poulenc 5A at various temperatures (open symbols: Garcin work [1991]; closed symbols: present work)
The theoretical equilibrium constants of argon, nitrogen and oxygen in 4A and 5A zeolites at 40, 70 and 95 °C can be estimated from the predicted isosteric adsorption heats and constants at 24 °C and the results are shown in Table 5.10. As a comparison the experimental values obtained in Laporte 4A and 5A and Rhône Poulenc 4A and 5A are also shown in this table. All equilibrium constants are expressed in dimensionless form. The experimental values, $K_\text{expt}$ (volume of macropore / volume of microparticle ) calculated by equation (4.31) can be transformed to the dimensionless, $\mathcal{K}$, by a multiplicative factor:

$$\mathcal{K} = K \frac{1 - \Theta_a}{\Theta_a}$$  \hspace{1cm} (5.30)

Table 5.10 Comparison between predicted and experimental dimensionless adsorption equilibrium constants of gases in zeolites A

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lap 4A</th>
<th>Lap 5A</th>
<th>RP 4A</th>
<th>RP 5A</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pred</td>
<td>expt</td>
<td>pred</td>
<td>expt</td>
</tr>
<tr>
<td>N$_2$</td>
<td>40 °C</td>
<td>13.02</td>
<td>12.34</td>
<td>26.27</td>
</tr>
<tr>
<td></td>
<td>70 °C</td>
<td>8.574</td>
<td>8.428</td>
<td>15.93</td>
</tr>
<tr>
<td></td>
<td>70 °C</td>
<td>5.510</td>
<td>5.081</td>
<td>5.754</td>
</tr>
</tbody>
</table>

The conversion of the adsorption Henry constants, $K$, expressed in molecule/cavity/cm$^3$/pressure$^{-1}$ to dimensionless form can be completed by the following relationship:

$$\mathcal{K} = K \frac{N_c}{N_o} \frac{RT}{V}$$  \hspace{1cm} (5.31)

where $N_c$ is the number of cavities per unit crystal volume that can be evaluated by taking the crystal cell constant of zeolite A as 12.29 Å [Breck, 1974].

The experimental results are a bit smaller than the theoretical values. This is expected because there is some binding material in Laporte and Rhône Poulenc zeolite particles and the contribution of binding material to the adsorbed amount is negligible. Usually the content of binding material is different from each manufacturer. Typically it varies from 10% to 20%. If we subtract this inert component, the experimental adsorption Henry constants agree well with the theoretically predicted values.
The coincidence of the adsorption Henry constants determined using the shallow bed diffusion cell and by the gravimetric method and these predicted theoretically confirms the reliability of the experimental technique.

D. Effective Diffusivities inside Particles and the Simulation of Transient Responses

In the mass transport model developed in last chapter for the shallow bed diffusion cell packed with a bidisperse porous solid the geometric parameter, $N_p$, particle and bed porosity parameters, $\omega_a$ and $\omega_b$, are available before experiment. $C_t$ and $C_b$ are measured from the transient response curves. $\mathcal{F}$ should be adjusted to estimate the mass transfer parameters. Because the chamber structure is the same as the single pellet diffusion cell, the dead volume should be also the same. The mass transport rate parameter $N_p$ can be obtained from the binary molecular diffusivities and a theoretical bulk phase tortuosity and $N_t$ can be obtained from the steady state response concentrations of top and bottom chambers. The mass transport rate parameters inside the particle, $N_a$ and $N_b$, have no effects on the steady state responses and thus they can be extracted only from the transient responses by matching the theoretical response values of both chambers calculated by the model including these two parameters to the experimental response curves. The model equations were numerically solved by inversion of the Laplace domain solutions using fast Fourier transform (FFT). We tested the accuracy of the FFT by using different number of points; 1024 points is enough for all these cases. The curve matching was carried out by using the weighted orthogonal distance regression technique (ODRPACK software). In the user supported subroutine we set some restrictions for the parameters to be estimated like being greater than zero and micropore effective diffusivity smaller than macropore effective diffusivity. As a comparison the orthogonal collocation numerical technique was also used for solving mass transport rate equations. Four internal collocation points were used for the discretization of both microparticle and particle radial variables and twelve internal collocation points for the discretization of the cell axial direction. By balancing the calculation precision and computation work these discretizing conditions are reasonable. We tested the solution accuracy by increasing the number of collocation points and found no visible improvements. The response curve simulation results using these two numerical solution methods shown that the difference is much smaller than the experimental measurement error. From the point of view of computation work, the former was preferred. For the same solution precision, the computation work for the FFT technique is about less than 10% for the collocation technique. The parameter regression using ODRPACK software needs to solve the mass transport equations more than once and thus an improvement of efficiency will greatly reduce the computation work. A good initial guess for the macropore and micropore diffusivities and a reasonable setting for some parameter restrictions can dramatically improve the process. We used theoretical predicted values for zeolite micropore diffusivity and measured values of macropore diffusivities for single alumina pellets as initial guesses. After obtaining some regressed values for one system we used such values as initial guess for other systems.

Table 5.11 shows the regressed results for the effective macropore and micropore diffusivities of argon, nitrogen and oxygen at 40, 70 and 95 °C in Laporte 4A and 5A, Rhône Poulenc 4A and 5A and Rhône Poulenc and LaRoche alumina samples. For alumina samples the microparticle diameters are unknown and thus only the dimensionless mass transport rate parameters are shown. The pore network structure properties of alumina are entirely determined by the manufacturing process and the values listed in Table 5.6 for pore volume, densities and average pore diameter for both alumina samples are quite different and thus the adsorption and diffusion properties should not be the same. For zeolite samples of the same type, adsorption and micropore diffusion
characteristics are similar because the microparticle dimensions for Laporte and Rhône Poulenc samples are close and the adsorption and micropore diffusion properties are mainly controlled by the zeolite crystal structure. The macropore structure is influenced by the agglomeration of synthetic crystals, binding material type and content and manufacturing conditions. For different sources the macropore structures will largely differ. The original synthetic zeolite A is in 4A form, that is, the exchangeable cations are Na⁺. The 5A zeolite is usually obtained by ion exchange. For the same agglomeration process, the macropore structure of 4A and 5A zeolites should be the same. Due to the similar macropore network structures of 4A and 5A zeolites obtained from the same source, the macropore diffusivities for 4A zeolite were taken as the same as for 5A zeolite. The micropores for 5A or 4A zeolite from different sources are the same and thus the diffusivities in micropores should be more or less similar if the crystal defaults can be neglected.

In our mass transport model for the shallow bed diffusion cell the mass transport resistances for bulk phase, macropores and micropores were taken in series and thus when one of them is much larger than the others this resistance becomes the rate controlling step. The relative importance between any two diffusion resistances linked in series can be illustrated by considering the time constant ratios, \( \tau_{ab} = N_s/N_b \) and \( \tau_{ai} = N_i/N_s \). In all our cases the variation of \( N_s \) and \( N_a \) is small compared to the variation of \( N_i \) for different solid samples, gases and temperatures. \( \tau_{ab} \) is in the range of 1.3 to 5.5 (shown in Table 5.8) and thus both bulk and macropore diffusional resistances make similar contributions to the total mass transport resistance. The variation of \( \tau_{ai} \) covers a large range. When \( \tau_{ai} > 1 \) the micropore diffusion becomes the rate controlling step. When \( \tau_{ai} << 1 \), the micropore diffusion resistance can be neglected. In the middle range both resistances are important. In the range of the macropore (micropore) rate controlling the variation of micropore (macropore) diffusional resistance has little effect on the response curves. Because of the blocking of the diffusion path in 4A zeolite, the intracrystalline diffusivities of argon and nitrogen in 4A become very small. Table 5.11 shows that the ratios for these two gases, \( \tau_{ai} \), are far larger than 1 for both 4A zeolites and the diffusion rates are controlled by micropore diffusion. In such cases the macropore diffusional resistance may be negligible. Figures 5.48 and 5.49 show the responses curves of nitrogen at 40 °C in Laporte and Rhône Poulenc 4A zeolites by keeping the micropore and bulk phase diffusional resistance and varying the macropore diffusivities from the values listed in Table 5.11 to infinity. The calculated response curves for both chambers are coincident for the various macropore diffusivities. This coincidence confirms the conclusion that the macropore diffusional resistance for nitrogen in 4A zeolites is negligible when compared to the micropore diffusional resistance. The case of argon in 4A particles is similar because its intracrystalline diffusivity is smaller than for nitrogen and thus the micropore diffusional resistance is even more dominating. For oxygen the situation is different. The intracrystalline diffusivities of oxygen in 4A are much greater than these for argon and nitrogen at the same operating conditions. The mass transport rate controlling step varies from the micropore to the transient region. In such cases both macropore and micropore diffusional resistances are important contributions to the total diffusional resistance.
Table 5.11 Effective macropore and micropore diffusivities (cm²/sec) and dimensionless mass transport rate parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lap 4A</th>
<th>Lap 5A</th>
<th>RP 4A</th>
<th>RP 5A</th>
<th>RP Al</th>
<th>La Al</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nₐ</td>
<td>Nᵲ</td>
<td>Dₐ</td>
<td>Dᵰ</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>40 °C</td>
<td>0.438</td>
<td>0.438</td>
<td>0.649</td>
<td>0.649</td>
<td>0.334</td>
<td>0.190</td>
</tr>
<tr>
<td></td>
<td>0.00262</td>
<td>&gt;12.8</td>
<td>0.0219</td>
<td>&gt;11.3</td>
<td>&gt;200</td>
<td>&gt;2.20</td>
</tr>
<tr>
<td></td>
<td>0.0156</td>
<td>.0156</td>
<td>0.0259</td>
<td>.0259</td>
<td>.0360</td>
<td>.0288</td>
</tr>
<tr>
<td></td>
<td>5.2 x 10⁻¹¹</td>
<td>2.6 x 10⁻⁷</td>
<td>6.9 x 10⁻¹¹</td>
<td>3.6 x 10⁻⁷</td>
<td>0.0070</td>
<td>0.0121</td>
</tr>
<tr>
<td></td>
<td>0.0087</td>
<td>0.0093</td>
<td>0.0112</td>
<td>0.0133</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>70 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.430</td>
<td>0.430</td>
<td>0.610</td>
<td>0.610</td>
<td>0.329</td>
<td>0.188</td>
</tr>
<tr>
<td></td>
<td>0.00557</td>
<td>&gt;15.7</td>
<td>0.00489</td>
<td>&gt;13.2</td>
<td>&gt;250</td>
<td>&gt;2.65</td>
</tr>
<tr>
<td></td>
<td>0.0167</td>
<td>.0167</td>
<td>0.0267</td>
<td>.0267</td>
<td>.0388</td>
<td>.0312</td>
</tr>
<tr>
<td></td>
<td>1.2 x 10⁻¹⁰</td>
<td>3.4 x 10⁻⁷</td>
<td>1.7 x 10⁻¹⁰</td>
<td>4.6 x 10⁻⁷</td>
<td>0.0061</td>
<td>0.0086</td>
</tr>
<tr>
<td></td>
<td>0.0066</td>
<td>0.0085</td>
<td>0.0119</td>
<td>0.0137</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>95 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.461</td>
<td>0.461</td>
<td>0.612</td>
<td>0.612</td>
<td>0.313</td>
<td>0.179</td>
</tr>
<tr>
<td></td>
<td>0.00943</td>
<td>&gt;18.0</td>
<td>0.00861</td>
<td>&gt;14.7</td>
<td>&gt;300</td>
<td>3.00</td>
</tr>
<tr>
<td></td>
<td>0.0193</td>
<td>.0193</td>
<td>0.0287</td>
<td>.0287</td>
<td>.0396</td>
<td>.0319</td>
</tr>
<tr>
<td></td>
<td>2.2 x 10⁻¹⁰</td>
<td>4.2 x 10⁻⁷</td>
<td>3.8 x 10⁻¹⁰</td>
<td>5.4 x 10⁻⁷</td>
<td>0.0082</td>
<td>0.0113</td>
</tr>
<tr>
<td></td>
<td>0.0059</td>
<td>0.0144</td>
<td>0.0050</td>
<td>0.0071</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>40 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.621</td>
<td>0.621</td>
<td>0.649</td>
<td>0.649</td>
<td>0.424</td>
<td>0.270</td>
</tr>
<tr>
<td></td>
<td>0.00485</td>
<td>&gt;23.8</td>
<td>0.00363</td>
<td>&gt;11.3</td>
<td>&gt;1000</td>
<td>&gt;4.43</td>
</tr>
<tr>
<td></td>
<td>0.0221</td>
<td>.0221</td>
<td>0.0259</td>
<td>.0259</td>
<td>.0456</td>
<td>.0410</td>
</tr>
<tr>
<td></td>
<td>9.7 x 10⁻¹¹</td>
<td>4.8 x 10⁻⁷</td>
<td>1.1 x 10⁻¹⁰</td>
<td>3.6 x 10⁻⁷</td>
<td>0.0033</td>
<td>0.0089</td>
</tr>
<tr>
<td></td>
<td>0.0116</td>
<td>0.0149</td>
<td>0.0117</td>
<td>0.0128</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>70 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.642</td>
<td>0.642</td>
<td>0.573</td>
<td>0.573</td>
<td>0.431</td>
<td>0.265</td>
</tr>
<tr>
<td></td>
<td>0.00684</td>
<td>&gt;27.2</td>
<td>0.00467</td>
<td>&gt;22.8</td>
<td>&gt;1500</td>
<td>&gt;5.53</td>
</tr>
<tr>
<td></td>
<td>0.0250</td>
<td>.0250</td>
<td>0.0229</td>
<td>.0229</td>
<td>.0508</td>
<td>.0441</td>
</tr>
<tr>
<td></td>
<td>1.5 x 10⁻¹⁰</td>
<td>5.9 x 10⁻⁷</td>
<td>1.6 x 10⁻¹⁰</td>
<td>7.2 x 10⁻⁷</td>
<td>0.0097</td>
<td>0.0085</td>
</tr>
<tr>
<td></td>
<td>0.0076</td>
<td>0.0124</td>
<td>0.0116</td>
<td>0.0125</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>95 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.581</td>
<td>0.617</td>
<td>0.581</td>
<td>0.581</td>
<td>0.436</td>
<td>0.179</td>
</tr>
<tr>
<td></td>
<td>0.00867</td>
<td>&gt;19.7</td>
<td>0.00554</td>
<td>&gt;26.7</td>
<td>&gt;2000</td>
<td>&gt;3.00</td>
</tr>
<tr>
<td></td>
<td>0.0258</td>
<td>.0258</td>
<td>0.0254</td>
<td>.0254</td>
<td>.0552</td>
<td>.0319</td>
</tr>
<tr>
<td></td>
<td>2.0 x 10⁻¹⁰</td>
<td>7.0 x 10⁻⁷</td>
<td>2.0 x 10⁻¹⁰</td>
<td>9.2 x 10⁻⁷</td>
<td>0.0084</td>
<td>0.0097</td>
</tr>
<tr>
<td></td>
<td>0.0065</td>
<td>0.0133</td>
<td>0.0063</td>
<td>0.0122</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>40 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.542</td>
<td>0.542</td>
<td>0.556</td>
<td>0.556</td>
<td>0.403</td>
<td>0.263</td>
</tr>
<tr>
<td></td>
<td>0.401</td>
<td>&gt;37.8</td>
<td>0.234</td>
<td>&gt;20.5</td>
<td>&gt;1000</td>
<td>&gt;3.58</td>
</tr>
<tr>
<td></td>
<td>0.0193</td>
<td>.0193</td>
<td>0.0222</td>
<td>0.0222</td>
<td>.0433</td>
<td>.0399</td>
</tr>
<tr>
<td></td>
<td>8.0 x 10⁻⁹</td>
<td>7.6 x 10⁻⁷</td>
<td>7.4 x 10⁻⁹</td>
<td>6.5 x 10⁻⁷</td>
<td>0.0075</td>
<td>0.0075</td>
</tr>
<tr>
<td></td>
<td>0.0055</td>
<td>0.0078</td>
<td>0.0094</td>
<td>0.0066</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>70 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.538</td>
<td>0.538</td>
<td>0.583</td>
<td>0.583</td>
<td>0.409</td>
<td>0.243</td>
</tr>
<tr>
<td></td>
<td>0.777</td>
<td>&gt;48.6</td>
<td>0.468</td>
<td>&gt;26.1</td>
<td>&gt;1500</td>
<td>&gt;4.40</td>
</tr>
<tr>
<td></td>
<td>0.0210</td>
<td>.0210</td>
<td>0.0255</td>
<td>0.0255</td>
<td>.0483</td>
<td>.0405</td>
</tr>
<tr>
<td></td>
<td>1.7 x 10⁻⁸</td>
<td>1.1 x 10⁻⁶</td>
<td>1.6 x 10⁻⁸</td>
<td>9.0 x 10⁻⁷</td>
<td>0.0088</td>
<td>0.0099</td>
</tr>
<tr>
<td></td>
<td>0.0039</td>
<td>0.0051</td>
<td>0.0095</td>
<td>0.0044</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>95 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.561</td>
<td>0.561</td>
<td>0.586</td>
<td>0.586</td>
<td>0.416</td>
<td>0.254</td>
</tr>
<tr>
<td></td>
<td>1.24</td>
<td>&gt;57.7</td>
<td>0.762</td>
<td>&gt;30.8</td>
<td>&gt;2000</td>
<td>&gt;5.06</td>
</tr>
<tr>
<td></td>
<td>0.0234</td>
<td>.0234</td>
<td>0.0275</td>
<td>0.0275</td>
<td>.0526</td>
<td>.0480</td>
</tr>
<tr>
<td></td>
<td>2.9 x 10⁻⁸</td>
<td>1.4 x 10⁻⁶</td>
<td>2.8 x 10⁻⁸</td>
<td>1.1 x 10⁻⁶</td>
<td>0.0069</td>
<td>0.0104</td>
</tr>
<tr>
<td></td>
<td>0.0067</td>
<td>0.0029</td>
<td>0.0023</td>
<td>0.0047</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.48 Influence of varying the macropore diffusivity in Laporte 4A when the micropore resistance is the controlling step (N₂/He system at 40 °C)

Figure 5.49 Influence of varying the macropore diffusivity in Rhône Poulenc 4A when the micropore resistance is the controlling step (N₂/He system at 40 °C)
The macropore and micropore diffusional time constants are proportional to the square of particle diameter and the square of microparticle diameter and thus the variation of particle diameter will significantly change the macropore and microparticle diffusional resistances. In our experimental system these two diameters were limited by the solid sample supplied and we were unable to change these diameters to examine the relative importance of macropore and microparticle diffusional resistances. The non sensitivity of response curves to the macropore diffusivity implies that the macropore diffusivities of gases in 4A zeolite can not be obtained by the parameter regression method. We used the values of macropore diffusivities obtained for the 5A to simulate the response curves of gases in 4A zeolite.

When micropore diffusion is the rate controlling step, the response curves will be sensitive to the variation of micropore diffusivity. Figures 5.50 and 5.51 show the comparison of calculated response curves for nitrogen at 40 °C in Laporte and Rhône Poulenc 4A by fixing macropore and bulk phase diffusional resistances and varying the micropore diffusivity. The micropore diffusivities used for the calculation of these curves were respectively $4 \times 10^{-11}$, $10 \times 10^{-11}$, $100 \times 10^{-11}$ and $500 \times 10^{-11}$ cm$^2$/sec. With small micropore diffusivities the response curves become steeper at the beginning and have long tails. The response curves have greater sensitivity to the micropore diffusivities when $D_i$ is less than $10 \times 10^{-11}$. This sensitivity ensures the parameter regression has enough sensitivity to calculate the micropore diffusivity from the experimental response curves. The micropore diffusivities obtained by parameter regression are in this range and thus the results should be reliable. When $D_i$ is greater than $100 \times 10^{-11}$ the time constants of macropore and micropore diffusion become of the same order of magnitude and thus it is difficult to calculate the micropore diffusivity by regression.

![Graph showing response curves for different micropore diffusivities](image)

Figure 5.50 Comparison of response curves for different micropore diffusivities when macropore effective diffusivity and film mass transport coefficients are kept constant (Laporte 4A - N$_2$/He at 40 °C)

240
Figure 5.51 Comparison of response curves for different micropore diffusivities at constant macropore effective diffusivity and film mass transport coefficients (Rhône Poulenc 4A - N₂ / He at 40 °C)

The theoretical self intracrystalline diffusivities of permanent gases in 4A zeolite can be calculated by the technique developed in Chapter III. As a rough comparison between the theoretical self intracrystalline diffusivities and the experimental counter intracrystalline diffusivities in Laporte and Rhône Poulenc 4A are show in Table 5.12. The theoretical values at 40 °C, 70 °C and 95 °C were calculated by extrapolation of the values given at 24 °C using the predicted activation energy. The results presented in Table 5.12 show that experimental counter diffusivities are smaller than these theoretically predicted. There is a counter diffusion of the carrier gas, helium, and the existence of carrier gas molecules in the diffusion path will block the diffusion of the solute molecules. Such blocking results in counter diffusivities smaller than the corresponding self diffusivities. The possible crystal defaults in practical synthetic zeolites will also reduce the intracrystalline diffusivities.

Table 5.12 Comparison of predicted and experimental intracrystalline diffusivities (cm²/s)

<table>
<thead>
<tr>
<th></th>
<th>Predicted Values</th>
<th>Laporte 4A</th>
<th>Rhône Poulenc 4A</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ar</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 °C</td>
<td>3.2 x 10⁻¹⁰</td>
<td>5.2 x 10⁻¹¹</td>
<td>6.9 x 10⁻¹¹</td>
</tr>
<tr>
<td>70 °C</td>
<td>8.1 x 10⁻¹⁰</td>
<td>1.2 x 10⁻¹⁰</td>
<td>1.7 x 10⁻¹⁰</td>
</tr>
<tr>
<td>95 °C</td>
<td>1.6 x 10⁻⁹</td>
<td>2.2 x 10⁻¹⁰</td>
<td>3.8 x 10⁻¹⁰</td>
</tr>
<tr>
<td><strong>N₂</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 °C</td>
<td>1.5 x 10⁻⁹</td>
<td>9.7 x 10⁻¹¹</td>
<td>1.1 x 10⁻¹⁰</td>
</tr>
<tr>
<td>70 °C</td>
<td>3.4 x 10⁻⁹</td>
<td>1.5 x 10⁻¹⁰</td>
<td>1.6 x 10⁻¹⁰</td>
</tr>
<tr>
<td>95 °C</td>
<td>6.0 x 10⁻⁹</td>
<td>2.0 x 10⁻¹⁰</td>
<td>2.0 x 10⁻¹⁰</td>
</tr>
<tr>
<td><strong>O₂</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 °C</td>
<td>4.6 x 10⁻⁸</td>
<td>8.0 x 10⁻⁹</td>
<td>7.4 x 10⁻⁹</td>
</tr>
<tr>
<td>70 °C</td>
<td>7.0 x 10⁻⁸</td>
<td>1.7 x 10⁻⁸</td>
<td>1.6 x 10⁻⁸</td>
</tr>
<tr>
<td>95 °C</td>
<td>9.5 x 10⁻⁸</td>
<td>2.9 x 10⁻⁸</td>
<td>2.8 x 10⁻⁸</td>
</tr>
</tbody>
</table>

241
The theoretical prediction of micropore diffusivities of small molecules such as argon, nitrogen and oxygen in 5A zeolite crystals shows that micropore diffusion is much faster than in 4A. The theoretically predicted diffusivity of nitrogen in 5A zeolite at 313.15 K is \(6.22 \times 10^{-7} \text{ cm}^2/\text{s}\) (calculated by extrapolating the diffusivities using the Ahrenius equation) and the corresponding \(N_e\) for Laporte 5A is about 10 and thus larger than the experimental one due to the difference between self and counter diffusivities and we used the \(N_e\) given in Table 5.11 and equal to 0.438. For this case the time constant ratio is about 0.05 and thus the micropore diffusional resistance is smaller than the bulk and macropore diffusional resistances. For negligible micropore resistance the accurate values of effective micropore diffusivity can not be obtained by the curve matching technique because there is no sensitivity. Figure 5.52 shows the theoretical response curves for both chambers for nitrogen at 40 °C in Laporte 5A keeping the macropore and molecular diffusion parameters and varying the micropore diffusivities from \(1. \times 10^{-7} \text{ cm}^2/\text{s}\) to infinity. The curves in Figure 5.52 are almost coincident and this confirms the above analysis about the relative importance of micropore and macropore diffusional resistances. For the cases of argon, oxygen and nitrogen in Laporte 5A at higher temperature the micropore diffusional resistance becomes even less important because the micropore diffusional resistance decreases more quickly than macropore resistance with the increase of temperature, that is the time constant decreases with increasing temperature. The particle dimension of Rhône Poulenc 5A is larger than Laporte 5A and roughly the macropore resistance is also larger (the macropore diffusivities are close). In such situation the micropore diffusivity can not be obtained by this method.

![Graph showing dimensionless concentration C vs. dimensionless time θ]

**Figure 5.52** Comparison of the cell responses for different micropore diffusivities in Laporte 5A for system \(N_2/\text{He}\) at 40 °C

242
The theoretical study of permanent gas diffusion in blocked zeolite micropores shown that such diffusion is an activated process and that the temperature dependency of diffusivities can be expressed by Ahrenius equation. Figure 5.53 shows the experimental temperature dependency of micropore diffusivities of Ar, N₂ and O₂ in Laporte and in Rhône Poulenc 4A and the corresponding activation energies obtained from the experimental curves are listed in Table 5.13. All these experimental data agree well with the Ahrenius equation. Because the temperature range of experimental data is not enough wide and there are possible experimental and parameter regression errors the absolute values of activation energies for these systems are very rough. Nevertheless the tendency is qualitatively good.

![Figure 5.53 Temperature dependency of experimental micropore diffusivities of Ar, N₂ and O₂ in Laporte (solid lines) and in Rhône Poulenc 4A (dashed lines)](image)

Table 5.13 Experimental activation energies of micropore diffusivities

<table>
<thead>
<tr>
<th></th>
<th>Laporte 4A</th>
<th>Rhône Poulenc 4A</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ar</td>
<td>N₂</td>
</tr>
<tr>
<td>Activation energy KJ/mol</td>
<td>25.14</td>
<td>21.02</td>
</tr>
</tbody>
</table>

The micropore dimension of alumina is not uniform and the typical pore radius is in the range of 15 - 60 Å depending on the preparation process [Yang, 1987]. This value is
much larger than the permanent gas dimensions and so the micropore diffusion resistance may be unimportant to the total resistance. Our simulations also confirm the difficulty in obtaining the micropore mass transport rate parameters by the matching technique due to the negligible micropore resistance. For alumina samples the simulation also shown that the micropore diffusion resistance is small and negligible.

The time constant ratios of bulk phase diffusion and macropore diffusion for all these cases are in the range of 0.15 to 0.6 and thus both bulk and macropore diffusional resistances make similar contributions to the total mass transport resistance. The accuracy of parameter regression to calculate the macropore effective diffusivity by curve matching is less effective than in the case of the micropore diffusivity in 4A zeolite for nitrogen and argon. As an illustration Figures 5.54 to 5.57 show the effect of different macropore effective diffusivities on the calculated response curves of argon, nitrogen and oxygen at 40 °C in Laporte 5A, Rhône Poulenc 5A, Rhône Poulenc alumina and LaRoche alumina. In these figures the dimensionless micropore mass transport parameter, $N_b$, was kept in the low limit values of Table 5.12 and the $N_a$ was varied as 1/9, 1/3, 3, 9 of the values in that table. Decreasing $N_a$ means an increase of the importance of macropore diffusional resistance when compared with the bulk phase resistance and the sensitivity for parameter regression of the macropore effective diffusivity also increases.

\[
\begin{align*}
\text{top chamber} \\
\text{bottom chamber}
\end{align*}
\]

\[D_i = 4.8 \times 10^{-7} \text{cm}^2/\text{s} \]

\[N_i = 23.8 \]

\[k_f = 11.42 \text{ cm/s} \]

\[N_f = 5.46 \]

Figure 5.54 Cell responses for different macropore diffusivities in Laporte 5A for system O$_2$ / He at 40 °C
Figure 5.55 Cell responses for different macropore diffusivities in Rhône Poulenc 5A for system Ar / He at 40 °C

Figure 5.56 Cell responses for different macropore diffusivities in Rhône Poulenc alumina for system N₂ / He at 40 °C
The effect of the variation of macropore diffusion resistance with temperature is similar to these figures. The mechanism of bulk phase diffusion is the molecular diffusion and the mechanism of macropore diffusion is mainly molecular diffusion too. In a small temperature range the temperature dependency of the ratio between the bulk phase diffusional resistance and macropore diffusional resistance is small.

As an illustration Figures 5.58 to 5.65 show the experimental and simulated response curves of both chambers for argon, nitrogen and oxygen at different temperatures in Laporte 4A and 5A, Rhône Poulenc 4A and 5A, Rhône Poulenc alumina and LaRoche alumina. The dashed lines in these figures are simulated values and the solid lines are experimental data. The simulated curves fit well the experimental ones for 4A zeolite and alumina systems. The simulated results are poor for 5A. The results for other cases of gases at different temperatures are similar. The differences of macropore effective diffusivities among argon, nitrogen and oxygen are small. The adsorption equilibrium constants of nitrogen in 5A visibly differ from other gases in 5A. While the difference on adsorption equilibria of gases in 4A and alumina is small.
Figure 5.58 Simulated (dashed lines) and experimental (solid lines) results for nitrogen in Laporte 4A at 40 °C.

Figure 5.59 Simulated (dashed lines) and experimental (solid lines) results for argon in Laporte 5A at 95 °C.
Figure 5.60 Simulated (dashed lines) and experimental (solid lines) results for nitrogen in Laporte 5A at 40 °C.

Figure 5.61 Simulated (dashed lines) and experimental (solid lines) results for argon in Rhône Poulenc 4A at 70 °C.
Figure 5.62 Simulated (dashed lines) and experimental (solid lines) results for oxygen in Rhône Poulenc 4A at 70 °C

Ni = 0.468
Na = 0.583
Nf = 5.66
Ns = 17.88

Figure 5.63 Simulated (dashed lines) and experimental (solid lines) results for nitrogen in Rhône Poulenc 5A at 40 °C

Ni = 30.8
Na = 0.586
Nf = 5.73
Ns = 17.81
Figure 5.64 Simulated (dashed lines) and experimental (solid lines) results for nitrogen in Rhône Poulenc alumina at 40 °C

Figure 5.65 Simulated (dashed lines) and experimental (solid lines) results for argon in LaRoche alumina at 40 °C
The simulated results for both Laporte and Rhône Poulenc 5A were poorer than for the corresponding 4A since for 5A zeolite the microparticle diffusional resistance is negligible when compared to macropore diffusional resistance; the whole mass transport process of gases in 5A is faster than in 4A and 5A zeolites have larger adsorption capacity than 4A. These factors result in that there are more difficulties to determine experimental responses. The standard deviations, $\delta_i$, of the simulated results to the experimental data for all systems were shown in Table 5.11.

### 2.2 Optimization of Cell Dimensions and Operating Conditions

The previously simulated results shown that the effective micropore diffusivities can not be obtained by the parameter regression when the micropore diffusional resistance is unimportant compared with macropore and bulk phase diffusional resistances. The parameter to express the relative importance of individual diffusional resistances in series is the diffusional time constant ratio and in our system this ratio can be expressed by using the dimensionless mass transport parameters. In order to determine the effective micropore diffusivity it is expected that the time constant ratios $\tau_{ai} = N_d/N_i$ and $\tau_{bi} = N_b/N_i$ are far greater than unity. For a given solid sample and cell geometric dimensions lower experimental temperatures are beneficial to increase sensitivity since micropore diffusion is usually an activated process and thus the effective micropore diffusivity decreases more than the effective macropore and bulk phase diffusivities. When the experimental temperature is given, in order to increase sensitivity a small particle size should be used and the cell dimensions should be designed to obtain large values of $N_b$. It is more difficult to change the microparticle dimensions and keep the physical and chemical properties than to change the particle dimensions. The easier way to increase the value of $\tau_{ai}$ is using a small particle because $\tau_{ai}$ is inversely proportional to the square of the particle diameter. Because the diffusional resistances of bulk phase, macropores and micropores are in series, the sensitivity to the effective micropore diffusivity is also limited by the bulk phase resistance. Increase of the time constant ratio, $\tau_{bi}$ is relatively difficult since the reduction of the cell thickness is limited by experimental constraints. In order to illustrate the situation let us make the simplification of neglecting the film resistance and then the equations (4.78) and (4.79) reduce to

$$C_t(\infty) = \frac{1 + N_bN_s}{1 + 2N_bN_s} \quad (4.78a)$$

$$C_s(\infty) = \frac{N_bN_s}{1 + 2N_bN_s} \quad (4.79a)$$

The variation of $N_b$ with different gases and solid samples is small and $N_s$ is only dependent on the cell dimensions and thus the steady state concentration responses are close to each other.

The product $N_bN_s$ is inversely proportional to the cell thickness. When $N_bN_s$ is much greater than the unity the film mass transport coefficient can not be determined because the top and bottom steady state responses are too close.

251
When micropore diffusion is the rate controlling step the variation of effective macropore diffusivity has little effects on the response curves and thus the matching technique gives less information about the macropore diffusion. In our experimental systems the diffusion of permanent gases in 4A zeolite is a typical case of the micropore rate controlling step. While the diffusion of permanent gases in 5A zeolite is a typical case of the macropore rate controlling step. The parameter regression sensitivity for the effective macropore diffusivity is less than for the micropore diffusivity even in the case of the macropore rate controlling step due to the existence of the bulk phase diffusional resistance. In our system the relative importance of the bulk phase diffusional resistance is similar to the macropore diffusional resistance.

The determination of adsorption equilibrium constants is independent of the mass transport equations and can be calculated by the global mass balance. So there is no requirement of linearity and high concentration can be used to make more accurate the measurements.

3 SINGLE PELLET STRING FIXED BED

Chromatography is a useful technique for the determination of adsorption equilibria and mass transport rate parameters of gases in porous solids. We use the single pellet string fixed bed method to determine the macropore and micropore diffusivities of argon, nitrogen and oxygen in Rhône Poulenc 4A and 5A zeolites and LaRoche alumina. The physical and pore network structural properties for these solid samples are listed in Table 5.7. The choice of the column diameter should satisfy the requirements of the single pellet string fixed bed [Scott et al., 1974], that is, the ratio of the column internal diameter to the particle diameter should be 1.1 ~ 1.4. According to the solid sample dimensions we used as column dimensions 2.0 × 1500 mm (internal diameter × length) for Rhône Poulenc 4A and 5A and 4.5 × 1500 mm (internal diameter × length) for LaRoche alumina. The choice of the column length was done considering the interest of having a reasonable Peclet number and space time and is discussed in detail later.

Similarly to the shallow bed diffusion cell technique, the adsorption equilibrium constants can be obtained by using the global mass balance between input and output. The results are shown in Table 5.14. As a comparison the adsorption equilibrium constants obtained by the shallow bed diffusion cell technique are also shown. They are fairly in agreement with each other.

The models in equations (4.96) to (4.104) developed for the single pellet string fixed bed in Chapter IV imply the conditions of linear adsorption isotherm and constant interstitial velocity. These conditions require a small tracer concentration in order to ensure linear isotherm and neglect the velocity variation due to tracer adsorption; also pressure drop is negligible when compared to the absolute pressure so that density variation can be neglected. In our experiments the inlet tracer concentration is lower than 5% and the maximum pressure drop is less than 60 mbar. So the velocity can be considered constant and the isotherms of argon, nitrogen and oxygen in these samples are linear in the experimental concentration range. Helium was used as the carrier and the desired concentration was achieved by controlling the flow rate of carrier and tracer. Table 5.15 lists the experimental conditions and regressed results. The microparticle diffusivities and corresponding dimensionless parameter, \( N_m \) in 5A are the minimum regressed values until the calculated response curves were not affected by varying more this parameter.
Table 5.14 Comparison of the dimensionless adsorption equilibrium constants determined by the shallow bed diffusion cell (SBDC) and by the single pellet string fixed bed (SPSB)

<table>
<thead>
<tr>
<th>Sample</th>
<th>RP 4A</th>
<th>RP 5A</th>
<th>LaRoche alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SBDC</td>
<td>SPSB</td>
<td>SBDC</td>
</tr>
<tr>
<td>Ar</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 °C</td>
<td>2.657</td>
<td>2.216</td>
<td>2.648</td>
</tr>
<tr>
<td>70 °C</td>
<td>1.981</td>
<td>1.773</td>
<td>2.084</td>
</tr>
<tr>
<td>95 °C</td>
<td>1.467</td>
<td>1.582</td>
<td>1.472</td>
</tr>
<tr>
<td>N₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 °C</td>
<td>5.271</td>
<td>5.341</td>
<td>10.47</td>
</tr>
<tr>
<td>95 °C</td>
<td>2.669</td>
<td>2.280</td>
<td>4.369</td>
</tr>
<tr>
<td>O₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 °C</td>
<td>3.125</td>
<td>3.488</td>
<td>3.593</td>
</tr>
<tr>
<td>70 °C</td>
<td>2.108</td>
<td>2.306</td>
<td>2.533</td>
</tr>
<tr>
<td>95 °C</td>
<td>1.938</td>
<td>2.113</td>
<td>1.837</td>
</tr>
</tbody>
</table>

Table 5.15 Effective macropore and micropore mass transport rate parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>40 °C</th>
<th>70 °C</th>
<th>95 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>u cm/s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>RP 4A</td>
<td>RP 5A</td>
<td>La Al</td>
</tr>
<tr>
<td>40 °C</td>
<td>9.12</td>
<td>6.264</td>
<td>6.15</td>
</tr>
<tr>
<td>RP 5A</td>
<td>9.12</td>
<td>6.264</td>
<td>6.15</td>
</tr>
<tr>
<td>La Al</td>
<td>7.81</td>
<td>2.882</td>
<td>2.676</td>
</tr>
<tr>
<td>70 °C</td>
<td>10.0</td>
<td>6.615</td>
<td>6.615</td>
</tr>
<tr>
<td>RP 4A</td>
<td>10.0</td>
<td>6.615</td>
<td>6.615</td>
</tr>
<tr>
<td>RP 5A</td>
<td>10.0</td>
<td>6.615</td>
<td>6.615</td>
</tr>
<tr>
<td>La Al</td>
<td>8.56</td>
<td>2.676</td>
<td>3.05</td>
</tr>
<tr>
<td>95 °C</td>
<td>10.7</td>
<td>7.033</td>
<td>7.033</td>
</tr>
<tr>
<td>RP 4A</td>
<td>10.7</td>
<td>7.033</td>
<td>7.033</td>
</tr>
<tr>
<td>RP 5A</td>
<td>10.7</td>
<td>7.033</td>
<td>7.033</td>
</tr>
<tr>
<td>La Al</td>
<td>9.18</td>
<td>2.687</td>
<td>3.65</td>
</tr>
<tr>
<td>N₂</td>
<td>RP 4A</td>
<td>RP 5A</td>
<td>La Al</td>
</tr>
<tr>
<td>40 °C</td>
<td>9.12</td>
<td>6.819</td>
<td>6.557</td>
</tr>
<tr>
<td>RP 5A</td>
<td>9.12</td>
<td>6.819</td>
<td>6.557</td>
</tr>
<tr>
<td>La Al</td>
<td>7.81</td>
<td>3.930</td>
<td>5.46</td>
</tr>
<tr>
<td>70 °C</td>
<td>10.0</td>
<td>6.557</td>
<td>6.557</td>
</tr>
<tr>
<td>RP 4A</td>
<td>10.0</td>
<td>6.557</td>
<td>6.557</td>
</tr>
<tr>
<td>RP 5A</td>
<td>10.0</td>
<td>6.557</td>
<td>6.557</td>
</tr>
<tr>
<td>La Al</td>
<td>8.56</td>
<td>3.861</td>
<td>6.48</td>
</tr>
<tr>
<td>95 °C</td>
<td>10.7</td>
<td>6.867</td>
<td>6.867</td>
</tr>
<tr>
<td>RP 4A</td>
<td>10.7</td>
<td>6.867</td>
<td>6.867</td>
</tr>
<tr>
<td>RP 5A</td>
<td>10.7</td>
<td>6.867</td>
<td>6.867</td>
</tr>
<tr>
<td>La Al</td>
<td>9.18</td>
<td>4.072</td>
<td>7.61</td>
</tr>
<tr>
<td>O₂</td>
<td>RP 4A</td>
<td>RP 5A</td>
<td>La Al</td>
</tr>
<tr>
<td>40 °C</td>
<td>9.12</td>
<td>7.314</td>
<td>7.314</td>
</tr>
<tr>
<td>RP 5A</td>
<td>9.12</td>
<td>7.314</td>
<td>7.314</td>
</tr>
<tr>
<td>La Al</td>
<td>7.81</td>
<td>3.908</td>
<td>4.35</td>
</tr>
<tr>
<td>70 °C</td>
<td>10.0</td>
<td>7.603</td>
<td>7.603</td>
</tr>
<tr>
<td>RP 4A</td>
<td>10.0</td>
<td>7.603</td>
<td>7.603</td>
</tr>
<tr>
<td>RP 5A</td>
<td>10.0</td>
<td>7.603</td>
<td>7.603</td>
</tr>
<tr>
<td>La Al</td>
<td>8.56</td>
<td>3.494</td>
<td>5.39</td>
</tr>
<tr>
<td>95 °C</td>
<td>10.7</td>
<td>7.598</td>
<td>7.598</td>
</tr>
<tr>
<td>RP 4A</td>
<td>10.7</td>
<td>7.598</td>
<td>7.598</td>
</tr>
<tr>
<td>RP 5A</td>
<td>10.7</td>
<td>7.598</td>
<td>7.598</td>
</tr>
<tr>
<td>La Al</td>
<td>9.18</td>
<td>3.694</td>
<td>5.93</td>
</tr>
</tbody>
</table>
The major inconvenience of the chromatographic methods for the determination of mass transport rate parameters is that the concentration response curves are affected by the flow pattern inside the column. Our model equations (4.96) to (4.104) include macropore and micropore effective diffusivities, film mass transport coefficient and axial dispersion. Theoretically, the effects of film mass transport resistance and axial dispersion on the concentration response curves can be isolated by varying the flow rate. One of the main advantages of the single pellet string bed is that there is a large space between the pellets and the column wall and thus high velocity of the gas can be achieved without visible pressure drop. In order to show the effects of varying the velocity on the concentration response curves, we use the Ranz - Marshall empirical correlation [ Yang, 1987 ] as a rough estimation of the film mass transport coefficient:

\[
\frac{2k_f R_o}{D_m} = 2.0 + 0.6 \left( \frac{v}{\rho D_m} \right)^{1/3} \left( \frac{2R_o G_f}{v} \right)^{1/2}
\]  

(5.32)

where \(G\) is the superficial mass flux based on the unit cross sectional area of the empty bed and \(\rho\) is the gas density. This correlation shows that the film mass transport coefficient is proportional to the square root of the flow rate. The particle radius for cylindrical geometry was calculated by the equivalent hydraulic radius defined as

\[
R_o = 3V_s/S_a
\]

(5.33)

where \(V_s\) and \(S_a\) are respectively the volume and surface area of the cylindrical particle. The estimated film mass transport coefficients, \(k_f\), and dimensionless film coefficients, \(N_o\), for argon, nitrogen and oxygen at 40 °C, 70 °C and 95 °C in Rhône Poulenc 5A and LaRoche alumina are shown in Table 5.16. The Ranz - Marshall empirical correlation for the calculation of the mass transport coefficient was developed for a column packed with small particles, that is, the ratio of column to the particle diameter is greater than 20 so that the wall effects are negligible. When applied to the single pellet string column does not give precise results. But we just use this correlation as an order of the magnitude estimation and the following simulation results show that the film mass transport resistance is unimportant even in a range much smaller than the estimated values by equation (5.33).

Figure 5.66 shows the theoretical concentration response curves of nitrogen at 40 °C in Rhône Poulenc 5A with different film mass transport coefficients going from 10 times smaller than the estimated value to infinity. Within this large range which should already cover the estimation error the response curves are coincident. Because the film mass transport resistance is in series with other diffusional resistances inside the particle, the relative importance can be illustrated by considering the ratios of the dimensionless mass transport parameters. For this system where macropore diffusion is the rate controlling step the ratio of \(N_f/N_a\) is of the order of 100 and thus the film can be safely neglected. For the case of gases in 4Å zeolite the main diffusional resistance is the micropore diffusion and the contribution of film mass transport resistance to total resistance becomes even less important. The differences of the film mass transport coefficients among argon, nitrogen and oxygen are small. The temperature dependency of the film mass transport coefficient is similar to that of the macropore diffusivity. As a conclusion for our experimental operating conditions and systems the film resistance effects on the concentration responses at the outlet can be neglected.
Table 5.16 Estimated film mass transport coefficients [Yang, 1987] and axial dispersion coefficients [Yang, 1987] and corresponding dimensionless parameters

<table>
<thead>
<tr>
<th></th>
<th>40 °C</th>
<th>70 °C</th>
<th>95 °C</th>
<th>40 °C</th>
<th>70 °C</th>
<th>95 °C</th>
<th>40 °C</th>
<th>70 °C</th>
<th>95 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ar</td>
<td>N₂</td>
<td>O₂</td>
<td>Ar</td>
<td>N₂</td>
<td>O₂</td>
<td>Ar</td>
<td>N₂</td>
<td>O₂</td>
</tr>
<tr>
<td></td>
<td>Rp 5A</td>
<td>La Al</td>
<td>Rp 5A</td>
<td>La Al</td>
<td>Rp 5A</td>
<td>La Al</td>
<td>Rp 5A</td>
<td>La Al</td>
<td>Rp 5A</td>
</tr>
<tr>
<td>u cm/s</td>
<td>9.12</td>
<td>10.0</td>
<td>10.7</td>
<td>9.12</td>
<td>10.0</td>
<td>10.7</td>
<td>9.12</td>
<td>10.0</td>
<td>10.7</td>
</tr>
<tr>
<td>k_f cm/s</td>
<td>4.91</td>
<td>5.72</td>
<td>6.43</td>
<td>4.91</td>
<td>5.72</td>
<td>6.43</td>
<td>4.91</td>
<td>5.72</td>
<td>6.43</td>
</tr>
<tr>
<td>N_f</td>
<td>504.</td>
<td>536.</td>
<td>562.</td>
<td>504.</td>
<td>536.</td>
<td>562.</td>
<td>504.</td>
<td>536.</td>
<td>562.</td>
</tr>
<tr>
<td>D_ass cm/s</td>
<td>7.86</td>
<td>9.15</td>
<td>10.3</td>
<td>7.86</td>
<td>9.15</td>
<td>10.3</td>
<td>7.86</td>
<td>9.15</td>
<td>10.3</td>
</tr>
<tr>
<td>P_e</td>
<td>174.</td>
<td>164.</td>
<td>156.</td>
<td>174.</td>
<td>164.</td>
<td>156.</td>
<td>174.</td>
<td>164.</td>
<td>156.</td>
</tr>
<tr>
<td></td>
<td>Rp 5A</td>
<td>La Al</td>
<td>Rp 5A</td>
<td>La Al</td>
<td>Rp 5A</td>
<td>La Al</td>
<td>Rp 5A</td>
<td>La Al</td>
<td>Rp 5A</td>
</tr>
<tr>
<td>u cm/s</td>
<td>7.81</td>
<td>8.56</td>
<td>9.18</td>
<td>7.81</td>
<td>8.56</td>
<td>9.18</td>
<td>7.81</td>
<td>8.56</td>
<td>9.18</td>
</tr>
<tr>
<td>k_f cm/s</td>
<td>2.07</td>
<td>2.41</td>
<td>2.71</td>
<td>2.07</td>
<td>2.41</td>
<td>2.71</td>
<td>2.07</td>
<td>2.41</td>
<td>2.71</td>
</tr>
<tr>
<td>D_ass cm/s</td>
<td>2.99</td>
<td>3.49</td>
<td>3.92</td>
<td>2.99</td>
<td>3.49</td>
<td>3.92</td>
<td>2.99</td>
<td>3.49</td>
<td>3.92</td>
</tr>
<tr>
<td>P_e</td>
<td>391.</td>
<td>368.</td>
<td>351.</td>
<td>391.</td>
<td>368.</td>
<td>351.</td>
<td>391.</td>
<td>368.</td>
<td>351.</td>
</tr>
</tbody>
</table>

Figure 5.66 Comparison of response curves using different film mass transport coefficients for N₂/He in Rhône Poulenc 5A at 40 °C
The experimental response curves of argon, nitrogen and oxygen in Rhône Poulenc 5A zeolite are coincident. The range of variation of the experimental flow rate is limited by pressure drop through the column and by flow meter controllers and it is about 3 - 5 times. The variation of the experimental flow rate will result in the variation of the flow pattern and thus the variation of the axial dispersion coefficient.

Similarly, the axial dispersion coefficients or Peclet numbers can be related to the flow rate and the gas physical properties by the empirical equation [Yang, 1987]

\[
\frac{\omega_b D_{ax}}{D_m} = 2.0 + 0.5 \left( \frac{\nu}{\rho D_m} \right) \left( \frac{2\tau_a G}{G} \right) \frac{1}{\nu} 
\] (5.34)

This correlation is principally applicable to an ordinary fixed bed. For the single string fixed bed the estimation may be very rough. The importance of the axial dispersion in the response curves can be verified by changing the flow rate. Figure 5.67 shows the breakthrough curves for different axial dispersion coefficients for nitrogen in LaRoche alumina at 40 °C. In Figure 5.67 the Peclet number was varied from a value five times smaller than the estimated value to a value five times larger. Because of the small macropore diffusion resistance and negligible micropore diffusional resistance response curves should be more sensible to axial dispersion. In the range studied the response curves are coincident meaning that the use of the rough estimated value for axial dispersion by equation (5.34) does not cause an observable error in the simulated response curves. For illustration Figure 5.68 shows the theoretically calculated response curves for nitrogen in Rhône Poulenc 4A zeolite at 40 °C when axial dispersion coefficients vary from a value five times smaller than the estimated value to infinity. The curves are also coincident. Because of the relatively large microparticle diffusional resistance the axial dispersion effect on the response variance is reduced in 4A zeolite and thus the curves are coincident in a so large range.

The dimensionless parameter that represents the importance of axial dispersion is the Peclet number, Pe. \(D_{ax}\) is proportional to the flow rate and thus the Peclet number is inversely proportional to it in the low flow rate range. In the high flow rate range it is independent of the flow rate. In our experiments, high flow rate and a long column were used so that the Peclet number was large.

The importance of axial dispersion, film mas transport resistance, macropore and micropore diffusional resistance contributions to total mass transport resistance can be examined using moment analysis. Similarly to the single pellet diffusion cell we define the system transfer function that describes the dynamic characteristics of the column as the ratio of the column outlet concentration response and the column inlet concentration in Laplace domain. From the system transfer function the first noncentral and second central moments can be calculated. Haynes and Sarma [1973] gave the results for a fixed bed model including axial dispersion, film mass transport resistances, macropore and micropore diffusional resistances and the similar results for our case models were given by Ruthven [Ruthven, 1984]

\[
\mu_1 = \frac{L}{u} \left[ 1 + \left( \frac{1 - \omega_b}{\omega_b} \right) \omega_a + \left( \frac{1 - \omega_b}{\omega_b} \right) (1 - \omega_a) K \right] = \frac{L}{u} \left[ 1 + \left( \frac{1 - \omega_b}{\omega_b} \right) K \right] 
\] (5.35)
Figure 5.67 Comparison of response curves using different axial dispersion coefficients for $\text{N}_2$/He in LaRoche alumina at 40 °C

Figure 5.68 Comparison of response curves using different axial dispersion coefficients for $\text{N}_2$/He in Rhône Poulenc 4A at 40 °C
where \( \mathcal{K} = \omega_a + (1 - \omega_a)K \)

\[
\sigma^2 = \frac{2L}{u} \frac{D_{ax}}{u^2} \left[ 1 + \left( \frac{1 - \omega_b}{\omega_b} \right)\mathcal{K} \right]^2 + \frac{2L}{3u} \frac{R_a}{k_f} \frac{1 - \omega_b}{\omega_b} \mathcal{K}^2 + \frac{2L}{15u} \frac{R_i^2}{1 - \omega_b} \frac{1 - \omega_b}{\omega_b} \mathcal{K}^2
\]
\[
+ \frac{2L}{15u} \frac{R_i^2}{D_i} \frac{1 - \omega_b}{\omega_b} (1 - \omega_a)K^2
\]  

(5.36)

When \( \mathcal{K} \gg \omega_a \), which is approximately true in our system, this expression can be simplified to:

\[
\frac{\sigma^2}{2\mu_i^2} = \frac{D_{ax}}{uL} \frac{u}{1 - \omega_b} \left( \frac{R_a}{3k_f} + \frac{R_i^2}{15\omega_aD_i} \right) [1 + \frac{\omega_b}{(1 - \omega_b)\mathcal{K}}]^2
\]  

(5.37)

The corresponding dimensionless form of these three equations expressed in our dimensionless variables are:

\[
\mu_i = \nu \left[ 1 + \phi \omega_a + \phi (1 - \omega_a)K \right] = \nu \left[ 1 + \phi \mathcal{K} \right]
\]  

(5.35a)

\[
\sigma^2 = \frac{2\nu^2}{P_e} \left[ 1 + \phi \mathcal{K} \right]^2 + \frac{2\nu^2}{3N_f} \phi \mathcal{K}^2 + \frac{2\nu^2}{15N_i} \phi \mathcal{K}^2 + \frac{2\nu^2}{15N_i} \phi (1 - \omega_a)K^2
\]  

(5.36a)

\[
\frac{\sigma^2}{2\mu_i^2} = \frac{1}{P_e} + \phi \nu^2 \left( \frac{1}{3N_f} + \frac{1}{15N_a} + \frac{1}{15KN_i} \right) [1 + \frac{1}{\phi \mathcal{K}}]^2
\]  

(5.37a)

The various terms in equation (5.37a) are equivalent to the corresponding mass transport resistances. The mass transport resistances for axial dispersion \( (R_{ax}) \), film \( (R_f) \), macropore \( (R_a) \) and microparticle \( (R_i) \) diffusion are, respectively:

\[
R_{ax} = \frac{1}{P_e}
\]  

(5.38)

\[
R_f = \frac{(\phi \mathcal{K})^2 \phi \nu^2}{3N_f (1 + \phi \mathcal{K})^2}
\]  

(5.39)

258
\[ R_a = \frac{(\phi_b \mathcal{K})^2 \phi_b v^2}{15 \sigma_a N_a (1 + \phi_b \mathcal{K})^2} \quad (5.40) \]

\[ R_i = \frac{(\phi_b \mathcal{K})^2 \phi_b v^2}{15 N_i (1 + \phi_b \mathcal{K})^2} \quad (5.41) \]

It is evident that the contributions of axial dispersion and the various mass transport resistances are linearly additive. Equation (5.34) shows that the first moment is independent of axial dispersion and of the various mass transport resistances and this conclusion is expected because the first moment only expresses the response gravity center. Because of the additivity of the various mass transport resistances we can examine them by comparing the relative size of the various terms. Table 5.17 shows the relative size of axial dispersion, film mass transport, macropore diffusional and micropore diffusional resistances at the experimental conditions listed in Table 5.15. The axial dispersion and film mass transport coefficients were estimated by equations (5.32) and (5.34). It should be mentioned that equations (5.35), (5.36) and (5.37) were obtained based on the mass transport model where one of the boundary conditions was set as \( C(z=\infty) \) limited. While for our model we considered the boundary condition at column outlet as \( \frac{\partial C}{\partial Z} = 0 \). For long columns the difference between the response concentrations using these two different boundary conditions are small. In our experimental systems the column length is quite long and we just used these tools to compare the relative importance of the various mass transport resistances.

Data also show that the microparticle diffusional resistances for argon and nitrogen in Rhône Poulenc 4A always dominate the various resistances. Whereas for all gases in 5A zeolite the microparticle diffusional resistances are negligible compare to the macropore diffusional resistances. The axial dispersion effects on the outlet concentration response variance are of the same order of magnitude as the macropore diffusional resistances. For LaRoche alumina the macropore diffusional resistances are larger than for Rhône Poulenc zeolite due to its larger particle dimension. One of our interests to compare the relative size of the various mass transport resistances is to illustrate that the film mass transport resistance is negligible when compared to other resistances. For 5A zeolite and alumina the main mass transport resistance is the macropore diffusion and thus the comparison between the film mass transport resistance term and macropore diffusional resistance can explain their relative importance. In our experimental conditions, the ratios between the macropore diffusional resistance and the film mass transport resistance are around 15 \~ 20, that is if we neglect the film mass transport resistance the error will be of the same order. If we further consider the axial dispersion term, the error will be smaller since the axial dispersion has also an important contribution to the response variance. For argon and nitrogen in 4A zeolite neglecting the film mass transport resistance will be much more safe because the microparticle diffusional resistance is much larger than all other resistances. Even for oxygen in 4A zeolite the existence of the microparticle diffusional resistance will reduce the relative importance of film mass transport resistance. The relative importance between macropore and microparticle diffusional resistances of argon and nitrogen shows that only the important resistance terms and the corresponding mass transport coefficients can be determined by our experimental and parameter regression technique. Only for oxygen in 4A zeolite, the macropore and microparticle diffusional resistances are of the same order of magnitude and both can be obtained by the technique. These conclusions are coherent with those obtained from the parameter regression.
Similarly to the shallow bed diffusion cell the precision on parameter estimation is dependent on the sensitivity of the concentration response curves to the parameters to be regressed. Only the diffusivity in the mass transport rate controlling step can be determined in the diffusion resistances in series model. Macropore diffusivity in 4A has negligible effect on the response curves. Figure 5.69 compares the response curves obtained for different macropore diffusivities for nitrogen at 40 °C in Rhône Poulenc 4A. The macropore diffusivities were varied from 1/100 to 50 times the values in Table 5.15. Only one curve is visibly different from the others. The effective macropore diffusivities of argon and nitrogen in 4A can not be obtained by this method. Taking into account of the similarity of macropore network structures of 4A and 5A particles, we used the values obtained for the 5A.

In order to illustrate the reliability of effective micropore diffusivities determined by the parameter regression technique Figure 5.70 shows the calculated response curves for nitrogen at 40 °C in Rhône Poulenc 4A using different effective microparticle diffusivities. The values used range from 1/25 to 25 times the value listed in Table 5.15.

When the micropore diffusivity decreases, the sensitivity of the concentration response curves increases and the curves breakthrough more early and have long tails. The sensitivity becomes small when microparticle diffusivities increase. When increasing $D_i$ while keeping constant the effective macropore diffusivity the mass transport rate controlling step changes from the micropore diffusion rate control to the intermediate regime.

<table>
<thead>
<tr>
<th></th>
<th>$R_{ax}$</th>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$R_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 °C</td>
<td>0.0057</td>
<td>0.00013</td>
<td>0.0022</td>
<td>0.156</td>
</tr>
<tr>
<td>RP 4A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RP 5A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La Al</td>
<td>0.0026</td>
<td>0.00098</td>
<td>0.0398</td>
<td></td>
</tr>
<tr>
<td>70 °C</td>
<td>0.0061</td>
<td>0.00011</td>
<td>0.0019</td>
<td>0.0773</td>
</tr>
<tr>
<td>RP 4A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RP 5A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La Al</td>
<td>0.0027</td>
<td>0.00089</td>
<td>0.0304</td>
<td></td>
</tr>
<tr>
<td>95 °C</td>
<td>0.0064</td>
<td>0.00010</td>
<td>0.0017</td>
<td>0.0701</td>
</tr>
<tr>
<td>RP 4A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RP 5A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La Al</td>
<td>0.0028</td>
<td>0.00079</td>
<td>0.0283</td>
<td></td>
</tr>
<tr>
<td>N2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 °C</td>
<td>0.0055</td>
<td>0.00018</td>
<td>0.0026</td>
<td>0.0601</td>
</tr>
<tr>
<td>RP 4A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RP 5A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La Al</td>
<td>0.0025</td>
<td>0.00098</td>
<td>0.0207</td>
<td></td>
</tr>
<tr>
<td>70 °C</td>
<td>0.0059</td>
<td>0.00014</td>
<td>0.0023</td>
<td>0.0657</td>
</tr>
<tr>
<td>RP 4A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RP 5A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La Al</td>
<td>0.0026</td>
<td>0.00089</td>
<td>0.0203</td>
<td></td>
</tr>
<tr>
<td>95 °C</td>
<td>0.0061</td>
<td>0.00012</td>
<td>0.0020</td>
<td>0.0618</td>
</tr>
<tr>
<td>RP 4A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RP 5A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La Al</td>
<td>0.0027</td>
<td>0.00081</td>
<td>0.0184</td>
<td></td>
</tr>
<tr>
<td>O2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 °C</td>
<td>0.0059</td>
<td>0.00015</td>
<td>0.0022</td>
<td>0.00118</td>
</tr>
<tr>
<td>RP 4A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RP 5A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La Al</td>
<td>0.0026</td>
<td>0.00088</td>
<td>0.0200</td>
<td></td>
</tr>
<tr>
<td>70 °C</td>
<td>0.0063</td>
<td>0.00012</td>
<td>0.0018</td>
<td>0.00071</td>
</tr>
<tr>
<td>RP 4A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RP 5A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La Al</td>
<td>0.0028</td>
<td>0.00081</td>
<td>0.0218</td>
<td></td>
</tr>
<tr>
<td>95 °C</td>
<td>0.0066</td>
<td>0.00011</td>
<td>0.0018</td>
<td>0.00048</td>
</tr>
<tr>
<td>RP 4A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RP 5A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La Al</td>
<td>0.0029</td>
<td>0.00074</td>
<td>0.0199</td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.69 Comparison of response curves using different macropore diffusivities for N₂/He in Rhône Poulenc 4A at 40 °C

Figure 5.70 Comparison of response curves using different microparticle diffusivities for N₂/He in Rhône Poulenc 4A at 40 °C
In the case of gas diffusion in 5A zeolite particles and alumina, the micropore diffusion resistance is negligible when compared with the macropore resistance. Figures 5.71 and 5.72 compare the calculated concentration response curves for different effective macropore diffusivities for nitrogen in Rhône Poulenc 5A and LaRoche alumina at 40 °C. The macropore diffusivities were varied from 1/25 to 25 times the values in Table 5.14. The various calculated curves have different shape and this means that the response curves have high sensitivity to the macropore diffusivity. This sensitivity is expected because the macropore diffusion is the rate controlling step and it ensures that the parameter regression have good precision.

Figures 5.73 and 5.74 show the influence of the microparticle diffusivity in the concentration response curves for nitrogen at 40 °C in Rhône Poulenc 5A and LaRoche alumina. The microparticle diffusivities were varied from the values listed in Table 5.15 to infinity. Because of the negligible microparticle diffusional resistance the variation of microparticle diffusivities from the values listed in the Table 5.15 to infinity have little influence on the response curves and the calculated curves are almost coincident and thus the microparticle diffusivity can not be determined by this chromatographic experimental technique.

![Figure 5.71 Comparison of response curves using different macropore diffusivities for N₂/He in Rhône Poulenc 5A at 40 °C](image)
Figure 5.72 Comparison of response curves using different macropore diffusivities for N₂/He in LaRoche alumina at 40 °C

Figure 5.73 Comparison of response curves using different microparticle diffusivities for N₂/He in Rhône Poulenc 5A at 40 °C
Figure 5.74 Comparison of response curves using different microparticle diffusivities for \( \text{N}_2 / \text{He} \) in LaRoche alumina at 40 °C

In the experimental apparatus there is a concentration detector at both inlet and outlet of the column and the same tubing, connectors and tubing length were used for the connection between the column and detectors in order to maintain the same delays and effects on concentration responses. In our mass transport model for the single pellet string fixed bed we assumed that the inlet perturbation is an ideal concentration step. In practice the input step dispersion is unavoidable. The experimental input can be approximately expressed using the following equation

\[
C = 1 - \exp\left(-\frac{\theta}{\theta_0}\right)
\]  

(5.42)

where \( \theta_0 \) is the dimensionless time at dimensionless concentration \( C = 0.6321 \). Figure 5.75 shows the inputs obtained by measurement and calculation using equation (5.42) for argon at 40 °C. This plot shows that equation (5.42) can represent well the measured input. The input is independent of the solid sample and for different gases the difference should be small. In our experiments the range of flow rates is small and thus we used equation (5.42) with different measured \( \theta_0 \) to simulate the real input steps. The influence of non ideal step input in the response can be shown by comparing the corresponding breakthrough curves. Table 5.18 shows the experimental \( \theta_0 \) and calculated standard deviation between the responses of the fixed bed to an ideal step and a real input for argon, nitrogen and oxygen in Rhône Poulenc 4A, 5A and LaRoche alumina at different temperatures.
Figure 5.75 Simulated (dashed line) and experimental (solid line) input concentration for oxygen in Rhône Poulenc 4A at 70 °C

Table 5.18 Experimental $\theta_o$ and calculated standard deviations between the responses of the fixed bed to an ideal step and a real input

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th>RP 4A</th>
<th>RP 5A</th>
<th>La Al</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ar</strong></td>
<td>40 °C</td>
<td>$\theta_o$</td>
<td>0.0730</td>
<td>0.0728</td>
<td>0.0625</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$S$</td>
<td>0.0052</td>
<td>0.0112</td>
<td>0.0351</td>
</tr>
<tr>
<td></td>
<td>70 °C</td>
<td>$\theta_o$</td>
<td>0.0813</td>
<td>0.0806</td>
<td>0.0684</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$S$</td>
<td>0.0076</td>
<td>0.0146</td>
<td>0.0360</td>
</tr>
<tr>
<td></td>
<td>95 °C</td>
<td>$\theta_o$</td>
<td>0.0856</td>
<td>0.0867</td>
<td>0.0734</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$S$</td>
<td>0.0085</td>
<td>0.0139</td>
<td>0.0378</td>
</tr>
<tr>
<td><strong>N₂</strong></td>
<td>40 °C</td>
<td>$\theta_o$</td>
<td>0.0721</td>
<td>0.0719</td>
<td>0.0611</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$S$</td>
<td>0.0067</td>
<td>0.0127</td>
<td>0.0317</td>
</tr>
<tr>
<td></td>
<td>70 °C</td>
<td>$\theta_o$</td>
<td>0.0834</td>
<td>0.0821</td>
<td>0.0692</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$S$</td>
<td>0.0059</td>
<td>0.0141</td>
<td>0.0330</td>
</tr>
<tr>
<td></td>
<td>95 °C</td>
<td>$\theta_o$</td>
<td>0.0862</td>
<td>0.0851</td>
<td>0.0747</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$S$</td>
<td>0.0084</td>
<td>0.0156</td>
<td>0.0366</td>
</tr>
<tr>
<td><strong>O₂</strong></td>
<td>40 °C</td>
<td>$\theta_o$</td>
<td>0.0736</td>
<td>0.0716</td>
<td>0.0634</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$S$</td>
<td>0.0083</td>
<td>0.0133</td>
<td>0.0381</td>
</tr>
<tr>
<td></td>
<td>70 °C</td>
<td>$\theta_o$</td>
<td>0.0876</td>
<td>0.0844</td>
<td>0.0673</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$S$</td>
<td>0.0071</td>
<td>0.0161</td>
<td>0.0402</td>
</tr>
<tr>
<td></td>
<td>95 °C</td>
<td>$\theta_o$</td>
<td>0.0844</td>
<td>0.0858</td>
<td>0.0741</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$S$</td>
<td>0.0088</td>
<td>0.0158</td>
<td>0.0394</td>
</tr>
</tbody>
</table>
In the calculation of standard deviations listed in Table 5.18 the macropore, microparticle and axial dispersion parameters listed in Tables 5.15 and 5.16 were used. As an illustration Figure 5.76 shows the calculated breakthrough curves for an ideal step and for a real input for oxygen in LaRoche alumina at 70 °C. We illustrated this case since the calculated standard deviation for this case is the largest. The standard deviation is less than 0.05 which is of the same order of magnitude of experimental measurement error for the concentration responses. The concentration detector for the input stream is fixed in an oven and thus the input concentration dispersion measured by the detector includes the tubing and detector dispersions. The true input should be somewhere between the ideal and measured inputs and thus we can use the responses to the ideal step to calculate the model parameters. Figures 5.77 to 5.79 show the experimental and simulated results of argon, nitrogen and oxygen in Laporte 4A, 5A and LaRoche alumina at different temperatures. These plots and the standard deviations listed in Table 5.15 show that the model for the single pellet string fixed bed represent well the experimental breakthrough curves and the errors between the calculated and experimental data are of the same size as the experimental errors.

The matching technique is the same as discussed for the shallow bed diffusion cell. Macropore and micropore diffusivities for Laporte and Rhône Poulenc systems obtained using the single pellet string fixed bed are in good agreement with those obtained by the shallow bed diffusion cell method.

![Breakthrough curve graph](image)

Figure 5.76 Breakthrough curves with ideal (dashed line) and real (solid line) input steps for oxygen in LaRoche alumina at 70 °C
Figure 5.77 Simulated (dashed line) and experimental (solid line) results for nitrogen in Rhône Poulenc 4A at 40 °C.

Figure 5.78 Simulated (dashed line) and experimental (solid line) results for oxygen in Rhône Poulenc 5A at 70 °C.
4 CONCLUSIONS

In this chapter, the experimental and simulated results for single pellet diffusion cell, shallow bed diffusion cell and single pellet string fixed bed were discussed and explained. The mass transport parameters including effective bulk phase, film, macropore and microparticle diffusivities were obtained using the time domain fitting technique.

The single pellet diffusion cell technique is a useful experimental tool for the determination of gas diffusion and convective flow coefficients inside a single pellet. By controlling the pressure difference across the pellet to zero the mass flux through the pellet for a mixture of gases just results from diffusion. The perfectly mixing assumption in both top and bottom chambers in our model was verified experimentally with the blank chamber responses. From the experimental blank chamber responses the chamber volume including the connection tubing between chamber and concentration detector can be determined. The special shape of the chamber and special inlet port configuration technically ensure the perfectly mixing. The importance of film mass transport resistance was determined. The system transfer function which links top and bottom chamber responses is a generating function and thus it can be expanded by means of all moments. Assuming that the global errors between the responses when the film diffusional resistance is considered or not are equally weighted to the various moments, a set of criteria for neglecting the film diffusional resistance were established. In our experimental conditions, the zeroth moment criterion is always satisfied. The first
moment criterion is almost satisfied. Whereas the second moment criterion is never met. This is expected because the zeroth and first moments are respectively the steady state gain and gravity center and only the second moment represents the system dispersion. The presence of the film diffusional resistance increases the system dispersion.

The time domain comparison of the responses with and without film diffusion shows that an error dumping effect occurs when passing the response from Laplace to time domain. Even if in the Laplace domain the system fails to satisfy the various moment criteria it is possible that the time domain responses satisfy those criteria. In our case the time domain responses meet the requirements to neglect film mass transport resistance, that is, the error is of the same size as the experimental error.

The diffusivities inside the pores can be calculated by using the steady state responses of both top and bottom chambers and by matching the theoretical responses obtained with the models to the experimental ones. The mass transport parameters are the adjustable parameters in the model. The weighted orthogonal distance regression technique was used to perform the minimization and the software package ODRPACK carried out this function. The differences between the simulated and experimental responses for Ar, O2 and N2 in 5 single pellets are within the experimental error and confirm that the technique is reliable. Due to the presence of dead end pores the effective diffusivities obtained from the transient responses are always larger than those obtained from the steady state responses because the dead end pores do not make a contribution to the steady state flux. The difference between them can be considered as the dead end pore contribution to the transient response. For our solid samples the differences are in the range of 7% - 12%.

When there is a pressure difference across the pellet a convective flow occurs. For monocomponent systems and convective pores the total flux through the pellet may include ordinary flow, wall and gravity effect contributions. The gravity effects are usually negligible due to the gas low density. In our experimental conditions the calculated results shown that the wall effects are also negligible. The comparison of the experimental and calculated results shown that Darcy equation can be used to express the relationship between the pressure difference across the pellet and the flux at steady state for convective pores. The apparent convective coefficient is independent of average pressure for large pores. When pore diameter reduces the Knudsen and slip flow contributions to the total flow are non negligible. In this case the apparent convective coefficient is no longer independent of the average pressure. Theoretically as long as the pressure is enough low, the Knudsen diffusivity can be obtained from the plots of the apparent convective coefficient against the average pressure.

Traditionally, the diffusion cell is used in the determination of the bidisperse mass transport parameters of single pellets. The successful determination of adsorption equilibria and macropore and micropore effective diffusivities of gases in a diffusion cell packed with small particles broadens the diffusion cell applications in the field of mass transport parameter measurement. The main problem in this technique is that the pressure difference through the cell must be kept zero otherwise the convective flow will change the total flux. In our experimental apparatus a self - made pressure difference keeper carries out this job. Using a global mass balance for an experimental run the adsorption equilibrium constant can be calculated. The measured equilibrium constants are in agreement with the theoretically predicted values. We specially compared the data for nitrogen and oxygen in Rhône Poulenc 5A at 40 °C that can be found for the same adsorbate - adsorbent systems in other sources using different methods and they are well in agreement.

The effective bulk phase diffusivities can be estimated by using a theoretical tortuosity ( \( \sqrt{2} \) ) and the film mass transport coefficients can be evaluated by combining this
estimated effective bulk phase diffusivity and the steady state responses of both chambers. The comparison of the effective bulk phase diffusivities obtained by theoretical estimation and experimental response curve regression confirmed that theoretical estimation is enough accurate for all our cases. The macropore and micropore diffusivities can be obtained by matching the theoretical responses to the experimental ones. The obtained macropore diffusivities for argon, nitrogen and oxygen in two types of zeolite A series and alumina are within the recognized ranges. The microparticle diffusivities are of the same order as the predicted theoretically and agree with the published data. The relative importance of macropore and micropore diffusional resistances can be shown by comparing their time constants. Our experimental and calculated results show that the diffusion of nitrogen and argon in Rhône Poulenc 4A is a typical case of micropore rate control. While the diffusion of argon, nitrogen and oxygen in Rhône Poulenc 5A is a typical case of macropore rate control. The difference between the simulated and experimental responses is within the experimental error range. All these results show that the experimental technique and the model for shallow bed diffusion cell are reasonable. As a conclusion, we must emphasize the meaning of the micropore diffusivity determined by this method. Due to the fact that the concentration of carrier gas is always dominant over the adsorbate concentration, the diffusion of the adsorbate into micropores is accompanied by carrier diffusion out of the micropores. So this effective diffusivity is counter diffusivity and should be different from these determined by the gravimetric method.

The fixed bed method is widely used to determine the adsorption equilibria and diffusion characteristics of gases in porous solids. A drawback of this technique is that the response values are strongly dependent on the gas flow pattern in bulk phase. Because there is a large amount of void between the pellets and column wall in the single pellet string fixed bed, the gas flow velocity can reach very high values without the problems of column large pressure drop. The relative importance among the various mass transport resistances including axial dispersion, film, macropore and micropore diffusion were examined by the moment analysis and time domain responses. The high velocity can largely reduce the importance of the film mass transport resistance that can be safely neglected in our system. The Peclet number that expresses the axial dispersion can reach a high value. In the experimental apparatus there is a concentration detector at both column inlet and outlet and thus the input step can be measured. This measured input includes the dispersion effects in the connecting tubes and detector and it is worse than the true input. We used this measured input to compare the breakthrough curves with an ideal step input and the results shown that the difference between them is negligible. The good agreement between the diffusivities obtained by this method and by the diffusion cell shows that these two experiments and corresponding models are reliable.

For bidispersed pore solids the effective macropore diffusivities in the case when the micropore diffusion is the rate controlling step can not be obtained by all our experimental techniques due to low sensitivity of the responses to macropore diffusivities. On the other hand the effective micropore diffusivities can not be obtained when macropore diffusion is the rate controlling step. Zeolites 4A and 5A produced by the same manufacturer have the same macropore network structure and thus the macropore diffusivities obtained for 5A can be used for the 4A.

The solution and matching of the mass transport model equations were carried out in the time domain. The inversion of the solution to the time domain was done using FFT and collocation techniques. Because the parameter regression process needs a lot of iterations, the computation is a heavy task. The comparison between these two solution methods shown that the former has a much lighter computation work. In our calculation we used 1024 FFT points to do the numerical inversion from Laplace to time domain and this number is enough for all cases.
For comparison the orthogonal collocation method was also used. There is little difference on the simulated concentration response curves obtained by these two numerical methods.

The experimental methods used in this chapter belong to the macroscopic techniques that can not be applied to determine the micropore diffusivities of small molecular gases in relatively large micropores due to the small micropore diffusional resistance compared to the macropore diffusional resistance.

REFERENCES


Breck, D.W., Zeolite Molecular Sieves, Wiley, 1974


Garcin, E., Periodic report of Project JOULE 0052 - C, Rhone Poulenc Recherches, 1991


Micromeritics, Operator's Manual for PoreSizer 9320, V1.01, 1990

271


Schneider, P. and J.M. Smith, Adsorption Rate Constants from Chromatography, AIChE J., 14, 762, 1968


VI CONCLUSIONS AND FURTHER PLANS

A methodology for predicting the adsorption isotherms, adsorption heats and adsorption thermodynamic functions of gases in zeolite A series at low coverage was developed. The adsorption equilibria and thermodynamic functions are related to the molecular and system partition functions of the gas and adsorbed phases by means of statistical thermodynamics. The central work of the theoretical model is the calculation of the molecular partition function of the adsorbate in the adsorbed phase. At low coverage the interaction potential among adsorbate molecules can be neglected and the potential field between adsorbate molecule and cavity wall atoms was simulated by pairwise summation of the various individual interactions including dispersion, repulsion, induction and quadrupole moment. The calculated results for nonpolar adsorbate Ar, weak quadruple adsorbate O$_2$ and strong quadruple adsorbate N$_2$ in zeolites A shown that the interaction potential field inside the cavity is close to a spherically symmetrical field in the interesting spatial region. The steady state Schrödinger equation was applied to describe the motion of the adsorbate molecule inside the zeolite A cavity. That potential function was then substituted into the steady state Schrödinger equation that describes the adsorbate molecular motion states and it can be reduced to a set of second order ordinary differential equations with Sturm-Liouville form using a variable separation technique. The numerical solution of this Sturm-Liouville problem gives an infinite set of eigenvalues and the corresponding eigenfunctions. The partition function describing the number of microscopic states can be calculated from the eigenvalues. Furthermore, the average total potential and kinetic energies and the average position of an adsorbate molecule inside a cavity can be evaluated at given macroscopic system conditions such as temperature and pressure. The model is independent of the experimental data and no any adjustable parameter exists, thus the model is truly predictive. Theoretically, this model is ready to be used in the adsorption of complicated structure molecules as long as the calculation method of the interaction potential can be established. The calculated results of adsorption isotherms and adsorption heats for argon, oxygen and nitrogen in 4A and 5A zeolites are in good agreement with the published experimental data. The comparison of the molecular partition functions calculated by classical and quantum mechanics shown that the differences are negligible for moderate temperatures and relative large cavities. At low temperatures the classical method loses applicability, specially for small size cavities where the deviation becomes more serious.

The drawback of this methodology is that the model only can deal with cases where the adsorbed amount is less than in average one molecule per cavity in order to be able to use the spherically symmetrical potential distribution. One of the potential applications of this methodology is as a criterion for theoretical design and improvement of adsorbent separation characteristics prior to any experimental determinations. The combination of this model with the Monte Carlo simulation is possible to develop a model which can deal with high coverage cases. At low coverage the influence between adsorbate molecules inside different cavities is negligible and thus the adsorption equilibria of multicomponent systems can be handled in the same way as a pure component. Faujasite zeolite series include synthetic X, Y and natural faujasite which are widely used in the gas-solid heterogeneous catalytic reactions and in the separation of xylene isomers. They have the same microscopic crystal structures that also includes windows (twelve membered ring) and cavities and thus our model is easy to be applied to them. In principle this methodology is not limited to the case with a spherically symmetrical interaction potential. For zeolites with a cylindrical path microscopic structure, such as ZSM series, the interaction potential between adsorbate molecule and the path wall atoms
may be expressed in a cylindrical approximation. In such case the motion of adsorbate molecules in adsorbed phase can be described by the steady state Schrödinger equation in cylindrical coordinates and can also be reduced to the one dimensional Sturm-Liouville problem. So the adsorption isotherms, adsorption heat and adsorption thermodynamic functions can be evaluated using the same principle. One interesting case is the application of this methodology to some amorphous micropore adsorbents, such as carbons, alumina oxides and silica gels. The detailed microscopic structures of the surface are not so clear as in zeolites and the lacking of structure information will give rise to difficulties in the calculation of the interaction potential. As a rough approximation one or more parameters to represent the interaction potential may be left in the model as adjustable parameters which can be finally determined by comparing the calculated results such as adsorption Henry constants and isosteric adsorption heats with the experimental ones. The truly predictive models are helpful for providing useful information on the modification, improvement and synthesis of adsorbents.

The prediction of the intracrystalline diffusivities of gases in zeolites is another important issue in heterogeneous catalysis and adsorption separation of gases involving porous solids. According to the relative size of diffusing molecule and the path, there are two kinds of mechanisms. One is when the dimension of the diffusion path is larger than the molecule size. The interaction potential between diffusing molecule and the adsorbent surface atoms shows that at the window central region the interaction potential is lower than inside the cavity. The diffusion process of a molecule from cavity to window is under an attractive force. Out of the vicinity of the window central region there is a strong repulsion force to prevent the molecule from crossing the window. So only when the diffusing molecule strikes the central region it can escape the cavity. The dimension of the central region can be considered as the average position of the molecule at the window plane. The window dimension of 5A is a bit larger than the molecular kinetic dimensions of small molecules and the molecule can temporally move with two degrees of freedom. The stability of this temporary state can be evaluated by means of the ratio of the molecular partition functions of the diffusing molecule at the window and inside the cavity. The diffusing molecule at the window can go to the next cavity or return to the original one as long as the molecule has a translational kinetic energy greater than the energy barrier which exists between the window and the cavity. The probability of these jumps should be equal at very low adsorbed amounts. The whole diffusion process can be considered as three steps in series: the molecule diffuses from the cavity to the window and this is a random process; temporally moves at the window plane, overcomes the energy barrier and diffuses to the next window or returns to the original one. The last step is a really activated process. The intermediate state is quite unstable and thus the contribution of this step to the total diffusion resistance can be neglected. The relative importance of the first and last steps to determine the diffusion resistance is dependent on the interaction potential between adsorbate molecule and adsorbent atoms and temperature. For weak interaction molecules, the energy barrier is small, the last step may be less important to the total resistance. Increasing the temperature, the resistances of both steps will reduce but the decrease in importance of the last step is more sensitive to the temperature. The predicted diffusivities and activation energies for permanent gases in 5A zeolite are fairly in agreement with the experimental results. Due to the quick diffusion of small molecules like helium, argon, oxygen and nitrogen in the relatively large unblocked eight membered ring, the usual macroscopic experimental techniques can not be used to determine these diffusivities.

The diffusion process of gases in blocked windows is different. The existence of a cation in the eight membered ring greatly reduces the free diameter. Only when the diffusing molecule strike the window with enough translational kinetic energy it can
overcome the energy barrier and cross the window to finish a jump. Otherwise it will be bounded back to the original cavity. The larger the adsorbate molecule, the stronger repulsion potential. When dealing with activated diffusion processes, one of the most important issues is the calculation of the translational kinetic energy distribution. The use of the classical approach to evaluate the translational kinetic energy distribution will introduce large errors at the high energy area. The activated diffusion processes involve the higher part of the distribution and thus the distribution of kinetic energies at high energies is important. The calculated results shown that the difference of activated diffusivities of argon and nitrogen in 4A by classical and quantum approaches is as high as one more order of magnitude. The predicted diffusivities and activation energies for permanent gases in 4A zeolites are in the same order of magnitude as published experimental results. The calculation error may result from the simplifying assumptions relative to the real interaction potential field and the uncertainty of the molecular parameters.

In this methodology for the prediction of the intracrystalline diffusivities, the calculations of the interaction potential and of the intracrystalline diffusivities are independent of any adsorption kinetic experimental data and thus the models are truly predictive. The zeolite structure and the adsorbate molecule characteristics are included in the models and thus they should be able to translate to other systems in which the zeolites have similar cavity and window structures. The most similar system may be the diffusion of gases in X and Y zeolites. This methodology is also ready to be used in other zeolite systems by adjusting the calculation of the interaction potential. For high coverage the interaction potential among different adsorbate molecules must be included and the spherically symmetrical potential distribution may need more approximation so that the three-dimensional steady state Schrödinger equation can be solved. The probability of an adsorbate molecule staying at the window plane of 5A zeolite going to next cavity and return the original one may be different and this probability can be related to the interaction potential energies in these two cavities. The motion direction of an adsorbate molecule inside cavity will be affected by other adsorbate molecules in the same cavity and in neighboring cavities. The concentration dependency of intracrystalline diffusivity for small molecules in relative large windows will rely on the interaction potential distribution variation among adsorbate molecules. The existence of the cation at the window plane relatively isolates the interaction between adsorbate molecules in adjacent cavities and thus when the coverage is less than one molecule per cavity in average the interaction potential can be still considered as similar to the case of zero coverage. It may be expected that the activated diffusivities are concentration-independent in the range of less than one molecule per cavity in average. At higher coverage the interaction potential resulting from other adsorbate molecules in the same cavity must be considered. One of the most attractive topics is the prediction of self and counter intracrystalline diffusivities of multicomponent gaseous systems. The diffusional path dimensions of zeolites are in the order of molecular magnitude. The existence of adsorbate molecules in the diffusional path will block the diffusion of other molecules. For multicomponent systems the different directions of the concentration gradients for different components result in that some components diffuse inside the crystal and other components diffuse out of the crystal. These two opposite diffusional processes will block each other. From the concentration distributions inside the crystal some probabilities for determining possible moving directions of the individual molecules of each component can be calculated by our model from the microscopic energy states of the individual molecules at various positions. The counter intracrystalline diffusivities can be related to these probabilities. The diffusion of gases in amorphous micropore adsorbents is much complicated due to the irregular micropore network structures. Theoretically, if the micropore dimension is small and the network structure can be quantitatively described, our model is helpful to analyze the diffusional resistances.
The experimental measurements are still the main way to obtain the mass transport rate parameters in porous solids. The limited pore structure information from the ordinary experimental means and the irregularity of shapes and dimensions of pore structures result in the that it is impossible in practice to completely describe the pore structure. The development and design for estimating the mass transport rate of gases in porous solids require some parameters to describe the mass transport dynamic characteristics. In this work we developed the corresponding mathematical models for describing the mass transport processes and transient responses for the diffusion cell packed with a single pellet, packed with small pellets and for the single pellet string fixed bed. In these models the pore structure was considered as bidispersed and a cylindrical pore shape with an average pore diameter was assumed to approximate the practical pore network. The mass transport rate parameters in the models were adjustable parameters and determined by fitting the theoretical calculated responses to the experimental ones. Two effective diffusivities were respectively used to represent the macropore and micropore diffusions.

The single pellet diffusion cell technique is a useful experimental tool for the determination of gas diffusion and convective flow coefficients inside a single pellet. By controlling the pressure difference across the pellet to zero the mass flux through the pellet for a mixture of gases just results from diffusion. The perfectly mixing assumption in both top and bottom chambers in our model was verified experimentally with the blank chamber responses. From the experimental blank chamber responses the chamber volume including the connection tubing between chamber and concentration detector can be determined. The special shape of the chamber and special inlet port configuration technically ensure the perfectly mixing. The importance of film mass transport resistance was determined. A set of criteria for neglecting the film diffusional resistance under the experimental operating conditions were established using moment analysis. In our experimental conditions, the zeroth moment criterion is always satisfied. The first moment criterion is almost satisfied. Whereas the second moment criterion is never met. This is expected because the zeroth and first moments are respectively the steady state gain and gravity center and only the second moment represents the system dispersion. The presence of the film diffusional resistance increases the system dispersion. The time domain comparison of the responses with and without film diffusion shows that an error dumping effect occurs when passing the response from Laplace to time domain. In our case the time domain responses meet the requirements to neglect film mass transport resistance, that is, the error is of the same size as the experimental error. The diffusivities inside the pores can be calculated by using the steady state responses of both top and bottom chambers and by matching the theoretical responses obtained with the models to the experimental ones. The weighted orthogonal distance regression technique was used to perform the optimization and parameter regression. The differences between the simulated and experimental responses for Ar, O₂ and N₂ in 5 single pellets are within the experimental error and confirm that the technique is reliable. Due to the presence of dead end pores the effective diffusivities obtained from the transient responses are always larger than these obtained from the steady state responses because the dead end pores do not make a contribution to the steady state flux. The difference between them can be considered as the dead end pore contribution to the transient response. For our solid samples the differences are in the range of 7% - 12%.

When there is a pressure difference across the pellet a convective flow occurs. For monocomponent systems and convective pores the total flux through the pellet may include ordinary flow, wall and gravity effect contributions. The gravity effects are usually negligible due the gas low density. In our experimental conditions the calculated results shown that the wall effects are also negligible. The comparison of
the experimental and calculated results shown that Darcy equation can be used to express the relationship between the pressure difference across the pellet and the flux at steady state for convective pores. The apparent convective coefficient is independent of average pressure for large pores. When pore diameter reduces the Knudsen and slip flow contributions to the total flow are non negligible. In this case the apparent convective coefficient is no longer independent of the average pressure.

Traditionally, the diffusion cell is used in the determination of the bidisperse mass transport parameters of single pellets. The successful determination of adsorption equilibria and macropore and micropore effective diffusivities of gases in a diffusion cell packed with small particles broadens the diffusion cell applications in the field of mass transport parameter measurement. The main problem in this technique is that the pressure difference through the cell must be kept zero otherwise the convective flow will change the total flux. In our experimental apparatus a self - made pressure difference keeper carries out this job. Using a global mass balance for an experimental run the adsorption equilibrium constant can be calculated. The measured equilibrium constants are in agreement with the theoretically predicted values. We specially compared the data for nitrogen and oxygen in Rhône Poulenc 5A at 40 °C that can be found for the same adsorbate - adsorbent systems in other sources using different methods and they are well in agreement. The effective bulk phase diffusivities can be estimated by using a theoretical tortuosity ( $\sqrt{2}$ ) and the film mass transport coefficients can be evaluated by combining this estimated effective bulk phase diffusivity and the steady state responses of both chambers. The comparison of the effective bulk phase diffusivities obtained by theoretical estimation and experimental response curve regression confirmed that theoretical estimation is enough accurate for all our cases. The macropore and micropore diffusivities can be obtained by matching the theoretical responses to the experimental ones. The obtained macropore diffusivities for argon, nitrogen and oxygen in two types of zeolite A series and alumina are within the known range. The microparticle diffusivities are of the same magnitude as these predicted theoretically and agree with the published data. The relative importance of macropore and micropore diffusional resistances can be shown by comparing their time constants. Our experimental and calculated results show that the diffusion of nitrogen and argon in Rhône Poulenc 4A is a typical case of micropore rate control. While the diffusion of argon, nitrogen and oxygen in Rhône Poulenc 5A is a typical case of macropore rate control. The difference between the simulated and experimental responses is within the experimental error range. All these results show that the experimental technique and the model for the shallow bed diffusion cell are reasonable.

The fixed bed method is widely used to determine the adsorption equilibria and diffusion characteristics of gases in porous solids. A drawback of this technique is that the response values are strongly dependent on the gas flow pattern in bulk phase. Because there is a lot of voids between the pellets and column wall in the single pellet string fixed bed, the gas flow velocity can reach very high values without the problems of column large pressure drop. The relative importance among the various mass transport resistances including axial dispersion, film, macropore and micropore diffusion were examined by the moment analysis and time domain responses. The high velocity can largely reduce the importance of the film mass transport resistance that can be safely neglected in our system. The Peclet number that expresses the axial dispersion can reach a high value. In the experimental apparatus there is a concentration detector at both column inlet and outlet and thus the input step can be measured. We used this measured input to compare the breakthrough curves with an ideal step input and the results shown that the difference between them is negligible. The good agreement between the diffusivities obtained by this method and by the
diffusion cell shows that these two experiments and corresponding models are reliable.

For bidispersed pore solids the effective macropore diffusivities in the case when the micropore diffusion is the rate controlling step can not be obtained by all our experimental techniques due to low sensitivity of the responses to micropore diffusivities. On the other hand the effective micropore diffusivities can not be obtained when macropore diffusion is the rate controlling step. The experimental methods used in this chapter belong to the macroscopic techniques that can not be applied to determine the micropore diffusivities of small molecular gases in relatively large micropores due to the small micropore diffusional resistance compared to the macropore diffusional resistance.

Although we used gas tracer systems in order to meet the linear adsorption isotherm requirement of mathematical model, the experimental techniques are not limited to the tracer systems. For nonlinear adsorption isotherms and variable velocity (higher bulk phase concentration and large adsorption capacity) the mass transport equations become nonlinear, the orthogonal collocation method can be directly used to solve such equations. So the present work can be easily applied to the nonlinear mass transport systems. The experimental determination of effective diffusivities of multicomponent systems by ordinarily macroscopic techniques is a challenging task. If the detection of the responses of each individual component can be solved, diffusion cell and fixed bed experimental techniques can be applied to the multicomponent systems. The corresponding mass transport models must include all mass balance equations of the various components and the orthogonal collocation method is applicable for solving such equations.
NOMENCLATURE

A_

A_{ik}
Surface or cross section area, cm²

 Dispersion constants for the interaction between atoms or molecules i and k

A_{London}
London dispersion constants for the interaction between atoms or molecules i and k, erg·cm⁻⁶

A_{Kirkwood - Muller}
Kirkwood - Muller dispersion constants for the interaction between atoms or molecules i and k, erg·cm⁻⁶

A_{Slater - Kirkwood}
Slater - Kirkwood dispersion constants for the interaction between atoms or molecules i and k, erg·cm⁻⁶

\bar{A}
Dimensionless adsorption amount

\bar{B}_{ik}
Laplace transform of the dimensionless adsorption amount

B_{ik}
Repulsion constants for the interaction between atoms or molecules i and k, erg·cm⁻¹²

B_o
Convective flow coefficient, cm²

B_{ce}
Effective convective flow coefficient, cm²

\bar{B}_{ce}
Apparent effective convective flow coefficient, cm²

C
Dimensionless concentration; or system concentration, mol·cm⁻³

\bar{C}
Laplace transform of the dimensionless concentration

\bar{C}_b
Laplace transform of the dimensionless bottom chamber concentration

\bar{C}_t
Laplace transform of the dimensionless top chamber concentration

D
Diffusivity, cm²·sec⁻¹

D_a
Effective macropore diffusivity, cm²·sec⁻¹

D_{ax}
Axial dispersion coefficient, cm²·sec⁻¹

D_b
Effective bulk phase diffusivity, cm²·sec⁻¹

D_{cw}
Self diffusivity of adsorbate molecule when travelling from cavity to window, cm²·sec⁻¹

D_e
Effective diffusivity, cm²·sec⁻¹

D_i
Effective micropore diffusivity, cm²·sec⁻¹

D_K
Knudsen diffusivity, cm²·sec⁻¹

D_{Ke}
Effective Knudsen diffusivity, cm²·sec⁻¹

D_m
Molecular diffusivity, cm²·sec⁻¹

D_{me}
Effective molecular diffusivity, cm²·sec⁻¹

D_{uw}
Unsteady state diffusivity defined in equation (1.111), cm²·sec⁻¹

D_{wc}
Self diffusivity of adsorbate molecule when travelling from window to cavity, cm²·sec⁻¹

\bar{D}
Average effective pore diffusivity defined in equation (1.126), cm²·sec⁻¹

D^*
Preexponential factor defined in equation (1.129)

D_o
Self diffusivity at zero coverage, cm²·sec⁻¹

E
Energy, J

E_{ad}
Adsorption energy barrier, J·mol⁻¹

E_{des}
Desorption energy barrier, J·mol⁻¹
\( \Delta E \) Diffusional energy barrier, J\text{-molecule}^{-1} \\
\( \Delta E_{\text{rot}} \) Rotational energy barrier, J\text{-molecule}^{-1} \\
\( \mathcal{E} \) Activation energy, J\text{-mol}^{-1} \\
\( F \) Molar Helmholtz free energy, J\text{-mol}^{-1} \\
\( F_a \) Molar Helmholtz free energy of adsorbate in gas phase, J\text{-mol}^{-1} \\
\( F_{\text{ad}} \) Molar Helmholtz free energy of adsorbate in adsorbed phase, J\text{-mol}^{-1} \\
\( F_s \) Molar Helmholtz free energy of adsorbent, J\text{-mol}^{-1} \\
\( F_{\text{os}} \) Molar Helmholtz free energy of adsorbent without adsorbate, J\text{-mol}^{-1} \\
\( \Delta F \) Molar adsorption Helmholtz free energy change, J\text{-mol}^{-1} \\
\( \Delta F_{\text{tr}} \) Translational molar adsorption Helmholtz free energy change, J\text{-mol}^{-1} \\
\( \mathcal{F} \) Volumetric flow rate, cm\(^3\text{-sec}^{-1}\) \\
\( G \) Molar Gibbs free energy, J\text{-mol}^{-1} \\
\( G_a \) Molar Gibbs free energy of adsorbate in gas phase, J\text{-mol}^{-1} \\
\( G_{\text{ad}} \) Molar Gibbs free energy of adsorbate in adsorbed phase, J\text{-mol}^{-1} \\
\( G_s \) Molar Gibbs free energy of adsorbent, J\text{-mol}^{-1} \\
\( G_{\text{os}} \) Molar Gibbs free energy of adsorbent without adsorbate, J\text{-mol}^{-1} \\
\( \Delta G \) Molar adsorption Gibbs free energy change, J\text{-mol}^{-1} \\
\( \Delta G_{\text{tr}} \) Translational molar adsorption Gibbs free energy change, J\text{-mol}^{-1} \\
\( H \) Molar enthalpy, J\text{-mol}^{-1} \\
\( H_a \) Molar enthalpy of adsorbate in gas phase, J\text{-mol}^{-1} \\
\( H_{\text{ad}} \) Molar enthalpy of adsorbate in adsorbed phase, J\text{-mol}^{-1} \\
\( H_s \) Molar enthalpy of adsorbent, J\text{-mol}^{-1} \\
\( H_{\text{os}} \) Molar enthalpy of adsorbent without adsorbate, J\text{-mol}^{-1} \\
\( H'_a \) Adsorbent partial molar enthalpy, J\text{-mol}^{-1} \\
\( \Delta H \) Molar adsorption enthalpy change, J\text{-mol}^{-1} \\
\( I \) Ionization potential, J\text{-mol}^{-1} \\
\( J \) Inertial moment, g\cdot cm\(^2\) \\
\( J_K \) Diffusional mass flux, mole\text{-cm}^{-2}\text{-sec}^{-1} \\
\( J_{\text{con}} \) Knudsen diffusional mass flux, mol\text{-cm}^{-2}\text{-sec}^{-1} \\
\( J_{\text{total}} \) Convective mass flux, mol\text{-cm}^{-2}\text{-sec}^{-1} \\
\( J_{\text{rot}} \) Total mass flux, mol\text{-cm}^{-2}\text{-sec}^{-1} \\
\( J \) Rotation quantum number \\
\( K \) Henry adsorption equilibrium constant \\
\( \mathcal{K} \) Dimensionless adsorption equilibrium constant \\
\( L \) Length, cm \\
\( M \) Molecular mass, g\text{-molecule}^{-1} \\
\( \mathcal{M} \) Number of adsorption sites \\
\( N \) System number of molecules \\
\( N_0 \) Avogadro’s constant \\
\( N_c \) Number of cavities per unit crystal volume, cm\(^3\) \\
\( N_a \) Dimensionless mass transport constant in bulk phase \\
\( N_{\text{mac}} \) Dimensionless mass transport constant in macropores \\
\( N_{\text{eff}} \) Dimensionless effective mass transport constant \\
\( N_f \) Dimensionless mass transport constant in film \\
\( N_{\text{mic}} \) Dimensionless mass transport constant in microparticles \\
\( N_g \) Dimensionless geometrical factor
\( P \) System total pressure, Pa

\( P_e \) Peclet number

\( \Phi \) Density function of energy distribution

\( P \) Cumulative energy distribution

\( P_{rot} \) Rotation probability

\( P_{ew} \) Probability of a molecule escaping the cavity

\( P_{wc} \) Probability that a molecule returns to cavity from window

\( Q \) Adsorption heat, J

\( \Omega \) System partition function

\( R \) Gas constant

\( R_0 \) Particle radius

\( R \) Radial wave function

\( R^* \) Conjugate radial wave function

\( S \) Molar entropy, J\( \cdot \)mol\(^{-1}\)\( \cdot \)K\(^{-1}\)

\( S_a \) Molar entropy of adsorbate in gas phase, J\( \cdot \)mol\(^{-1}\)\( \cdot \)K\(^{-1}\)

\( S_{ad} \) Molar entropy of adsorbate in adsorbed phase, J\( \cdot \)mol\(^{-1}\)\( \cdot \)K\(^{-1}\)

\( S_s \) Molar entropy of adsorbent, J\( \cdot \)mol\(^{-1}\)\( \cdot \)K\(^{-1}\)

\( S_{os} \) Molar entropy of adsorbent without adsorbate, J\( \cdot \)mol\(^{-1}\)\( \cdot \)K\(^{-1}\)

\( \Delta S \) Molar adsorption entropy change, J\( \cdot \)mol\(^{-1}\)\( \cdot \)K\(^{-1}\)

\( \Delta S_{tr} \) Translational molar adsorption entropy change, J\( \cdot \)mol\(^{-1}\)\( \cdot \)K\(^{-1}\)

\( S \) Standard deviation

\( T \) Absolute temperature, K

\( U \) Molar internal energy, J\( \cdot \)mol\(^{-1}\)

\( U_a \) Molar internal energy of adsorbate in gas phase, J\( \cdot \)mol\(^{-1}\)

\( U_{ad} \) Molar internal energy of adsorbate in adsorbed phase, J\( \cdot \)mol\(^{-1}\)

\( U_s \) Molar internal energy of adsorbent, J\( \cdot \)mol\(^{-1}\)

\( U_{os} \) Molar internal energy of adsorbent without adsorbate, J\( \cdot \)mol\(^{-1}\)

\( U_s^* \) Adsorbent partial molar internal energy, J\( \cdot \)mol\(^{-1}\)

\( \Delta U \) Molar internal energy change, J\( \cdot \)mol\(^{-1}\)

\( \Delta U_{tr} \) Translational molar internal energy change, J\( \cdot \)mol\(^{-1}\)

\( V \) Volume, cm\(^3\)

\( V_a \) Adsorbate volume in gas phase, cm\(^3\)

\( V_b \) Bed volume, cm\(^3\)

\( V_c \) Diffusion cell chamber volume, cm\(^3\)

\( V_s \) Adsorbent volume, cm\(^3\)

\( V_{os} \) Adsorbent volume without adsorbate, cm\(^3\)

\( \mathcal{U} \) Interaction potential, erg\( \cdot \)mol\(^{-1}\)

\( \mathcal{U}_{dis} \) Total dispersion potential, erg\( \cdot \)molecule\(^{-1}\)

\( \mathcal{U}_{ele} \) Total multipole moment potential, erg\( \cdot \)molecule\(^{-1}\)

\( \mathcal{U}_{ind} \) Total induction potential, erg\( \cdot \)molecule\(^{-1}\)

\( \mathcal{U}_{eq} \) Total quadrupole potential, erg\( \cdot \)molecule\(^{-1}\)

\( \mathcal{U}_{rep} \) Total repulsion potential, erg\( \cdot \)molecule\(^{-1}\)

\( \mathcal{U}_{isp}^{ik} \) Dispersion interaction potential, erg\( \cdot \)molecule\(^{-1}\)

\( \mathcal{U}_{ik}^{eq} \) Interaction potential between a linear quadrupole and a charge, erg\( \cdot \)molecule\(^{-1}\)
\( U_{rk} \)  
Repulsion interaction potential, erg-molecule\(^{-1}\)

\( U_c \)  
Average interaction potential inside the cavity, erg-molecule\(^{-1}\)

\( U_i \)  
Average interaction potential at i level, erg-molecule\(^{-1}\)

\( U_{iq} \)  
Average interaction potential between a linear quadrupole and a charge over all orientations, erg-molecule\(^{-1}\)

\( U_w \)  
Average interaction potential at the window, erg-molecule\(^{-1}\)

\( U_{rep} \)  
Average repulsion interaction potential of cations, erg-molecule\(^{-1}\)

\( \bar{U} \)  
Total average interaction potential, erg-molecule\(^{-1}\)

\( \psi_\eta \)  
Angular wave function in \( \eta \) direction

\( \psi_\xi \)  
Angular wave function in \( \xi \) direction

\( Z \)  
Ion charge, esu

\( Z_e \)  
Electron charge, esu

\( Z_c \)  
Configuration integral

\( a \)  
Adsorbed amount, g/100g

\( a_m \)  
Adsorbed amount, mol-cm\(^{-3}\)

\( a_0 \)  
Adsorbed amount at \( t = 0 \), mol-cm\(^{-3}\)

\( a_t \)  
Adsorbed amount at \( t = t \), mol-cm\(^{-3}\)

\( a_\infty \)  
Adsorbed amount at \( t = \infty \), mol-cm\(^{-3}\)

\( c \)  
Molar concentration, mol-cm\(^{-3}\)

\( c_a \)  
Macropore molar concentration, mol-cm\(^{-3}\)

\( c_b \)  
Bottom chamber molar concentration, mol-cm\(^{-3}\)

\( c_i \)  
Inlet molar concentration, mol-cm\(^{-3}\)

\( c_l \)  
Micropore molar concentration, mol-cm\(^{-3}\)

\( c_m \)  
Molar concentration in the cell bottom boundary, mol-cm\(^{-3}\)

\( c_t \)  
Mobile phase molar concentration, mol-cm\(^{-3}\)

\( c_{total} \)  
Top chamber molar concentration, mol-cm\(^{-3}\)

\( c_o \)  
Total molar concentration including both mobile and immobilized solute, mol-cm\(^{-3}\)

\( c_v \)  
Molar concentration in the cell top boundary, mol-cm\(^{-3}\)

\( c_v \)  
Speed of light, m-sec\(^{-1}\)

\( \delta \)  
Pore diameter, cm

\( f_g \)  
Shape geometric factor

\( g \)  
Degeneracy

\( g_i \)  
Degeneracy at level \( i \)

\( h \)  
Planck constant

\( h \)  
Modified Planck constant defined as \( h/2\pi \)

\( i \)  
Imaginary unit (\( \sqrt{-1} \))

\( k \)  
Boltzmann constant

\( k_f \)  
Film mass transport coefficient, cm-sec\(^{-1}\)

\( k_{des} \)  
Desorption rate constant, molecules-cm\(^{-2}\)-sec\(^{-1}\)

\( k_e \)  
Molecular kinetic energy, erg-molecule\(^{-1}\)

282
Total average molecular translational kinetic energy, erg-mole-1

Total average molecular translational kinetic energy in gas phase, erg-mole-1

Total average molecular kinetic energy in adsorbed phase, erg-mole-1

Average molecular kinetic energy at i level, erg-mole-1

Average molecular rotation kinetic energy, erg-mole-1

Average molecular translational kinetic energy, erg-mole-1

Quantum number defined in equation (1.85)

Adsorbent weight, g

Electron mass, g

Adsorbent weight at t = t, g

Adsorbent weight at t = ∞, g

Molar quantity, mol

Adsorbate molar quantity, mol

Adsorbent molar quantity, mol

Number of the outer shell electrons

Gas number density, molecules·cm⁻³

Number of molecules associated with energy level ε_i

Partial pressure, Pa

Vapor pressure, Pa

Momentum, g·cm·sec⁻¹

Component of momentum in x direction, g·cm·sec⁻¹

Component of momentum in y direction, g·cm·sec⁻¹

Component of momentum in z direction, g·cm·sec⁻¹

Molar adsorption heat, J·mol⁻¹

Differential adsorption heat, J·mol⁻¹

Isosteric adsorption heat, J·mol⁻¹

Molecular partition function

Molecular partition function of adsorbate in bulk phase

Molecular partition function of adsorbate in adsorbed phase

Molecular partition function inside the cavity

Electronic partition function of a molecule

Internal motion partition function of a molecule including vibration, nuclei and electronic

Nuclei partition function of a molecule

Rotation partition function of a molecule

Molecular total partition function

Translational partition function of a molecule

Vibration partition function of a molecule
\( \varphi_w \)
Molecular partition function at the window

Spherical coordinate variable, cm

\( r_c \)
Effective convective flow pore radius, cm

\( r_p \)
Knudsen pore radius, cm

\( r_w \)
Cavity or window radius, cm

\( r_{\text{win}} \)
Radius of the eight membered ring window, cm

\( r_z \)
Distance when the interaction between two particles is zero, cm

\( r_o \)
Microparticle radius, cm

\( \bar{r} \)
Average moving radius of an adsorbate molecule in the cavity or at the window

\( r_i \)
Average radial position at the \( i \) level, cm

\( \overline{r} \)
Total average radial position, cm

\( r_s \)
Ratio of macropore and micropore diffusional time constant s

\( s_t \)
Laplace domain variable

\( t_e \)
Time variable, sec

\( t \)
Experimental tend time, sec

\( t_o \)
Observation time, sec

\( u \)
Velocity, cm-sec\(^{-1}\)

\( w \)
Number of ways

\( w_i \)
Number of ways for level \( i \)

\( x \)
Cartesian coordinate variable, cm

\( x \)
Hopping distance of a molecule inside a crystal, cm

\( y \)
Cartesian coordinate variable, cm

\( z \)
Cartesian coordinate variable, cm

\( \dot{\gamma} \)
Effective collision rate resulting in adsorption, molecules-cm\(^{-2}\)-sec\(^{-1}\)

\( \dot{\gamma} \)
Total collision rate, molecules-cm\(^{-2}\)-sec\(^{-1}\)

\( \dot{\gamma}'' \)
Total desorption rate, molecules-cm\(^{-2}\)-sec\(^{-1}\)

\( \Gamma \)
Adsorbed amount per unit surface area, mol-cm\(^{-2}\)

\( \Gamma_s \)
Adsorbed amount per unit surface area at monolayer coverage, mol-cm\(^{-2}\)

\( \Omega_{AB} \)
Collision function between molecules A and B

\( \Omega_v \)
Collision integral

\( \Pi \)
Three-dimensional spreading pressure, J-mol\(^{-1}\)-cm\(^{-3}\)

\( \Psi \)
Wave function

\( \Psi^* \)
Conjugate wave function

\( \Theta \)
Quadrupole moment, cm\(^3\)

\( \alpha \)
Polarizability, cm\(^3\)

\( \varepsilon \)
Molecular energy, erg-molecule\(^{-1}\)

\( \varepsilon_a \)
Molecular energy in gas phase, erg-molecule\(^{-1}\)

\( \varepsilon_{\text{ele}} \)
Electronic energy of a molecule, erg-molecule\(^{-1}\)

\( \varepsilon_i \)
Molecular energy at \( i \) level or molecular energy level, erg-molecule\(^{-1}\)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_{\text{int}}$</td>
<td>Internal motion energy of a molecule including vibration, nuclei and electronic, erg-molecule$^{-1}$</td>
</tr>
<tr>
<td>$\varepsilon_{\text{nu}}$</td>
<td>Nuclei energy of a molecule, erg-molecule$^{-1}$</td>
</tr>
<tr>
<td>$\varepsilon_{\text{rot}}$</td>
<td>Rotation energy of a molecule, erg-molecule$^{-1}$</td>
</tr>
<tr>
<td>$\varepsilon_{\text{int,pot}}$</td>
<td>Molecular total energy including internal and potential energies, erg-molecule$^{-1}$</td>
</tr>
<tr>
<td>$\varepsilon_{\text{total}}$</td>
<td>Molecular total internal energy, erg-molecule$^{-1}$</td>
</tr>
<tr>
<td>$\varepsilon_{\text{tr}}$</td>
<td>Translational energy of a molecule, erg-molecule$^{-1}$</td>
</tr>
<tr>
<td>$\varepsilon_{\text{vib}}$</td>
<td>Vibration energy of a molecule erg-molecule$^{-1}$</td>
</tr>
<tr>
<td>$\bar{\varepsilon}$</td>
<td>Average translational molecular energy, erg-molecule$^{-1}$</td>
</tr>
<tr>
<td>$\bar{\varepsilon}$</td>
<td>Total average translational molecular energy, erg-molecule$^{-1}$</td>
</tr>
<tr>
<td>$\phi_a$</td>
<td>Microparticle to macropore ratio</td>
</tr>
<tr>
<td>$\phi_b$</td>
<td>Solid to fluid ratio</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Spherical coordinate variable</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>Surface tension, dyne-cm</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>de Broglie wave length, cm; or molecular mean free path, cm</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Chemical potential, J-mol$^{-1}$</td>
</tr>
<tr>
<td>$\mu_a$</td>
<td>Adsorbate chemical potential, J-mol$^{-1}$</td>
</tr>
<tr>
<td>$\mu_{\text{ad}}$</td>
<td>Adsorbate chemical potential in adsorbed phase, J-mol$^{-1}$</td>
</tr>
<tr>
<td>$\mu_s$</td>
<td>Adsorbent chemical potential, J-mol$^{-1}$</td>
</tr>
<tr>
<td>$\mu_{\text{os}}$</td>
<td>Adsorbent chemical potential without adsorbate, J-mol$^{-1}$</td>
</tr>
<tr>
<td>$\mu_n^i$</td>
<td>$n$th non central moment</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Residence time, sec</td>
</tr>
<tr>
<td>$\pi$</td>
<td>Two-dimensional spreading pressure, J-mol$^{-1}$-cm$^{-2}$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density, mol·ml$^{-1}$</td>
</tr>
<tr>
<td>$\rho_s$</td>
<td>Adsorbent particle density (per unit particle volume), g·ml$^{-1}$</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Molecular diameter, cm</td>
</tr>
<tr>
<td>$\sigma_{\text{AB}}$</td>
<td>Lennard-Jones diameter of molecules A and B, cm</td>
</tr>
<tr>
<td>$\sigma^2$</td>
<td>Second central moment</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Tortuosity</td>
</tr>
<tr>
<td>$\tau_a$</td>
<td>Single pellet tortuosity</td>
</tr>
<tr>
<td>$\tau_{\text{bulk}}$</td>
<td>Bulk phase tortuosity</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Adsorption coverage; or dimensionless time variable</td>
</tr>
<tr>
<td>$\upsilon$</td>
<td>Gas viscosity, g·cm$^{-1}$·sec$^{-1}$</td>
</tr>
<tr>
<td>$\varrho$</td>
<td>Porosity</td>
</tr>
<tr>
<td>$\varrho_a$</td>
<td>Bulk phase porosity</td>
</tr>
<tr>
<td>$\varrho_b$</td>
<td>Macropore porosity</td>
</tr>
<tr>
<td>$\chi$</td>
<td>Magnetic susceptibility, cm$^3$</td>
</tr>
<tr>
<td>$\xi$</td>
<td>Spherical coordinate variable, Rad</td>
</tr>
</tbody>
</table>
\[ \zeta \]

Negative chemical potential increment of adsorbent defined in equation 1.4, J·mol\(^{-1}\)