

A Graduate Course in . . .

FUNDAMENTALS OF ADSORPTION

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Adsorption is a unit operation that exploits the ability of solid surfaces to concentrate species from fluid phase onto its surface. It is used quite extensively in the chemical processing industry for purification (drying of gaseous and liquid streams, recovery of solvents) and for bulk separation of mixtures such as normal and iso-paraffins, and air into nitrogen and oxygen by pressure swing adsorption.

The course on fundamentals of adsorption was first developed in 1986 to complement our department's research interests in the areas of zeolite sorption, kinetics, and applications.^[1] It is taken by chemical engineering graduate students nearing completion of the master's degree program or who are in the early stages of the doctoral program. They have previously had graduate-level courses in transport phenomena, thermodynamics, reactor design, and application of numerical methods in engineering. The course is offered once every two years and averages about ten students.

COURSE OBJECTIVES

The course has two main objectives:

- To provide a fundamental background in adsorption, including adsorbent characterization, adsorption equilibria, kinetics of adsorption, adsorption column dynamics, and industrial applications of adsorption.
- To provide an understanding of the present state-of-the-art of adsorption research.

The course is offered over a ten-week period, with two classes each week of 110 minutes duration. It emphasizes zeolites or molecular sieves as adsorbents, with only a brief treatment of other adsorbents. The course content is divided into five parts, described in Table 1.

Introduction • The course begins with an introduction to the general concepts of adsorption. The selectivity parameter is defined in a manner similar to the definition of the relative volatility parameter in distillation. The unit operation of distillation is compared with adsorption, and some general criteria are developed regarding when the adsorption process is a viable unit operation for separation.



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This introduction is followed by a discussion of common adsorbents, such as activated carbon, alumina, silica, and zeolites. The main focus during these introductory lectures is an emphasis on the differences between zeolites and other commonly encountered adsorbents, both in terms of their physical characteristics (monodispersed versus bidispersed), adsorptive properties (differences in shape of the sorption equilibrium isotherms), and diffusive properties (configurational diffusion in zeolites versus molecular and Knudsen diffusion in other microporous adsorbents). These differences also bring into focus the unique features of zeolites, such as their ability to differentiate molecules based on their size and shape.

These lectures are followed by a brief discussion on synthesis of various adsorbents. The crystal structures of commonly used zeolites such as A, X, Y, and pentasil zeolites are also discussed. At this point in the course we emphasize that the main focus of the course will be zeolites as adsorbents.

Sorption Equilibria • Van der Waals forces and various electrostatic forces arising from polarization, dipole, and quadrupole interactions are responsible for physical adsorption. Atom-atom interactions are used to calculate the potential function between an adsorbate molecule and an adsorbent surface. The potential function is then used to calculate the heat of adsorption and the Henry's constant. These theoretical calculations are compared with the experimental data reported in the literature for inert gases on zeolite X and a variety of hydrocarbons in 5A.^[2] The Brunauer classification of isotherms (Type I through V) is discussed next. Langmuir's theoretical model for monolayer adsorption is derived and experimental data for zeolite systems that conform to the Langmuir formulation are presented. The multilayer BET adsorption isotherm is discussed along with a qualitative explanation of the relationship between the type of isotherm and the pore-size distribution.

A thermodynamic approach is then used to study the sorption equilibrium. The concept of spreading pressure is introduced, and it is shown that four independent variables need to be specified to define an extensive thermodynamic property for the two-dimensional adsorbed phase. Gibbs formulation is used to derive the Gibbs adsorption isotherm which is used to derive different adsorption isotherms by assuming different equations of state for the adsorbed phase. The Dubinin-Polanyi concept of correlating experimental data in terms of adsorption potential is also developed.

The major underlying assumptions, the advantages, and the limitations of each adsorption isotherm are discussed in depth. Prediction of binary sorption equilibria from single component equilibria is explored along with the ideal adsorbed solution theory,^[3] the vacancy solution theory,^[4] and the statistical thermodynamic approach.^[2,5] Examples of adsorbent-adsorbate systems that fit the underlying physical principles of each isotherm model (for pure component as well as binary mixtures) are provided. The advantages and limitations of experimental methods of measuring pure component and binary equilibria are then discussed.^[6]

TABLE 1
Course Outline

1. Introduction

- Nature of adsorption: physisorption, chemisorption
- Microporous adsorbents and their characterization

2. Sorption Equilibrium

- Energetics of adsorption
- Thermodynamics of adsorption
- Different isotherm equations
- Adsorption of mixtures
- Correlation, analysis, and prediction of adsorption equilibria
- Experimental techniques

3. Sorption Kinetics

- Different Types of diffusivities
- Experimental techniques
- Models for kinetics of sorption
- Review of diffusion in zeolites

4. Adsorption Column Dynamics

- Mathematical models for single-transition systems
 - General model
 - Linear driving-force approximation
 - Chromatographic response of packed columns
 - Constant pattern behavior
- Mathematical models for multiple-transition systems
 - General model for isothermal systems
 - General model for nonisothermal systems
 - Equilibrium theory

5. Adsorption Process Applications

- Cyclic processes
 - Thermal-swing adsorption
 - Pressure-swing adsorption
 - Displacement desorption
- Chromatographic processes
- Continuous processes
- Simulated countercurrent processes

Sorption Kinetics • Design of adsorption columns requires information on kinetics of sorption. Different types of diffusivities (molecular, Knudsen, configurational) that characterize transport in a porous material are brought out from the semi-logarithmic plot of the values of diffusivity versus pore opening.^[7] The various types of configuration diffusivities in zeolites are defined at this point. The transport diffusivity is defined in terms of concentration gradient, whereas the corrected diffusivity is defined in terms of the chemical potential gradient. These two diffusivities are then related to one another by the Darken's correction factor. The self-diffusivity is defined in terms of the rate of tracer exchange of tagged molecules under no net concentration gradient.

The macroscopic and microscopic experimental techniques of measuring diffusivities in zeolites are discussed next. The macroscopic static methods that are discussed at length include gravimetric, volumetric, and single-crystal membrane methods. The macroscopic dynamic methods that students are exposed to include pulse chromatography, zero-length column, and breakthrough experiments. The basic principles behind each one of these methods are outlined, and students are given a tour of our laboratories where they can examine the experimental setups associated with these methods. Both the advantages and the limitations of each experimental technique are discussed, and the guidelines on the range of diffusivities that can be measured with any given method and the precautions that have to be taken in the analysis of data are given. The microscopic methods such as Nuclear Magnetic Resonance (NMR) and pulsed-field gradient methods are discussed at a more introductory level.

The experimental data on micropore diffusion of various gases in A, X, Y, and pentasil zeolites, and carbon molecular sieves are then reviewed. The monograph of Karger and Ruthven^[8] on diffusion in zeolites thoroughly reviews the field and provides an extensive bibliography of the work done in the field until 1990. The discussion on micropore diffusion in class focuses on variation of transport and corrected diffusivities with 1) loading and 2) temperature. Experimental data for adsorbent-adsorbate systems that exhibit constant corrected diffusivity (*i.e.*, n-heptane-5A, CO₂-4A)^[2] and varying corrected diffusivity with loading (benzenesilicalite)^[8] are presented.

The dispute in the literature on the several orders of magnitude difference in the values of micropore diffusivities determined by NMR and by other macroscopic techniques is highlighted next. This has spawned a debate in the literature on whether the diffusivities determined by the macroscopic techniques are truly micropore diffusivities or some other extraneous mass or heat transfer resistance masks the effect of micropore diffusion. There are numerous cases in the literature where the data were interpreted under the assumption of intracrystalline diffusion control, but further analysis showed that other resistances controlled the overall transport

process. Ruthven, *et al.*,^[9] showed that the results from the uptake experiments carried out with small crystals are more likely to be affected by the intrusion of heat transfer resistance than those obtained with large crystals. Another system where the combined effects of heat transfer and bed diffusion controlled the uptake curve was *i*-octane-13X zeolite.^[10]

Concerted efforts have been made over the last fifteen years to reconcile the differences between NMR diffusivities and those determined from macroscopic method.^[2,8,11] Some adsorbent-adsorbate systems have been identified for which diffusivities determined by both NMR and macroscopic techniques are consistent (Xe and CO₂ in 5A).^[12] There are, however, a number of systems for which discrepancies still exist.^[8,11]

Adsorption Column Dynamics • Since most industrial applications of adsorption processes are performed in a packed-bed configuration with a cyclic mode of operation (adsorption and regeneration), it is imperative that we be able to predict the time of the breakthrough and the shape of the breakthrough curve. In this section of the course, the most commonly used mathematical models are developed to describe the dynamic behavior of an adsorption column.

A realistic mathematical model should account for the nature of the isotherm (linear or nonlinear), feed concentration (dilute or concentrated), nature of adsorption (one component or multicomponent, isothermal or nonisothermal), nature of the fluid flow (plug flow or dispersed-plug flow), and the mass-transfer resistances present in the system (external, macropore, and micropore diffusional resistance). The pedagogical development of the mathematical model is started with the simplest model that assumes

- *linear adsorption isotherm*
- *dilute system*
- *no external mass transfer resistance*
- *fluid in plug flow*
- *adsorption of a single component*
- *isothermal operation*
- *linear driving force approximation*

When these assumptions are relaxed one by one, the mathematical models become progressively more complex.

For linear isotherms, analytical solutions are available for many of these models, but they involve evaluating oscillating integrals which converge rather slowly.^[6] Therefore, it is emphasized that for a linear or a nearly linear isotherm the numerical solution of the simplest model equations with the linear driving force approximation provides a reasonably good representation of the dynamic behavior of an adsorption column. The constant-pattern behavior of the mass transfer zone for a favorable isotherm is discussed for isothermal and non-isothermal conditions. For a nonlinear isotherm, numerical solution of the mass balance equations is required. The complexities introduced by the presence of more than

one adsorbable component and non-isothermal adsorption are discussed. These include: difficulty in representing multicomponent equilibria; variation of sorption equilibrium and transport parameters with temperature; and the increase in number of differential equations that need to be solved since the energy balance and several mass balances have to be included.

For multicomponent systems, the use of equilibrium theory to understand the movement of solutes through the column under isothermal conditions is emphasized. A cursory treatment of equilibrium theory is presented for adiabatic systems.

Process Applications • The process applications of adsorption are divided into

- *Batch cyclic processes that include pressure-swing adsorption (PSA), temperature-swing adsorption (TSA), and displacement desorption*
- *Chromatographic processes*
- *Continuous countercurrent processes*
- *Simulated moving bed processes*

The PSA processes (especially separation of air into nitrogen and oxygen) and TSA processes (sweetening of sour gas) are treated more fully with a detailed discussion of theory, experimental data, and design considerations. The treatment of other processes is limited to a qualitative discussion of principles and design aspects and their applications in the process industry. Examples of the chromatographic separation processes discussed are separation of xylene isomers, pinenes, and linear paraffins. The continuous process discussed is the now-obsolete hypersorption process, and the simulated moving-bed system represented by Sorbex processes.

BOOKS AND READING MATERIAL

In general, it is difficult to find a book that will cover the majority of the material covered in a graduate course. Fortunately, several excellent books in the area of adsorption have recently been published that cover many of the topics discussed in this course. Ruthven's book^[2] covers the major sections of the course and, hence, is used as a textbook. Since it was published in 1984, its material is complemented with other more recently published books.^{[[6,8,13-15]} These books also provide a listing of appropriate journal articles.

GRADING

Grading is based on student performance in homework assignments, an in-class midterm examination, a take-home final examination, and an end-of-the-term project. The project requires the students to review a state-of-the-art research subject that is of interest to the student and that falls within the scope of the course. Since the number of students in the class is small, active student participation is encouraged and sought.

CONCLUSION

Adsorption represents an important unit operation in the chemical industry. It is a fertile area with research opportunities in both fundamental and applied aspects. For those students who are interested in pursuing research in this area, the course is designed to provide sufficient fundamental background and an appreciation of the status of current research efforts in different areas. After taking the course, the graduate students are in a better position to identify an area of research interest. For others, it provides an understanding of the fundamentals of adsorption and its place in industrial applications for separation and purification. The course has been well received by the students.

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Scaling Initial and Boundary Value Problems

Continued from page 241

we must have $\partial c_A^* / \partial r^* \ll 1$ at $r^* = 1$. But $\partial c_A^* / \partial r^*$ is largest at $r^* = 1$; hence $\partial c_A^* / \partial r^* \ll 1$ throughout the tube, and we conclude that $c_A^* \approx c_A(z^*)$. Since the radial concentration gradient is negligible, we can incorporate the heterogeneous reaction term directly into the species mass balance to obtain the classical plug flow reaction equation

$$\bar{v} \frac{dc_A}{dz} = -\frac{2k_1}{R} c_A \quad \text{for } 0 \leq z \leq L \quad (5.19)$$

$$c_A = c_{A_0} \quad \text{at } z = 0 \quad (5.20)$$

where \bar{v} is the average velocity.

SUMMARY

Hopefully these five examples have convinced the reader that the systematic approach to scaling analysis described here has real utility in teaching transport-related engineering courses as well as in engineering practice. Additional examples of scaling analysis were given in the earlier article by Krantz.^[1] Reprints of the latter article can be obtained by contacting the authors.

NOMENCLATURE

- c_A molar concentration of component A
- c_{A_0} initial molar concentration of component A
- D_{AB} binary diffusion coefficient of A in B
- g gravitational acceleration
- H spacing or half-spacing between parallel plates
- k thermal conductivity
- k_1 first-order heterogeneous reaction-rate constant
- K Darcy permeability of porous media
- L length of parallel plates or cylindrical tube
- L_e entry length to achieve fully developed laminar flow
- P pressure

- ΔP pressure drop over length L
- r radial coordinate in cylindrical coordinate system
- R radius of cylindrical tube
- Re Reynolds number
- t time
- T temperature
- T_f freezing temperature
- T_0 surface temperature
- U_s scale for velocity component in x-direction
- v_i velocity component in the i-direction
- \bar{v} mass-average velocity
- V_p velocity of the plate
- V_s scale for velocity component in y-direction
- W_s scale for velocity component in z-direction
- x, y rectangular coordinates
- z axial coordinate in cylindrical coordinate system

Subscripts

- r denotes a reference factor
- s denotes a scale factor

Superscripts

- $*$ denotes a dimensionless variable

Greek

- α thermal diffusivity
- δ boundary-layer or region of influence thickness
- λ latent heat of fusion of water
- μ shear viscosity
- ρ mass density

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