

SEPARATION PROCESSES: Particulate Systems And Column Operations

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CHEMICAL ENGINEERING 260 and 261 at UC Davis are each one quarter courses designed to introduce graduate students (and some seniors) to separation processes of particulate systems and column or cascade systems. Some students consider the courses as featuring applications of mass transfer, others, applications of mathematics. Some students hope to gain a deeper understanding for design of ChE unit operations, others desire a suitable background in a particular area so they may begin research or understand the research of others. In addition to these separate objectives the instructor hopes students in the courses are instilled with an appreciation for the interaction and interdependence of these subjects: mathematics, transport phenomena, design, and research.

Tables I and II show typical outlines of topics and lectures. These courses are not meant to overlap with other engineering courses at UC Davis, and therefore certain items are omitted that are adequately covered in the other courses. For the first course, a course in transport phenomena such as Section III in Bird, Stewart, and Lightfoot [1], is pre-requisite; for the second, an additional pre-requisite is a course in staged mass transfer operations.

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TABLE I

Outline of topics for ChE 260, Separation Processes: Particulate Systems

1. Membrane separations: colloid systems, reverse osmosis and ultrafiltration, problem of concentration polarization.
2. Distribution functions, population balances, moment equations.
3. Micro organisms; enzyme kinetics.
4. Birth, death, and fission kinetics.
5. Chemostat analysis: fermentation, activated sludge, sterilization.
6. Crystallization, nucleation, zone refining.
7. Liquid-liquid systems: particle agglomeration and breakage.
8. Aerosol dynamics: Knudsen, transition, continuum regimes.
9. Molecular velocity distribution functions, kinetic equations, hydrodynamic equations, constitutive equations.
10. Drag and thermal forces on aerosols; precipitators.
11. Evaporation and growth of aerosols.

PARTICULATE SYSTEMS

BRIEFLY, THE FIRST COURSE is an analysis of particulate systems in, for example, pollution abatement and chemical process equipment. Macromolecules, micro-organisms, colloids, crystals, and aerosols are discussed. Population balances and distribution functions are mathematical concepts that tie the topics together and help maintain continuity. Variations of the classic ChE models, the plug flow and continuous stirred tank reactors, recur frequently as well.

Usually ChE 260 begins with the membrane separations: reverse osmosis (hyper filtration), ultrafiltration, dialysis, etc. The students inspect various membrane devices, and thermodynamics of osmotic pressure is reviewed (e.g. van't Hoff equation). Flux equations for solvent or solute transfer through the membrane are based on principles of irreversible thermodynamics. The



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role of concentration polarization is emphasized, and the film theory with rejection efficiency is introduced. We review correlations for mass transfer coefficients in various configurations for laminar and turbulent flow. For example, we show the Leveque model provides an analytical path to the laminar-flow form of the relation between Sherwood and Peclet numbers and the diameter to length ratio [2]:

$$Sh \propto Pe^{1/3} (d/x)^{1/3}$$

Techniques for increasing mass transfer and decreasing concentration polarization are discussed [3], including the effect of heating [4] and of pulsed operation [5]. For dewatering of certain food materials, the fluid is non-Newtonian. Thus the effect of the power law stress relation on transfer coefficients is studied [6]. For a mathematically more detailed description of the convective mass transfer in concentration polarization, the partial differential equations are written and solved by separation of variables [7]. The velocity profiles for the convective model are provided by the perturbation solution of the Navier-Stokes equation for the stream function [8].

Enzymes are macromolecules (proteins) that can be concentrated by ultra-filtration [9]. Their catalytic properties are first described by Michaelis-Menten kinetics, derived via the Briggs-Haldane model [10]. Expressions for conversion of substrate in plug flow, batch and continuous stirred tank reactors are compared. Rate equations for various competitive reactions, as well as methods of data analyses, are developed.

Various immobilized-enzyme reactors are compared. Rate equations for various competitive reactions, as well as methods of data analyses, are developed. Various immobilized-enzyme reactors are analyzed: for example, the differential equation for steady state diffusion and reaction of substrate in a porous spherical particle is solved for zeroth and first order kinetics due to an enzyme attached to the pore surfaces. Effectiveness factors are used to determine conversion for packed bed and slurry reactors of these porous particles [11].

Solubility and stability of proteins and colloids are discussed in terms of the electrical double layer [12]. The Debye-Huckel theory, which makes use of diffusion-like differential equations for electrostatic potential, is reviewed for the activity coefficients of dissolved enzymes [13]. The equilibrium theory of protein solubility shows how dissolved protein concentration depends on ionic strength [14]. Recent developments in affinity

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chromatography to separate proteins are interpreted in terms of protein solubility in salt solutions [15].

Microencapsulated enzyme is an example of the simplest model of a microorganism. Substrate diffuses through the encapsulating membrane to react with the entrapped enzyme. Monod kinetics for bacterial growth follow naturally, and are used to derive equations for the operation of the steady state chemostat. Brief mention is made of the chemostat's relation to fermentation, activated sludge, and sterilization processes. The diffusion field in and around a single spherical cell is studied for zeroth and first order approximations to Michaelis-Menten kinetics inside the cell [16].

POPULATION BALANCE

THE COMPACT SECTION in Himmelblau and Bischoff [17] is followed closely to introduce and use population balance equations. A general

Reynolds transport theorem is used in this context, and the population balance equation is shown to be a generalization of the more familiar multicomponent mass balance. Moment equations are derived from the equation for the population distribution function. A macroscopic equation for the average distribution is shown to have obvious similarities with macroscopic equations in transport phenomena. The chemostat model for bacteria with time dependent mass is considered for special forms of birth, death, and fission terms. We briefly touch on problems of particle agglomeration and breakage in liquid-liquid systems.

Crystallizer product size distributions for the "mixed suspension, mixed product removal" model are discussed. Reading from the book on particulate processes by Randolph and Larson [18] is recommended. The basic picture of homogeneous nucleation with free energy depending on embryo size provides for a discussion of effects of supersaturation, interfacial tension, and critical cluster diameter [19]. We also discuss a model of zone refining [20].

The final major section of ChE 260 is based on rarefied gas transport phenomena and aerosol systems. First, the three rarefied gas regimes are defined: the Knudsen, transition, and continuum regimes with, respectively, the mean free path λ much greater than, about the same as, or much less than the characteristic geometrical length L , e.g., the particle diameter. We note qualitatively different phenomena are exhibited in the extreme regimes, but that a gradual transition bridges between. This is compared to sharp qualitative leaps between regimes of other phenomena, e.g. phase changes, or laminar-turbulent transition. All this is to emphasize physical laws have limits: mathematical equations fail to describe physical reality outside the range of the model's application.

Because it appears in so many contexts, the equation for flux of molecules to a surface in free-molecule (Knudsen) flow is carefully developed.

$$j = p/\sqrt{2\pi mkT}$$

This equation is related to effusion, catalyst pore diffusion, the Knudsen vapor pressure cell, thermal transpiration, and deposition and evaporation at the surface of a particle—all processes in the Knudsen regime. Condensation and accommodation coefficients are defined. Knudsen regime formulas for heat transfer from a sphere, and for drag on a sphere are presented (reference is made to Kogan's book [21] for details).

The continuum gas regime is next treated, where intermolecular collisions dominate entirely over molecule/wall collisions. The Boltzmann kinetic equation is shown to have the same general form as population balance equations. The velocity distribution function has moments related to the observable mass density, velocity, and temperature of the gas. The moment equations are the point (hydrodynamic) equations of change. We introduce the simple relaxation (Krook) form of the intermolecular collision operator [22] and use the Chapman-Enskog technique to derive Newton's law of stress with viscosity coefficient,

$$\mu_c = \tau_c p$$

and Fourier's law of heat conduction with thermal conductivity coefficient,

$$\kappa_c = \frac{5}{2} \frac{k}{m} \tau_c p$$

in terms of the collision time τ_c , pressure p , molecular mass m , and Boltzmann's constant k . The subscript c indicates the continuum limit.

We treat the transition regime by assuming that the collision frequency is the sum of collision frequencies of molecule/wall and molecule/molecule collisions [23]:

$$\frac{1}{\tau} = \frac{1}{\tau_K} + \frac{1}{\tau_c}$$

Such a hypothesis leads to transport coefficients obeying a well-known expression; e.g. for the viscosity,

$$\frac{1}{\mu} = \frac{1}{\mu_K} + \frac{1}{\mu_c}$$

The second course concerns the analysis and design of separation processes in columns or cascaded systems: distillation, leaching, extraction, adsorption, chromatography, absorption. Applied mathematics is a prominent aspect of the course including finite difference equations, probability and random walk theories, method of characteristics, and moment analysis.

Expressions for fluxes Φ are usually of prime importance; we show that

$$\Phi/\Phi_c = \frac{1}{1 + GK}$$

where $K = \lambda/L$ is the Knudsen number, and G depends on geometry and molecular accommodation. Further,

$$GK = \Phi_c/\Phi_K = \mu_c/\mu_K = \tau_c/\tau_K$$

TABLE II

Outline of topics for ChE 261,
Separation Processes: Column Operations

1. Finite difference equations applied to staged operations: distillation, extraction, leaching, absorption. Derivation of Smoker, Fenske, and Kremser equations.
2. Rate processes in column operations: transfer unit analysis and unified design method for continuous contactors.
3. Axial dispersion: Taylor, random walk, other models.
4. Equilibrium theory of chromatography: binomial, Poisson, and Gaussian probability functions.
5. Breakthrough curve analysis: Goldstein J-function, Parex process.
6. Method of characteristics for solving first-order partial differential equations: chromatography, parametric pumping.
7. Moment analysis of pulse response experiments: adsorption, gas-liquid partition, gel permeation chromatography. Hermite polynomial representation of elution curves.
8. Chromatography resolution and optimization.

so that quite simple formulas describe the transition regime, formulas that are easily constructed if one knows the continuum and Knudsen flux expressions [23]. Transition range formulas are developed for heat and mass transport near a sphere, and drag on a sphere. The well-known Maxwell equation for evaporation or growth of a droplet is derived for simultaneous heat and mass transport [24]. Remarkably, when transition range diffusion and heat conductivity coefficients are inserted into the Maxwell formula, one obtains precisely the same equation derived by Fukuta and Walters [24] by quite a different approach.

COLUMN OPERATIONS

THE SECOND COURSE concerns the analysis and design of separation processes in columns or cascaded systems: distillation, leaching, extraction, adsorption, chromatography, absorption. Applied mathematics is a prominent aspect of the course, including finite difference equations, probability and random walk theories, method of characteristics, and moment analysis via Laplace transformation. The emphasis is on mathematics as a reflection of the physical world, and the usefulness (or necessity) of the derived equations for design of equipment is continually noted. The

students in ChE 261 are asked to purchase King's *Separation Processes* [25], from which numerous reading and problem assignments are made.

We begin with the calculus of finite differences applied to staged units [26]. Analytical methods for solving difference equations are compared to methods for differential equations. Murphrey efficiencies are included in the analysis of systems whose equilibrium can be described by a linear relation or by a constant separation factor (relative volatility). The Smoker, Fenske, and Kremser equations are derived, and a host of problems of industrial interest are solved for homework.

Depending on the interests of the students, we have sometimes treated multicomponent distillation for constant relative volatility systems. Here, matrix methods and computer techniques are discussed [24].

We review the analysis of two-phase separations controlled by interphase mass transfer when longitudinal dispersion can be ignored [1]. The resulting expression for number of transfer units (NTU) is related to height equivalent to a theoretical stage (HETP).

Descriptive notions of longitudinal dispersion in columns are introduced. The Danckwerts boundary conditions for a finite-length column are derived following the simple, yet general treatment by Bischoff [28]. A unified design method for continuous-contact mass transfer operations unifies a large class of operations with dispersion [29].

Following Feller [30], we introduce the probability concepts of binomial distribution and Bernoulli trials. The Poisson and normal Gaussian distributions are treated as approximations to the binomial distributions. The first and second moments of the three distributions are derived and compared.

We follow King's treatment [25] of the intermittent carrier flow model for equilibrium stages, to get the binomial distribution of solute among stages. We use a generating function method [30] to obtain the Poisson distribution solution to the difference-differential equation for the continuous-flow equilibrium-stage model of chromatographic separators. From the Gaussian approximation we extend this analysis to develop the relations for the equilibrium model of chromatography. We also use the generating function method to analyze a breakthrough curve for a cascade of equilibrium stages.

One-dimensional random walk theory is used

in the conventional manner to derive the diffusion equation,

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} .$$

A solution for a delta function initial condition is derived by means of the gaussian approximation to the binomial distribution [31]. This solution is used as a Green's function to get superposition solutions for several other initial conditions [32]. This material is then related to the convected dispersion problem in a tube, and conditions for the Peclet number are derived under which a chromatographic output curve is gaussian with respect to time [33]. Related topics, such as Fourier transform solutions, Brownian motion, and the Einstein formula for diffusion coefficients, have been dealt with in some years, depending on available time and student interest.

There is considerable interest . . . in using dynamic response methods (e.g. pulse response) to quantify parameters in a range of systems: packed-bed and slurry catalytic reactors, kidneys, distillation columns, chicken lungs, etc.

TREATMENT OF DISPERSION

WE NEXT TREAT dispersion in a more thorough manner by means of the Taylor-Aris model via the moment analysis of convection and diffusion [34]. Some other models and correlations of data are discussed [35-39].

The Goldstein J-function solution for the non-dispersed first order partial differential equations for breakthrough curves is derived by Laplace transforms [40]. The discussion of this model and the graphical presentation of the solution by Hougen and Watson [41] is noted. The application to the Parex adsorption process for recovering p-xylene from its mixtures with other C₈ hydrocarbons is discussed [42]. We also consider ion exchange processes.

The method of characteristics is also useful for time-dependent problems when diffusion effects can be ignored. Simple chromatography [35] and parametric pumping [43] are analyzed by this method.

There is considerable interest in our department in using dynamic response methods (e.g.

pulse response) to quantify parameters in a range of systems: packed-bed and slurry catalytic reactors, kidneys, distillation columns, chicken lungs, etc. The method is introduced by a pulse response analysis of an open tube; for the concentration $c(t,x)$ we have

$$\frac{\partial c}{\partial t} = -v \frac{\partial c}{\partial x} + D \frac{\partial^2 c}{\partial x^2} .$$

The equation is Laplace transformed, and the resulting ordinary differential equation is solved for $c(s,x)$. From the definition of the transformed concentration, $c(s,x)$, we prove that

$$\lim_{s \rightarrow 0} \frac{d^k c}{ds^k} = (-1)^k \int_0^{\infty} t^k c dt,$$

where the integral is the kth moment. Therefore, we can take limits of derivatives of the solution, $c(s,x)$, to relate the statistical moments to the parameters of the system. The moments may be calculated from experimental response data, and parameters evaluated. The technique is extended to breakthrough curve analysis (response to a step function input), and to frequency analysis (response to a sinusoidal input).

Considerable effort is put into the moment treatment of adsorption chromatography [44], of which (gel) permeation chromatography is the special case when adsorption is negligible. Adsorption (or a linear chemical reaction) may occur at the pore surfaces of porous particles in packed columns. Pore diffusion, interparticle mass transfer, and axial dispersion all play a role. Expressions of moments and methods of getting information out of pulse response data are presented [45, 46].

Since an output pulse is often nearly gaussian, hermite polynomials are defined and used to reconstruct the output curve in terms of moments, and thus in terms of system parameters [47]. For the separation of two solutes with gaussian outputs, a resolution criterion is defined for their separation, and optimization with regard to column length and operating velocity is discussed [48]. This approach has the advantage that considerable semi-empirical knowledge can be organized by one comprehensive method. The optimization is extended to apply to product value, and equipment and operating costs [48]. We point out the same methods can be applied to capillary chromatography or partition chromatography.

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CONCLUDING REMARKS

OUR EXPERIENCE INDICATES considerable material can be covered in the two 30-lecture quarters if tedious algebraic manipulations on the blackboard are kept to a minimum. Such manipulations are often assigned as homework so students may gain familiarity with the mathematical symbols and their meaning in terms of the physical world. Lecture notes are frequently xeroxed and handed out, so lectures emphasize concepts and conclusions. Many of the papers referenced here are assigned reading, to bring students up to the frontiers of research. □

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