Non-Equilibrium Transport (BSL, pg 753-755)

Suppose we flow through an adsorption or chromatograph column so fast that the adsorption is not at equilibrium at a given point in the column. This departure from equilibrium could be either due to diffusion resistance within the porous particles of the column or due to kinetic limitation of the adsorption process. Alternatively, you may wish to separate different size macromolecules by the difference in the diffusivity of the macromolecules. This is commonly known as size-exclusion chromatography. Another case is measurement of the saturation of a nonaqueous phase by partitioning tracers. We will first derive the analytical solution for the general case and then derive the mass transfer coefficients for specific cases.

The system is a homogeneous column with no dispersion in the direction of flow and uniform concentration on a macroscopic scale perpendicular to the direction of flow, i.e. the transverse direction.

The packing material of the column may be porous particles such that we need to distinguish between intra-particle porosity or micro-porosity and the inter-particle porosity or macro-porosity. The total porosity is the sum of the two porosities.

$$\phi_t = \phi_{flow} + \phi_{micro}$$
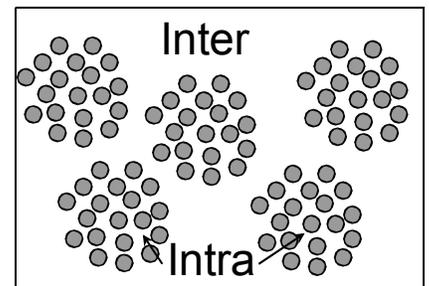
Convective transport occurs only in the inter-particle porosity so it will be referred to as the flowing porosity. At a given distance along the length of the column, it is always assumed that the concentration gradients in the inter-particle region are small enough so the concentration can be assumed to be uniform. If the process is diffusion limited, then there will be a concentration gradient within the particle. In this case, the concentration is uniform only in the inter-particle space and the porosity containing the uniform concentration is the flowing porosity, $\phi = \phi_{flow}$. The micro-porosity is considered to be the stationary phase.

On the other hand, if the process is adsorption kinetic limited, then the concentration profile of the fluid within the particle as well as in the inter-particle space is assumed to be uniform and the total porosity should be used to describe the convective and diffusive transport through the column. In this case the

porosity of uniform concentration is the total porosity, $\phi = \phi_t = \phi_{flow} + \phi_{micro}$. In either case, the column is modeled as consisting of a flowing phase (all of which may not be flowing) having a porosity ϕ with an interstitial velocity, v, and concentration, c, and a stationary phase with a concentration, c_s. The units of c_s is defined such that it is amount of material per unit of flowing volume, ϕ. Multiple fluid phases will be discussed later. This description of the column is illustrated below.

Flowing phase	$\mathbf{v} \longrightarrow$	$\mathbf{c}$
Stationary phase	v=0	$\mathbf{c}$
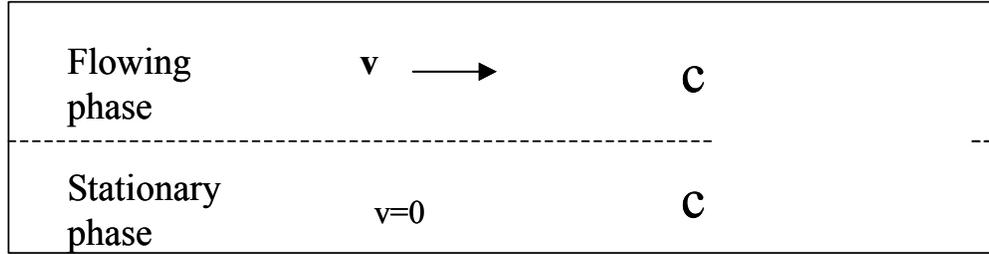
The overall concentration, flux, and the mass conservation equation are as follows.

$$C = \phi(c + c_s)$$
$$N = u\,c, \quad u = q/A$$
$$\frac{\partial C}{\partial t} + \frac{\partial N}{\partial x} = 0$$
$$\phi \frac{\partial(c + c_s)}{\partial t} + u \frac{\partial c}{\partial x} = 0$$

At equilibrium, assume the relation between the stationary and flowing phase can be described by a linear relationship. This linear relationship is expressed simply by a coefficient, K, which appears like an equilibrium constant but this coefficient must also include the parameters that express the concentration in the stationary phase as per unit volume of the flowing phase. Also, assume that the rate of transport between the flow and stationary phases is proportional to the departure of the flowing concentration from the concentration that would be in equilibrium with the surface. The mass transfer coefficient and specific area, $k_c\,a_\phi$, are defined with respect to the specific area per unit of pore volume. Small mass transfer rates, i. e., negligible convection, is assumed.

$$c_s^{eq} = K\,c^{eq}, \quad \text{at equilibrium}$$
$$\frac{\partial c_s}{\partial t} = k_c\,a_\phi\left(c - c^{eq}\right), \quad a_\phi = a/\phi$$
$$= k_c\,a_\phi\left(c - c_s/K\right)$$

This relationship is substituted into the conservation equation.

$$\phi \frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} = -\phi k_c a_\phi \left(c - c_s / K \right)$$

$$\frac{\partial c}{\partial t} + v \frac{\partial c}{\partial x} = -k_c a_\phi \left(c - c_s / K \right), \quad v = u / \phi$$

The following initial and boundary conditions are assumed.

$$c_s \left(t = 0 \right) = 0, \qquad x > 0$$

$$c \left(x = 0 \right) = c^{BC}, \qquad t > 0$$

Time is transformed to a transformed time,

$$t' = t - x / v .$$

This transformed time is zero at a point in the column at the time when the concentration wave would have reached that point if no mass transfer to the stationary phase was to occur. Expressing the time in terms of this transformed time transforms the conservation equations are as follows.

$$c(x,t) = c(x,t')$$

$$\left(\frac{\partial c}{\partial t} \right)_x = \left(\frac{\partial c}{\partial t'} \right)_x \left(\frac{\partial t'}{\partial t} \right)_x = \left(\frac{\partial c}{\partial t'} \right)_x$$

$$\left(\frac{\partial c}{\partial x} \right)_t = \left(\frac{\partial c}{\partial t'} \right)_x \left(\frac{\partial t'}{\partial x} \right)_t + \left(\frac{\partial c}{\partial x} \right)_{t'}$$

$$= \left(\frac{\partial c}{\partial t'} \right)_x \left(\frac{-1}{v} \right) + \left(\frac{\partial c}{\partial x} \right)_{t'}$$

$$\left(\frac{\partial c}{\partial t} \right)_x + v \left(\frac{\partial c}{\partial x} \right)_t = v \left(\frac{\partial c}{\partial x} \right)_{t'}$$

The conservation equations and initial and boundary conditions are now as follows.

$$v \left(\frac{\partial c}{\partial x} \right)_{t'} = -k_c a_\phi \left(c - c_s / K \right)$$

$$\frac{\partial c_s}{\partial t'} = +k_c a_\phi \left(c - c_s / K \right)$$

$$c_s \left(t' \le 0 \right) = 0, \quad x > 0$$

$$c \left(x = 0 \right) = c^{BC}, \quad t' > 0$$

The equations will be made dimensionless. Since there is no downstream boundary condition, it is convenient to treat the system as if it is infinite in length. The variables are made dimensionless as follows.

$$X = c/c^{BC}, \qquad Y = c_s/c_o$$

$$\varsigma = x/x_o, \qquad \tau = t'/t_o$$

$$\left[\frac{v c^{BC}}{k_c a_\phi c^{BC} x_o} \right] \frac{\partial X}{\partial \varsigma} = -\left(X - \left[\frac{c_o}{K c^{BC}} \right] Y \right)$$

$$\left[\frac{c_o}{k_c a_\phi c^{BC} t_o} \right] \frac{\partial Y}{\partial \tau} = +\left(X - \left[\frac{c_o}{K c^{BC}} \right] Y \right)$$

The dimensionless variables can be determined by specifying that the bracketed terms equal to unity.

$$c_o = K c^{BC}$$

$$x_o = \frac{v}{k_c a_\phi}$$

$$t_o = \frac{K}{k_c a_\phi}$$

$$X = c/c^{BC}, \qquad Y = \frac{c_s}{K c^{BC}}$$

$$\varsigma = \frac{k_c a_\phi x}{v}, \qquad \tau = \frac{k_c a_\phi}{K} t'$$

$$\frac{\partial X}{\partial \varsigma} = -(X - Y)$$

$$\frac{\partial Y}{\partial \tau} = +(X - Y)$$

$$X(0, \tau) = 1, \qquad Y(\varsigma, 0) = 0$$

We have a linear, first order initial value problem in the space and time variables. Thus it can be solved by Laplace transformation in the space and time variables. Hints to this solution is given in BSL Problem 23D.1. The solution for Y is derived in a similar manner by taking the Laplace transform of the equations with respect to the space variable, ς. The resulting analytical solution is as follows.

$$X = 1 - \int_0^\varsigma \exp\left(-\varsigma' - \tau\right) J_o\left(i\sqrt{4\tau\varsigma'}\right) d\varsigma'$$

$$Y = \int_0^\tau \exp\left(-\varsigma - \tau'\right) J_o\left(i\sqrt{4\tau'\varsigma}\right) d\tau'$$

$$\varsigma > 0, \quad \tau > 0$$

Suppose we wish to evaluate the effluent concentration at *x=L*. Then it is convenient to express time as pore volume throughput.

$$\varsigma(x = L) = \frac{k_c a_\phi L}{v}$$

$$t = t' + x/v$$

$$t(x = L) = \frac{K\tau}{k_c a_\phi} + \frac{L}{v}$$

$$\frac{Aut(x = L)}{A\phi L} = \frac{vK\tau}{k_c a_\phi L} + \frac{L}{L}$$

$$\frac{\phi_t}{\phi}\frac{Q}{V_p} = 1 + K\left(\frac{\tau}{\varsigma(x = L)}\right), \quad V_p = A\phi_t L, \quad Q = Aut, \quad \tau > 0$$

$$\frac{\tau}{\varsigma(x = L)} = \frac{1}{K}\left(\frac{\phi_t}{\phi}\frac{Q}{V_p} - 1\right), \quad \frac{\phi_t}{\phi}\frac{Q}{V_p} \geq 1$$

The last two equations give a mapping between the physical variable, the pore volume throughput, Q/V_p, and the dimensionless independent variables. If one wanted to calculate the effluent concentration as a function of the pore volumes of throughput, it is necessary to first calculate the dimensionless distance to the outflow end of the column, $\varsigma(x = L)$, and then keeping this parameter fixed calculate the effluent concentration and pore volume throughput as a function of dimensionless time.

The dimensionless effluent concentration is plotted below for several values of the dimensionless distance, $Z=\zeta$, corresponding to the length of the column.
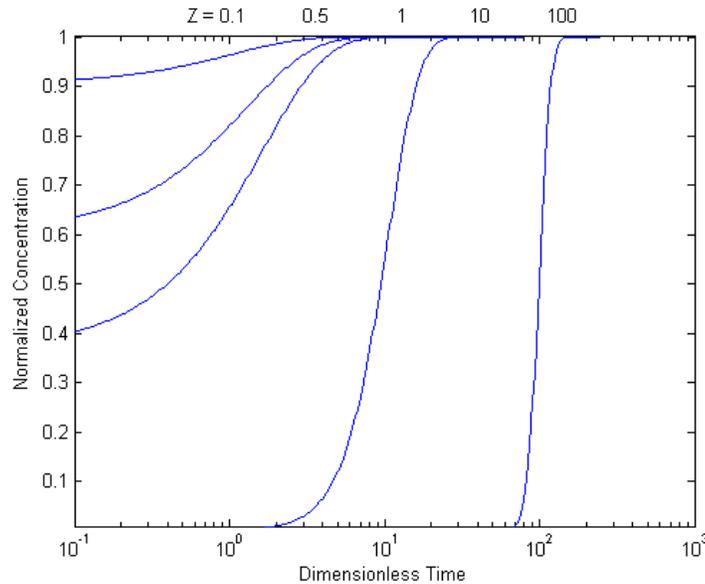
Notice that for a very short column, a column with a very small mass transfer coefficient, or very fast flow rate, the effluent concentration is very near the injected concentration soon after breakthrough at one pore volume of throughput. On the other hand, notice that for a very long column, a column with a very large mass transfer coefficient, or a very slow flow rate, the effluent concentration is very near zero for some time after one pore volume of throughput. It appears as if the effluent concentration is retarded due to the mass transfer of solute to the stationary phase.

The extent of retardation can be seen more explicitly if the effluent concentration is plotted as a function of the ratio of dimensionless time and dimensionless distance as shown below.

In this figure, we see that the retardation in the limit of large dimensionless length is approaching a dimensionless time equal to dimensionless length, i.e. ratio equal to unity. We can see from the expression for the pore volume throughput that when this ratio is equal to unity, the pore volume throughput (multiplied by the porosity ratio) exceeds unity by the parameter, K.

$$\left.\frac{\phi_t}{\phi}\frac{Q}{V_p}\right|_{\tau/\varsigma=1}=1+K$$

Thus the retardation of the effluent concentration in the limit of negligible mass transfer resistance is equal to the parameter, K. This limiting case corresponds to the retardation calculated assuming equilibrium adsorption with a linear adsorption isotherm.

Stationary phase concentration and equilibrium constant

Earlier we stated that the stationary phase concentration, c_s, is expressed as amount of material per unit of flowing volume, ϕ. This definition gives the stationary phase concentration the same units as the flowing phase concentration and thus simplifies the equations. However, we must remember that ϕ may be either the total porosity, ϕ_t or the flowing porosity, ϕ_{flow}. It will be the total porosity in case of adsorption rate controlling mass transfer and the flowing porosity or inter-particle porosity when mass transfer is controlled by diffusion within the particle.

Adsorption. If the mass transfer rate limiting process is adsorption on to the surface of the solid, then the stationary phase concentration is calculated from the surface concentration. Recall that the surface coverage could be expressed through the fractional coverage.

$$\phi=\phi_t,\quad \phi_t/\phi=1$$

$$c_s=\Sigma_s\,\rho_s\frac{1-\phi}{\phi}\Gamma$$

$$\Gamma=\frac{\theta}{b_2\,N_A}$$

where
Σ_s specific surface area, m^2/kg
ρ_s adsorbent matrix density, kg/m^3
b_2 coarea of molecule, m^2
θ fractional coverage, b_2/a
N_A Avogadro's number, 6.022×10^{23} molecules mole^{-1}
Γ surface concentration, mole/m^2

7

The value of the equilibrium constant is the limiting slope of the adsorption isotherm in the Henry's law limit.

$$K = \lim_{c \to 0} \frac{dc_s}{dc}$$

Absorption into a stationary oil phase. Suppose the flowing phase is water and the stationary phase is oil. The amount of the stationary or residual oil phase, S_{or}, can be determined by measuring the retardation of a partitioning tracer. The flowing porosity is the product of the total porosity and the water saturation.

$$\phi = \phi_{flow} = \phi_t (1 - S_{or})$$

$$\frac{\phi_t}{\phi} = \frac{1}{1 - S_{or}}$$

The concentration in the oil must be expressed as per unit of flowing volume.

$$c_s = c_{oil} \frac{S_{or}}{1 - S_{or}}$$

The equilibrium distribution of a solute between the oil and water phases is expressed as the equilibrium partition coefficient, $K_{o/w}$.

$$K_{o/w} = \frac{c_{oil}}{c_{water}}, \quad \text{at equilibrium}$$

The equilibrium ratio between the stationary and flowing phases can be determined from the above two equations.

$$c_s^{eq} = \frac{S_{or}}{1 - S_{or}} K_{o/w} c_{water}^{eq}$$

$$K = \frac{S_{or}}{1 - S_{or}} K_{o/w}$$

Size exclusion chromatography. Suppose an aqueous solution of a macromolecule is flowed through a column packed with micro-porous particles. If the size of the micro-pores is small enough, the macromolecule will be entirely excluded. We will consider the more interesting case of where the size of the pores are large enough for the macromolecules to enter but the macromolecules have a small diffusivity because of its size in the particular solvent. The flowing

porosity will be the inter-particle porosity. The micro-porosity is sometimes called the excluded pore volume.

$$\phi = \phi_{flow} = \phi_t - \phi_{micro} = \left(\frac{\phi_t - \phi_{micro}}{\phi_t} \right) \phi_t$$

$$\frac{\phi_t}{\phi} = \frac{\phi_t}{\phi_t - \phi_{micro}}$$

$$c_s^{eq} = \frac{\phi_{micro}}{\phi_{flow}} c^{eq} = \frac{\phi_{micro}}{\phi_t - \phi_{micro}} c^{eq}$$

$$K = \frac{\phi_{micro}}{\phi_t - \phi_{micro}}$$

<u>Mass transfer coefficient</u>. The mass transfer coefficient allows us to compute the diffusive mass flux as a function of a concentration difference over some length rather than a concentration gradient. The dimensionless group to correlate the mass transfer coefficient is the Sherwood number (BSL pg. 675). If the particles in a packed bed can be described as spheres with a diameter D_p, the Sherwood number gives an approximation for estimating the mass transfer coefficient (BSL pg 681, 686). The diffusivity in a particle, D_{As}, is reduced by the micro-porosity and tortuosity.

$$\text{Sh}_m = \begin{cases} \dfrac{k_c D_p}{D_{AB}} \approx 2, & \text{creeping flow past spheres} \\[2mm] \dfrac{k_{c,s} D_p}{D_{As}} \approx 10, & \text{diffusion inside a sphere} \end{cases}$$

If the particles diameter cannot be directly measured as in a consolidated porous medium, it can be estimated from the porosity and permeability through the Blake-Kozeny model.

$$D_p = \sqrt{\frac{150(1-\phi)^2 k}{\phi^3}}$$

The Blake Kozeny model can also be used to estimate the specific surface area if the porous media has a narrow pore size distribution i.e., no micro-porosity.

$$a = \sqrt{\frac{6\phi^3}{25k}}$$

$$a_\phi = \frac{a}{\phi} = \sqrt{\frac{6\phi}{25k}}$$

The product of mass transfer coefficient and specific area can be estimated from the above relations.

$$k_c \, a_\phi = \frac{\mathrm{Sh}_m \, D}{25 \, k} \frac{\phi^2}{(1-\phi)}$$

Assignments

NEQ-1. Perform the steps for the derivation of the analytical solution for the pair of dimensionless differential equations and boundary or initial conditions.

NEQ-2. Non-equilibrium adsorption. Details will be presented Wednesday.

NEQ-3. Non-equilibrium partitioning. . Details will be presented Wednesday.