

# Diffusion and Fluid Flow

## What determines the diffusion coefficient?

## What determines fluid flow?

1. **Diffusion:** Diffusion refers to the transport of substance against a concentration gradient.  $\Delta S > 0$

Mass transfer: movement of mass from one place to another

Diffusion: movement of mass from region of high concentration to low concentration.  $J = -D \frac{dN}{dz}$  (Flux of mass, D: diffusion coefficient)

2. Diffusion is an important process in chromatography in determining the mass transfer and band-broadening

### 3. Einstein diffusion equation:

$$t_d = d^2/(2D) \quad \text{Where, } t_d = \text{average time required to diffuse a distance } d$$

$d = \text{distance of travel}$

4. The change in distribution of a band of chromatography with time due to diffusion can be described as a function of distance and time by a Gaussian curve.

$$C_x = C_0 \left( \frac{1}{2\sqrt{\pi Dt}} \right) e^{-(x^2/4Dt)}$$

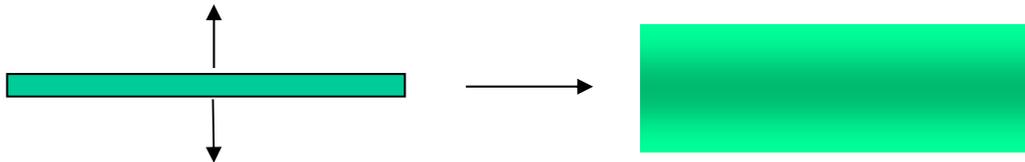
Where,  $C_x$  = concentration of A at position x and time t

$C_0$  = concentration of A at position at  $x = 0$  and time  $t = 0$

t = time

x = distance from A' s starting point

D = diffusion coefficient for A



Diffusion and band broadening

# What determines the diffusion coefficient?

## A. Diffusion in an open system

1. The value of  $D$  may vary over many orders of magnitude depending on the solute, solvent and temperature of the system of interest

## 2. Diffusion in gases:

(a) For solute in gases, diffusion is a rapid process due to the low density of the solvent.

(b) Typical value of  $D$  for solute in gas rang from 1 to 0.1  $\text{cm}^2/\text{sec}$  at 1 atm pressure.

(c) Examples of diffusion coefficients for various solutes in gases:

Solute	Solvent	T (k)	$D_{AB}$ ( $\text{cm}^2/\text{sec}$ )
water	Hydrogen	307	1.00
water	Air	313	0.277
Benzene	Air	298	0.096

**(d) The value of the diffusion coefficient for a solute A in a gas B depends on the temperature, pressure, and molecular weight or sizes of the solute and solvent.**

**The D can be estimated by using the following formula.**

$$D_{AB} = \frac{1.00 \times 10^{-3} T^{1.75}}{P[(\sum v_i)_A^{1/2} + (\sum v_i)_B^{1/2}]} \left( \frac{1}{MW_A} + \frac{1}{MW_B} \right)$$

**Where: T = absolute temperature**

**P = absolute pressure**

**MW<sub>x</sub>: molecular weight for A and B**

**(sum v<sub>i</sub>)<sub>x</sub> = sum of the “diffusion volumes” of all atoms in the molecule (i.e., a measure of A and B’ s size)**

**Question: The diffusion coefficient of water molecules in hydrogen (the carrier gas) at 307 k and 1 atm is 1 cm<sup>2</sup>/sec.**

**What is the average time that the water molecules to travel a distance of 1 mm in the gas chromatographic system? Assuming there no interactions between water and the system.**

### 3. Diffusion in liquids:

(a) Diffusion in liquids is much slower than in gases due to the high density of the solvent and the greater chance for interactions between the solute and solvent.

(b) Typical values of  $D$  for solute in liquid are  $10^{-5}$  to  $10^{-7}$   $\text{cm}^2/\text{sec}$

(c) The value of  $D$  for various solutes (A) in liquid solvent (B) are shown

#### Diffusion in liquids at 20 °C

Solute	Solvent	$D_{AB}$ ( $\text{cm}^2/\text{sec} \cdot 10^{-5}$ )
$\text{O}_2$	water	1.80
Acetic acid	water	0.88
Ethanol	water	1.00
phenol	water	0.84

(d) The value of  $D$  for a solute in a liquid depends on temperature, viscosity of liquid and size and shape of solute.

For spherical molecule A in a liquid B,  $D$  is given by stokes-Einstein equation:

$$D_{AB} = \frac{kT}{6\pi\eta_B r_A}$$

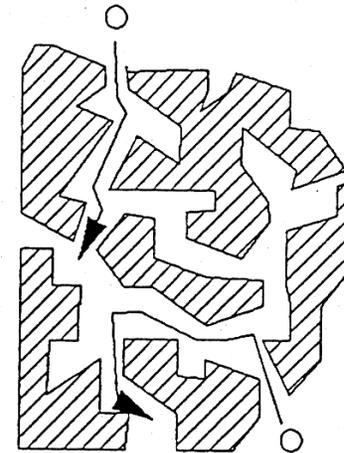
$k$  = Boltzmann constant;  $T$  = absolute temperature

$\eta_B$  = viscosity of the solvent,  $r_A$  = radius of the spherical molecule

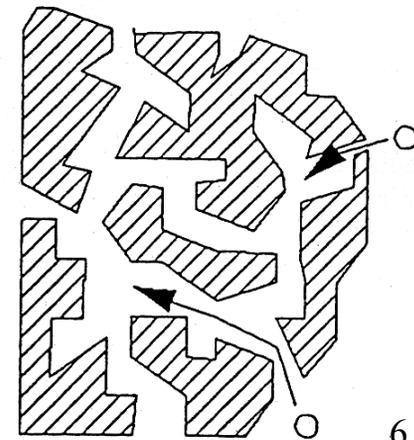
## B. Diffusion in a packed bed

1. Diffusion in a bed containing a porous support is typically slower than diffusion in an open system. This is created by tortuosity of the flow paths and bottleneck problems.

2. Tortuosity refers to the decrease in a solute's rate of diffusion due to the presence of wandering paths in the packed bed, whether within the pores of the support or around the support particles. The presence of such paths results in a slower rate of travel for the solute through the medium



3. The “bottleneck problem” refers to the decreases in the rate of solute diffusion due to the presence of ink bottle or narrow channels in the support.



**What determines the diffusion coefficient?**

**What determines fluid flow?**

## What determines fluid flow?

### A definition:

1. Fluid flow, or convective mass transfer, refers to the transport of solute through a system as they are being carried by the solvent.
2. Fluid flow is an essential part of chromatographic separation.

### B. Measures of fluid flow:

1. Flowrate (F): the volume of the solvent traveling through the column per unit time (units: mL/min, L/hr...).
2. Linear velocity (u): The distance of a solute or solvent travels in the column per unit time (units: cm/sec, cm/min).
3. The relationship between u and F is shown below:

(a) for mobile phase flowing through the column:

$$\begin{aligned} u_{mp} &= F (L/V_m) \\ &= L/t_m \end{aligned}$$

$V_m$  = column void volume; L = column length; and  $t_m$  = column void time

**(b) for a solute flowing through the column phase flowing through the column**

$$\begin{aligned}u_{\text{solute}} &= F(L/V_R) \\ &= L/t_R\end{aligned}$$

**$u_{\text{solute}}$  = solute's linear velocity through the column,  $t_R$  = solute's the retention time,  $V_R$  = solute's retention volume.**

### **C. Fluid flow in open tubes:**

- 1. Flow of a solvent through a circular tube can be one of three types (a) plug flow, (b) turbulent flow, or (c) laminar flow.**
- 2. The type of flow expected in a given system can be determined by using the Reynolds number ( $R_e$ ): the ratio of inertial force and viscous force**

$$R_e = \rho u d_p / \eta$$

**Where:  $\rho$  = solvent density (g/cm<sup>3</sup>)**

**$u$  = solvent linear velocity (cm/sec)**

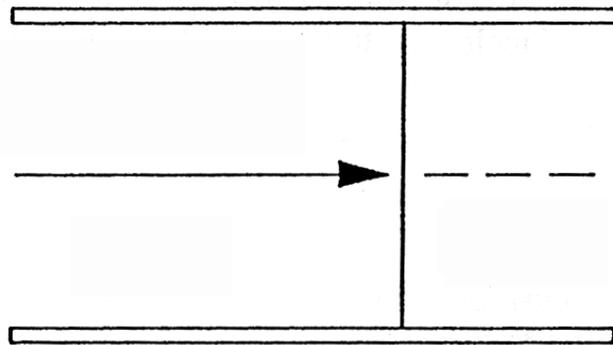
**$d_p$  = tube diameter (cm)**

**$\eta$  = solvent viscosity (poise)**

**Newtonian fluid: Inertial force and viscous force**

### 3. Types of Fluid Flow:

#### (a) Plug or ideal Flow ( $R_e = \text{infinity}$ )



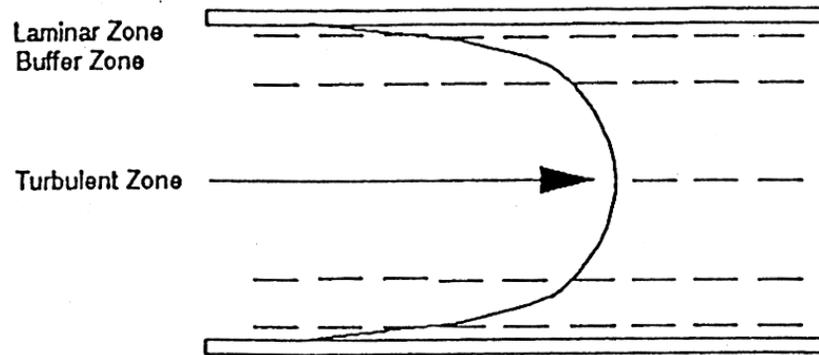
$$R_e = \rho u d_p / \eta$$

Inertial force and viscous force

Plug Flow

- i. This is the best type of flow in theory since all solute travel at the same speed through the flow-stream. As a result, they all reach the end of the tube at the same time and no additional band-broadening results.
- ii. However, this type of flow is not obtainable in practice and is used only as a model system to help understand factors that affect fluid flow.

**(b) Turbulent flow ( $R_e \geq 2100$ )**

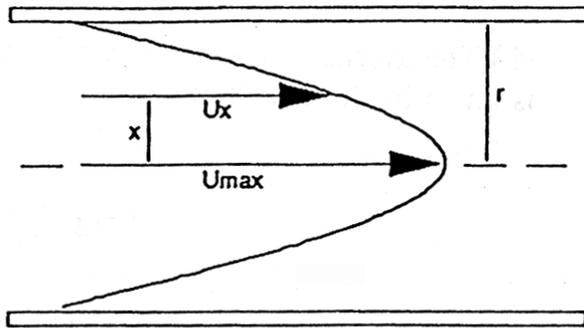


$$R_e = \rho u d_p / \eta$$

**Inertial force and viscous force**

- (i) This is the best type of fluid flow obtainable in practice.**
- (ii) Although there is some difference in the rate of travel for molecule in different parts of the flow-stream, the turbulent core has random eddies and currents that mix molecules from different parts of flow-stream. This helps to minimize differences in the rate of travels of molecules in the capillary, and helps prevent band-broadening.**

**(c) Laminar (parabolic) Flow ( $R_e < 2100$ )**



$$R_e = \rho u d_p / \eta$$

**Inertial force and viscous force**

Laminar Flow

- (i) This is the most common type of fluid flow and is that which is usually seen in chromatography.**
- (ii) Fluid in this type of flow has a well-characterized profile in the tube that can be described by a parabolic curve. The equation relating the speed at which a molecule travels to its position in the flowstream is as follows.**

$$u_x = u_{max} (1 - x^2/r^2)$$

**Where:  $r$  = radius of tube;  $x$  = distance of the molecule from the center of tube;  $u_{max}$  = Maximum linear velocity of a solute in the flow profile;  $u_x$  = linear velocity of a molecule at distance  $x$ .**

**(iii) Note in this equation that the maximum rate of flow for a molecule is at the center of tube, where  $x = 0$  and  $u_x = u_{\max}$**

**(iv) Since molecules at different location of the flowstream travel through the tube at different rates, some arrive at the end of the tube before others, producing band-broadening.**

**(v) The average linear velocity of a molecule in a laminar flow profile is give by the equation:**

$$u_{\text{avg}} = u_{\text{max}}/2$$

**Where  $u_{\text{avg}}$  = average linear velocity**

**(vi) The maximum and average linear velocities for laminar flow in an open tube can be related to the length and pressure drop across the tube by the Hagen-Poiseuille Equation**

$$u_{\text{max}} = \Delta P r^2 / (4\eta L)$$

$$u_{\text{avg}} = \Delta P r^2 / (8\eta L)$$

**Where:  $\Delta P$  = pressure drop across the tube (i.e.  $P$  at inlet –  $P$  at the outlet)  
 $\eta$  = solvent viscosity;  $L$  = tube length;  $r$  = tube radius**

**12. Determine what type of flow is present in each of the following systems. The density and viscosity of water at 20 °C are 1.00 g/cm<sup>3</sup> and 0.01 poise, respectively, and the density and viscosity of nitrogen at 100 °C and 1 atm are 0.08 g/cm<sup>3</sup> and 0.0002 poise, respectively.**

**(1) A LC system with a 2 m X 50 micron ID open tube using water as the mobile phase, flowing at 0.01 mL/min and at 20 °C.**

**(2) A GC system with a 25 m X 250 micron ID open tube using nitrogen as the mobile phase at a flow-rate of 2 mL/min at 2mL/min at 1 atm and 100 °C.**

**4. An open tubular column has a diameter of 207  $\mu\text{m}$  and the thickness of the stationary phase on the inner wall is 0.5  $\mu\text{m}$ . Unretained solute pass through in 63 s and a particular solute emerges in 433 s. Find the partition coefficient for this solute and find the fraction of time spent in the stationary phase.**

**5. A mixture of benzene, toluene, and air was injected in to an open tubular GC column that has an inner diameter of 250  $\mu\text{m}$  and is coated on the inside with a layer of stationary phase 1.0  $\mu\text{m}$  thick. Air gave a sharp peak spike in 42 s, whereas benzene required 251 s and toluene was eluted in 333 s. (1) Find the adjusted retention time and capacity factor for each solute. (2) Estimate the distribution coefficient ( $K = C_s/C_m$ ) for benzene and toluene between stationary and mobile phases. (3) State what fraction of time benzene and toluene spend in the mobile phase.**

**6. In a typical liquid, molecules jump randomly to one side or another about  $10^{10}$  times per second in steps of 0.3 nm length. Calculate the diffusion coefficient for such molecules.**