Rate of Diffusion through a Solution

**Diffusion** in a gas is the random motion of particles involved in the net movement of a substance from an area of high concentration to an area of low concentration. Each particle in a given gas continues to collide with other particles. In regions of the gas where the particle density is the highest, the particles bounce off each other and the boundary of their container at a greater rate than particles in less-dense regions.

**Introduction**

For a gas, the rate at which diffusion occurs is proportional to the square root of the density of the gas. The density of a gas is equal to the mass of the gas divided by the volume of the gas. If the volume is held constant one gas is compared with another with another,

\[
\frac{R_2}{R_1} = \sqrt{\frac{M_1}{M_2}}
\]

where \(R\) is the rate of diffusion in mol/s and \(M\) is the molar mass in g/mol. This is known as **Graham's law of diffusion**.

**Fick's First Law of Diffusion**

For a volume of solution that does not change:

\[
[J = -D\frac{dc}{dx}]
\]

- \(J\) is the flux, or movement, of the molecules in a given time interval denoted by units of moles/(time×area)
- \(D\) is the diffusivity constant, which describes the speed at which an object diffuses and has units of area/time
- \(\Delta c\) refers to the change in concentration from a point in time where no diffusion occurs to a point in time where the diffusion is complete, denoted by units of (moles/volume)
- \(\Delta x\) refers to the change in distance that a given particle undergoes during diffusion and has units of length.
Consider a cylinder with a region of high concentration and a region of low concentration. The volume of the region with no molecules can be designated as \( \text{Area}(\text{of a circle}) \times \text{L(length of the gap)} \).

- The high concentration point on the left may be treated as \( C(X-1/2L) \)
- The low concentration point on the right may be treated as \( C(X+1/2L) \)

If the time interval is designated as \( \Delta T \), then:

- Average concentration coming from the left \( \propto C(X-1/2L) \times \text{L} \times \text{Area} \times \Delta T \)
- Average concentration coming from the right \( \propto C(X+1/2L) \times \text{L} \times \text{Area} \times \Delta T \)

The total flux may be represented as:

\[
[J \propto \dfrac{[C(X-1/2L) \times \text{L} \times \text{Area} \times \Delta T] \cdot [C(X+1/2L) \times \text{L} \times \text{Area} \times \Delta T]}{(\text{Area}) \times (\Delta T)}]
\]

Using the following relationship:

\[
(C(X+1/2L) = C(X)+1/2L \times \frac{dc}{dx} \quad C(X-1/2L) = C(X)-1/2L \times \frac{dc}{dx})
\]

Then:

\[
[J \propto -L^2 \frac{dc}{dx}]
\]

\( L^2 \) may be incorporated into the diffusivity constant \( D \), and the equation for the flux may be rewritten as:

\[
[J = -D \frac{dc}{dx}]
\]

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**Fick's Second Law of Diffusion**

An incremental volume may have diffusion at both the rear and front surfaces of the volume. The rate at which the concentration changes with respect to the second derivative of the concentration gradient is given by the following formula:

\[
(\frac{dfrac \{partial \{C\}\}}{partial \{T\}} \times x \frac{dfrac \{partial \ \^2C\}}{partial \ x^2})
\]

If the front gradient allows (and thus drives) an uptake of solution into the incremental volume more quickly than the rear gradient allows for its dissipation, then the second derivative is positive. If the rear gradient allows for (and thus drives) the concentration out of the incremental volume more quickly than the front gradient allows for its uptake, then the second derivative is negative.

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**Diffusion and Activation**

When two different particles end up near each other in solution, they may be trapped as a result of the particles surrounding them, which is known as the *cage effect* or *solvent cage*.
Two different particles colliding may be represented as a 2nd order reaction: \((A + B \rightarrow AB)\)

\[\text{[AB] = K_d[A][B]}\]

Notice the use of \(K_d\) to denote the **diffusion rate constant**.

If circumstances change and either of the particles is able to diffuse out of the **solvent cage**, then the following 1st order reaction \((AB \rightarrow A + B)\) is possible, then:

\[\text{[AB] = K_d'[AB]}\]

There now exists a reaction for the formation of the AB complex as well as the breakdown of the AB complex into products.

\[k = \dfrac{K_aK_d}{K_a + K_d'}\]

\[V = K[A][B]\]

\[(A + B \rightarrow AB \rightarrow \text{Products})\]

The net rate of formation for AB can now be determined:

\[\dfrac{d[AB]}{dt} = (A + B \rightarrow AB) - (AB \rightarrow A + B) - (AB \rightarrow \text{Products})\]

\[\dfrac{d[AB]}{dt} = K_d[A][B] - K_d'[AB] - K_a[AB]\]

Assuming steady state conditions:

\[\dfrac{d[AB]}{dt} = K_d[A][B] - K_d'[AB] - K_a[AB] = 0\]

\[[AB] = \dfrac{K_d[A][B]}{K_a + K_d'}\]

The final rate of product formation taking into account both **diffusion** and **activation**:

\[V = \dfrac{K_d[A][B]}{K_a + K_d'}\]

**Diffusion-controlled limit**

If the rate at which particle A encounters particle B is much slower than the rate at which AB dissociates, then \(K_d'\) is essentially zero.

\[V = \dfrac{K_d[A][B]}{K_a}\]
Activation-controlled limit

The rate at which particle A encounters and reacts with particle B may exceed the rate at which the AB complex breaks apart into a product by a significant quantity. If the rate of at which AB decomposes is slow enough that $K_d$ in the denominator may be ignored, the following results:

$$V = \frac{K_d[A][B]}{K_d'}$$

The Rate Constant $K_d$

Viscosity and rate of diffusion may be related by the following formula:

$$K_d = \frac{8RT}{3n}$$

where $n$ is the viscosity of the solution.

Practice Problems

1. Compare the rate of diffusion between fluorine and chlorine gases. Fluorine gas, $F_2$, has a molecular mass of 32 grams. Chlorine gas, $Cl_2$, has a molecular mass of 70.90 grams.

2. Gas A is 0.75 times as fast as Gas B. The mass of Gas B is 32 grams. What is the mass of Gas A?

3. Determine the rate of diffusion (flux) for aspirin dissolving through the stomach lining. $C_1 = 50 \text{ mg/L}$ and $C_2 = 290 \text{ mg/L}$. The diffusivity constant of aspirin is $0.29 \times 10^{-9} \text{ cm}^2/\text{s}$ and the thickness of the stomach lining is approximately 0.5 cm.

4. How long will it take oxygen to diffuse 0.5 cm below the surface of a still lake if $D = 1 \times 10^{-5} \text{ cm}^2/\text{s}$?

5. If it takes 5 seconds for oxygen to diffuse to the center of a bacterial cell that is 0.02 cm in diameter, determine the diffusivity constant.

Solutions to Practice Problems

1. Using Graham's law of diffusion:

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \left(\frac{\text{Mass}_2}{\text{Mass}_1}\right)^{1/2}$$

$$(\text{Rate}_{F_2}/\text{Rate}_{Cl_2}) = (70.90\text{g}/32\text{g})^{1/2} = 1.49$$

Fluorine gas is 1.49 times as fast as chlorine gas.

2. Using Graham's law of diffusion:

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \left(\frac{\text{Mass}_2}{\text{Mass}_1}\right)^{1/2}$$

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(Rate_A/Rate_B) = (Mass_B/Mass_A)^{1/2}

0.75 = (32g/Mass_A)^{1/2}

0.75^2 = (32g/Mass_A)

Mass_A = (32g/0.5625)

**Mass_A = 56.8888g**

3. Using Fick's first law:

\[ J = -D \frac{dc}{dx} \]

Where:

- \( J \) = unknown flux
- \( D \) = 0.29 × 10^{-9} \text{ cm}^2/\text{s}
- \( dc = (C_1 - C_2) = 50 \text{mg/L} - 290 \text{mg/L} = -240 \text{mg/L} \), which is equivalent to -240mg/1000cm³ = -0.24mg/cm³
- \( dx = 0.5 \text{cm} \)

\[ J = (0.29 \times 10^{-9} \text{ cm}^2/\text{s})[-0.24 \text{mg/cm}^3/(0.5 \text{cm})] = 1.39 \times 10^{-10} \text{mg/s \times cm}^2 \]

**J = 1.39 \times 10^{-10} \text{mg/s \times cm}^2**

4. Using Fick's second law:

\[ T = \frac{x^2}{2D} \]

Where:

- \( T \) = our unknown (time)
- \( x \) = 0.5 cm
- \( D = 1 \times 10^{-5} \text{cm}^2/\text{s} \)

\[ T = (0.5 \text{cm})^2/[2(1 \times 10^{-5} \text{cm}^2/\text{s})] \]

**T = 1.25 \times 10^4 \text{ seconds}**
5. Using Fick's second law:

First, rearrange the equation $T = \frac{x^2}{2D}$ to solve for $D$ --> $D = \frac{x^2}{2T}$

Where:

$D =$ our unknown (diffusivity constant)

$x = 0.01 \text{ cm}$ (distance from the outside to the center of the cell)

$T = 5s$

$D = \frac{(0.01\text{cm})^2}{2(5s)}$

$D = 1 \times 10^{-5} \text{cm}^2/\text{s}$

References


Contributors

- Eric Stouffer (UCD), Anne Slisz (UCD)