

Fick's Laws

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1 Fick's First Law

- an analogy with the Fourier's laws for heat transfer
- rate of transfer of the diffusing substance through unit area of a section is proportional to the concentration gradient measured normal to the section

$$F = D \frac{\partial C}{\partial x} \quad (1)$$

- defines mass flux with respect to distance
- first law for cartesian co-ordinates

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$$J = -A * D * \frac{\partial C}{\partial z}$$

- J is flux per unit area

- A is area across which diffusion occurs
- C is concentration
- z is distance
- D is diffusion coefficient

2 Fick's Second Law

2.1 Derivation

- let's assume an isotropic medium
- consider the following volume - a rectangular parallelepiped with sides $2dx$, $2dy$, and $2dz$
- let concentration at the centre be C

$K + \text{-----} + K' \quad / / \quad 2dz \quad | \quad | \quad | \quad | \quad | \quad L + \text{-----}$
 $\text{---} + L' \quad | \text{-----} >$

$$4dydz(F_x + dF_x/dx dx)$$

$\text{-----} > | \quad | \quad |$

$$4dydz(F_x + dF_x/dx dx) \quad | \quad C \quad | \quad | \quad | \quad 2dy \quad | \quad J + \text{-----} | \text{---} + J'$$

$$I + \text{-----} + I'$$

- rate at which diffusing substance enters the control volume is given as

$$4dydz(F_x - \frac{\partial F_x}{\partial x} dx) \quad (2)$$

- rate at which diffusing substance exits the control volume is given as

$$4dydz(F_x + \frac{\partial F_x}{\partial x} dx) \quad (3)$$

- performing mass balance, net accumulation in the x direction is given as

$$- 8dx dy dz \frac{\partial F_x}{\partial x} \quad (4)$$

- similarly in y and z directions

$$- 8dxdydz \frac{\partial F_y}{\partial y} \quad (5)$$

$$- 8dxdydz \frac{\partial F_z}{\partial z} \quad (6)$$

- since average concentration is given as C, the rate at which diffusing amount changes is given as volume * concentration difference

$$8dxdydz \frac{\partial C}{\partial t} \quad (7)$$

- equating the above equations
- a more general conservation equation that gives change in concentration with time

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$$\frac{\partial C}{\partial t} = D * \frac{\partial^2 C}{\partial r^2} = D \left(\frac{\partial^2 C}{\partial z^2} + \frac{1}{A} + \frac{\partial A}{\partial z} \frac{\partial C}{\partial z} \right)$$

– t is time

- For a non-linear isotherm [?]

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$$\frac{\partial}{\partial z} \left(D \frac{\partial C}{\partial z} \right) = \frac{\partial C}{\partial t}$$

3 Anisotropic Media

4 Analogy with Heat Flow

5 Diffusion Constant

- much less sensitive to temperature than the rate constant of a chemical reaction or other phenomena
- also much less sensitive to the solute being studied, diffusion constant in a given system for a variety of solutes often fall within a factor of 10
- also much less sensitive to solute concentration, although there are exceptions
 - smaller solutes may show concentration dependent diffusion