

Foundations of Chemical Kinetics Lecture 26: Diffusion

Marc R. Roussel

November 22, 2021

Mathematical background: Gradient

- The **gradient operator** ∇ is defined by

$$\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)$$

- The **gradient of a function**

$$\nabla f = \left(\frac{\partial f}{\partial x}, \frac{\partial f}{\partial y}, \frac{\partial f}{\partial z} \right)$$

is a vector that points in the direction of greatest increase of f .

Mathematical background: Divergence

- The **divergence of a vector** is

$$\nabla \cdot \mathbf{v} = \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z}$$

- A positive value of the divergence at a point indicates that \mathbf{v} describes a locally expanding quantity; a negative value describes local compression.

Mathematical background: Laplacian

- The **Laplacian operator** is

$$\nabla \cdot \nabla = \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

- The Laplacian of a function is

$$\nabla \cdot \nabla f = \nabla^2 f = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2}$$

Mathematical background: Differential operators and coordinate systems

- The gradient, divergence and Laplacian can be expressed in other coordinate systems.
- The formulas are generally non-trivial and should be looked up.
- Example: The Laplacian in spherical polar coordinates is

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

i.e.

$$\nabla^2 f = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial f}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial f}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 f}{\partial \phi^2}$$

Background: Chemical potential

- In thermodynamics, you would have learned the equation

$$dG = V dp - S dT$$

which tells us how G depends on T and p for a closed system.

- Recall that the following relations follow from this equation:

$$\left. \frac{\partial G}{\partial p} \right|_T = V \qquad \left. \frac{\partial G}{\partial T} \right|_p = -S$$

Background: Chemical potential (continued)

- What if we add a very small amount of substance i to the system?

The **chemical potential** μ_i is defined as the partial derivative of G with respect to n_i :

$$\left. \frac{\partial G}{\partial n_i} \right|_{p, T, n_{j \neq i}} = \mu_i$$

Note that, if we allow material to be added to the system, $\partial G / \partial p$ and $\partial G / \partial T$ must be evaluated holding all the n_i constant.

- From the definition of the chemical potential, we get

$$dG = V dp - S dT + \sum_i \mu_i dn_i$$

where the sum is over all species in the system.

Background: Chemical potential (continued)

$$dG = V dp - S dT + \sum_i \mu_i dn_i$$

- Since G and n_i are extensive variables (depend on the size of the system), μ_i must be an intensive variable (doesn't depend on the size).
- μ_i can only depend on intensive variables (p , T , c_i , etc.).

Background: Chemical potential (continued)

$$dG = V dp - S dT + \sum_i \mu_i dn_i$$

- Suppose that we “make” a system by adding material while holding p , T and all the c_i constant, i.e. add all the system components in the correct, final proportions.

Note: the volume will have to increase as we do this.

- Then,

$$dG = \sum_i \mu_i dn_i$$
$$\therefore G = \sum_i \int_0^{n_i} \mu_i dn_i = \sum_i \mu_i n_i$$

Background: Chemical potential (continued)

$$G = \sum_i \int_0^{n_i} \mu_i dn_i = \sum_i \mu_i n_i$$

Interpretation: μ_i is the portion of the Gibbs free energy of a system that can be attributed to species i .

- That being the case, it should not be very surprising that μ_i obeys the equation

$$\mu_i = \mu_i^\circ + RT \ln a_i$$

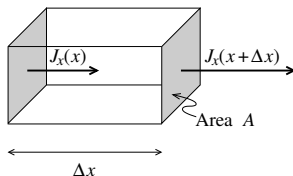
where μ_i° is the chemical potential under standard conditions and a_i is the activity of species i .

- Recall that $a_i = \gamma_i c_i / c^\circ$ for solutes.

Flux

- Imagine a small (imaginary) surface of area dA immersed in a fluid.
- The net number of molecules passing through this surface in a specified direction per unit time divided by the area is the **flux, J** .
- If the surface is oriented perpendicular to the x axis and we count the net number of molecules travelling to the right (i.e. right-travelling minus left-travelling), then we have J_x , the x component of the flux vector.

The transport equation



- What is the rate of change of the concentration in the prism shown above if there is a flux along the x direction of J_x ?
- J_x is the number of particles flowing through the surface per unit area per unit time, so

$$\frac{\Delta n}{\Delta t} = A [J_x(x) - J_x(x + \Delta x)]$$

- $\Delta n/V$ is the change in concentration, and $V = A\Delta x$, so

$$\frac{\Delta c}{\Delta t} = \frac{[J_x(x) - J_x(x + \Delta x)]}{\Delta x}$$

The transport equation (continued)

$$\frac{\Delta c}{\Delta t} = \frac{[J_x(x) - J_x(x + \Delta x)]}{\Delta x}$$

- If we let $\Delta x \rightarrow 0$ and $\Delta t \rightarrow 0$, we get

$$\frac{\partial c}{\partial t} = -\frac{\partial J_x}{\partial x}$$

- We only considered a flux along the x direction. If we consider the fluxes in the other directions, we get the **transport equation**

$$\frac{\partial c}{\partial t} = -\frac{\partial J_x}{\partial x} - \frac{\partial J_y}{\partial y} - \frac{\partial J_z}{\partial z} = -\nabla \cdot \mathbf{J}$$

Driving force of diffusion

- Suppose that we have an inhomogeneous system, so that the composition, and therefore the chemical potential, varies from point to point.
- Suppose that we take one molecule of substance i from the vicinity of position x along the x axis, and move it to position $x + dx$.

The corresponding change in free energy is

$$dG = [\mu_i(x + dx) - \mu_i(x)] / L$$

(μ_i is in J mol^{-1} , so division by L gives us the chemical potential per molecule.)

Driving force of diffusion (continued)

- Because the negative of the free energy change is the maximum work, we have

$$dw = - [\mu_i(x + dx) - \mu_i(x)] / L$$

- From the definition of work, $dw = F_{i,x} dx$, so

$$F_{i,x} = -\frac{1}{L} \frac{\mu_i(x + dx) - \mu_i(x)}{dx}$$

or, in the limit as $dx \rightarrow 0$,

$$F_{i,x} = -\frac{1}{L} \frac{\partial \mu_i}{\partial x}$$

Driving force of diffusion (continued)

- For an **ideal solute**,

$$\mu_i = \mu_i^\circ + RT \ln(c_i(x)/c^\circ)$$
$$\therefore F_{i,x} = -\frac{RT}{Lc_i} \frac{\partial c_i}{\partial x} = -\frac{k_B T}{c_i} \frac{\partial c_i}{\partial x}$$

or, in three dimensions

$$\mathbf{F}_i = -\frac{k_B T}{c_i} \nabla c_i$$

- The negative of this **virtual force** is the opposing force we would have to apply to prevent diffusion from occurring.
- Note that the force is directed opposite to the gradient, i.e. diffusion is equivalent to a force pushing the molecules toward regions of low concentration.

Driving force of diffusion (continued)

- A constantly applied force would cause molecules to accelerate.
- The virtual diffusion force is opposed by drag.
- At low speeds, the drag force is $\mathbf{F}_i^{(d)} = -f_i \mathbf{v}_i$ where f_i is a frictional (drag) coefficient and \mathbf{v}_i is the mean drift velocity.
- $\mathbf{F}_i^{(d)}$ should be equal to the negative of \mathbf{F}_i , i.e.

$$\mathbf{F}_i^{(d)} = -f_i \mathbf{v}_i = \frac{k_B T}{c_i} \nabla c_i$$

- The flux (molecules per unit area per unit time) is (molecules per unit volume) \times (distance travelled per unit time), i.e.

$$\mathbf{J}_i = c_i \mathbf{v}_i.$$

Thus,

$$\mathbf{J}_i = -\frac{k_B T}{f_i} \nabla c_i$$

Driving force of diffusion (continued)

$$\mathbf{J}_i = -\frac{k_B T}{f_i} \nabla c_i$$

- The drag coefficient f_i depends on the solute and solvent environment.
- Define the **diffusion coefficient**

$$D_i = k_B T / f_i$$

so that

$$\mathbf{J}_i = -D_i \nabla c_i$$

which is known as **Fick's first law**.

- Fick's first law states that the flux of species i runs in the opposite direction to its gradient.

Driving force of diffusion (continued)

- The derivation of Fick's first law involves a number of assumptions, some obvious, some less so. Accordingly, Fick's first law has a limited range of applicability (negligible forces between solutes, gradients not too large).

The diffusion equation

Transport equation: $\frac{\partial c_i}{\partial t} = -\nabla \cdot \mathbf{J}_i$

Fick's first law: $\mathbf{J}_i = -D_i \nabla c_i$

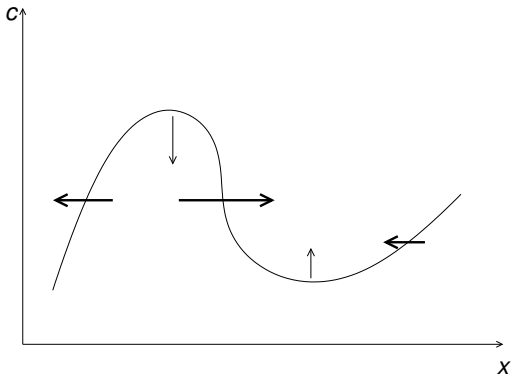
- Putting these two together, we get the **diffusion equation**, also known as **Fick's second law**:

$$\frac{\partial c_i}{\partial t} = D_i \nabla \cdot \nabla c_i = D_i \nabla^2 c_i$$

The diffusion equation (continued)

- In one dimension:

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2}$$



Example: Diffusive spread in one dimension

- Suppose that we put a small drop of material (e.g. a dye) in the centre of a very long, narrow tube.
- A drop of negligible width can be modeled as a **delta function**, with the following properties:
 - $\delta(x) = 0$ everywhere except at $x = 0$.
 - $\int_{-a}^a \delta(x) dx = 1$ for any $a > 0$.
- Take $c(x, t = 0) = \frac{n}{A}\delta(x)$, where n is the total number of moles of the material and A is the cross-sectional area of the tube.
- Solution of the diffusion equation requires special techniques. Many standard cases have already been solved, and the solutions can simply be looked up.
- In this case, the solution is

$$c(x, t) = \frac{n}{2A\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

Example: Diffusive spread in one dimension

(continued)

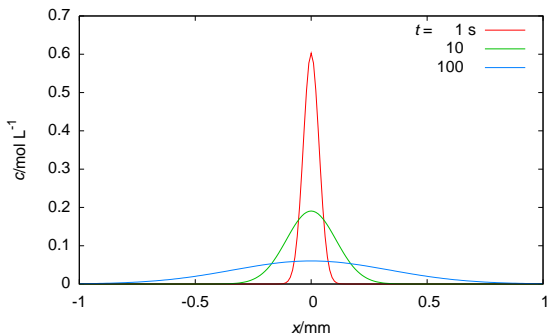
$$c(x, t) = \frac{n}{2A\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

Note: This is a Gaussian with time-dependent variance $2Dt$.

Example: Diffusive spread in one dimension

(continued)

- Diffusion coefficient of sucrose in water at 20 °C:
 $5.7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$
- Assume a cylindrical pipe with an internal diameter of 5.00 mm, giving $A = 1.96 \times 10^{-5} \text{ m}^2$, and $n = 1 \text{ } \mu\text{mol}$.



Stokes-Einstein theory

- Recall

$$D_i = k_B T / f_i$$

where f_i is a frictional coefficient.

- Equations for frictional coefficients exist for objects of various shapes immersed in a fluid.

In particular, for a sphere,

$$f_i = 6\pi r_i \eta$$

where r_i is the radius of the sphere, and η is the viscosity of the solvent.

- By combining the two, we get the **Stokes-Einstein equation**:

$$D_i = \frac{k_B T}{6\pi r_i \eta}$$

Stokes-Einstein theory: example

- C₆₀ has a diameter of 10.18 Å.
- Benzonitrile has a viscosity of 1.24 mPa s at 25 °C.
- According to the Stokes-Einstein theory, C₆₀ in benzonitrile should have a diffusion coefficient at 25 °C of

$$\begin{aligned} D &= \frac{k_B T}{6\pi r \eta} \\ &= \frac{(1.380\,6488 \times 10^{-23} \text{ J K}^{-1})(298.15 \text{ K})}{6\pi(5.09 \times 10^{-10} \text{ m})(1.24 \times 10^{-3} \text{ Pa s})} \\ &= 3.46 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \end{aligned}$$

- Experimental value: $(4.1 \pm 0.3) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$

Diffusive motion of ions in solution

- In addition to diffusion, ions in solution experience forces due to their charges.
- The force on an ion of charge z_i (in elementary units) in an electric field \mathbf{E} is

$$\mathbf{F}_i = z_i e \mathbf{E}$$

Diffusive motion of ions in solution (continued)

- The electric force is balanced by the drag force $\mathbf{F}_i^{(d)} = -f_i \mathbf{v}_i$,
so

$$f_i \mathbf{v}_i = z_i e \mathbf{E}$$

or

$$\mathbf{v}_i = z_i e \mathbf{E} / f_i$$

- Each component of the velocity is proportional to the corresponding component of the electric field.
Define the **mobility** of an ion as

$$u_i = v_i / E = |z_i| e / f_i$$

so that

$$\mathbf{v}_i = \text{sgn}(z_i) u_i \mathbf{E}$$

where $\text{sgn}(z_i)$ is the sign of the charge.

Diffusive motion of ions in solution (continued)

- The flux of ion i due solely to the electric field is

$$\mathbf{J}_i^{(E)} = c_i \mathbf{v}_i = \text{sgn}(z_i) c_i u_i \mathbf{E}$$

- Combining the flux due to the electric field with the flux due to diffusion, we get an overall flux

$$\mathbf{J}_i = -D_i \nabla c_i + \text{sgn}(z_i) c_i u_i \mathbf{E}$$

- Applying the transport equation, $\partial c_i / \partial t = -\nabla \cdot \mathbf{J}_i$, we get the **diffusion-conduction equation**:

$$\frac{\partial c_i}{\partial t} = D_i \nabla^2 c_i + \text{sgn}(z_i) u_i \nabla \cdot (c_i \mathbf{E})$$

Diffusion coefficient and mobility

- Recall

$$D_i = k_B T / f_i \quad \text{and} \quad u_i = |z_i| e / f_i$$

- Therefore,

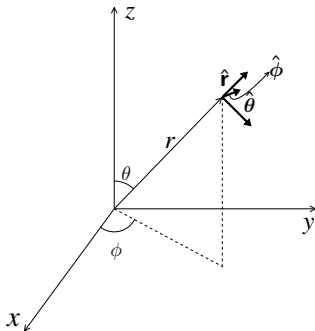
$$u_i = \frac{|z_i| e}{k_B T} D_i$$

Mathematical interlude: Gradient in spherical polar coordinates

In spherical polar coordinates,

$$\nabla = \hat{\mathbf{r}} \frac{\partial}{\partial r} + \frac{\hat{\boldsymbol{\theta}}}{r} \frac{\partial}{\partial \theta} + \frac{\hat{\boldsymbol{\phi}}}{r \sin \theta} \frac{\partial}{\partial \phi}$$

where $\hat{\mathbf{r}}$, $\hat{\boldsymbol{\theta}}$ and $\hat{\boldsymbol{\phi}}$ are unit vectors in the corresponding directions.



Equilibrium distribution in a spherically symmetric potential

- Suppose that an ion is placed in a spherically symmetric electrostatic potential (e.g. the potential due to another ion) with $V(r \rightarrow \infty) = 0$.
For a spherically symmetric potential, $V = V(r)$.
- The equilibrium solution of the diffusion-conduction equation will have the same symmetry, i.e. $c_i = c_i(r)$.
- At equilibrium, $\mathbf{J} = \mathbf{0}$.

Equilibrium distribution in a spherically symmetric potential (continued)

- $\mathbf{E} = -\nabla V$, so

$$\begin{aligned}\mathbf{J}_i &= -D_i \nabla c_i + \text{sgn}(z_i) c_i u_i \mathbf{E} \\ &= -D_i \nabla c_i - \text{sgn}(z_i) c_i u_i \nabla V\end{aligned}$$

- For spherically symmetric functions, the gradient reduces to

$$\nabla f = \frac{df}{dr}$$

- If c_i and V only depend on r , the equilibrium condition becomes

$$\mathbf{J}_i = \mathbf{0} = -D_i \frac{dc_i}{dr} - \text{sgn}(z_i) c_i u_i \frac{dV}{dr}$$

- Separation of variables:

$$\frac{dc_i}{c_i} = -\frac{\text{sgn}(z_i) u_i}{D_i} dV$$

Equilibrium distribution in a spherically symmetric potential (continued)

Substitute $u_i/D_i = |z_i|e/k_B T$:

$$\frac{dc_i}{c_i} = -\frac{z_i e}{k_B T} dV$$
$$\therefore \int_{c_i^0}^{c_i(r)} \frac{dc_i}{c_i} = -\frac{z_i e}{k_B T} \int_0^{V(r)} dV$$

Equilibrium distribution in a spherically symmetric potential (continued)

$$\therefore \ln \left(\frac{c_i(r)}{c_i^\circ} \right) = -\frac{z_i e}{k_B T} V(r) = -\frac{U(r)}{k_B T}$$

where $U(r)$ is the electrostatic potential energy of ion i in the potential $V(r)$.

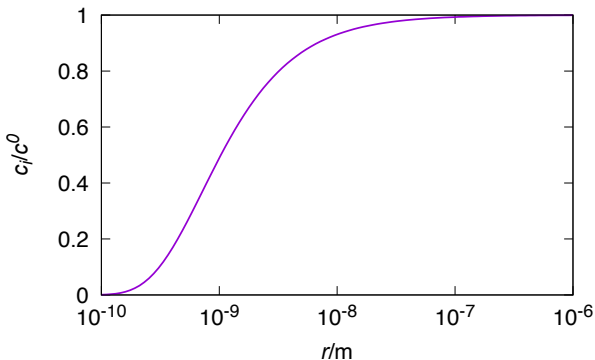
$$\therefore c_i(r) = c_i^\circ \exp \left(-\frac{U(r)}{k_B T} \right)$$

which is a Boltzmann distribution!

Equilibrium distribution in a spherically symmetric potential (continued)

$$q_1 = q_2 = e \quad \epsilon_r = 78.37$$

$$T = 298.15 \text{ K}$$



Equilibrium distribution in a spherically symmetric potential (continued)

$$q_1 = -q_2 = e \quad \epsilon_r = 78.37$$

$$T = 298.15 \text{ K}$$

