LESSON 2: MOLECULAR DIFFUSION

FICK LAW

Hp: - Fluid at rest: $\boldsymbol{u}(\boldsymbol{x}, t) = 0$

- Solute mass conservation: $\dfrac{\mathrm{d}M}{\mathrm{d}t} = \mathrm{const}$

Fick stated:

- The mass flux of solute depends on its concentration gradient.

$$\boldsymbol{q} = f(\nabla c)$$

- The process is isotropic (equal characteristics along all directions).
- The process is homogeneous (it does not depend on space and position).
- The process is linear.

$$\boldsymbol{q} = -D\ \nabla c$$

Definition of Gradient ∇

Scalar: $\nabla c = \begin{bmatrix} \dfrac{\partial c}{\partial x} & \dfrac{\partial c}{\partial y} & \dfrac{\partial c}{\partial z} \end{bmatrix}$

Vector: $\nabla \boldsymbol{a} = \begin{bmatrix} \dfrac{\partial a_1}{\partial x_1} & \dfrac{\partial a_1}{\partial x_2} & \dfrac{\partial a_1}{\partial x_3} \\ \dfrac{\partial a_2}{\partial x_1} & \dfrac{\partial a_2}{\partial x_2} & \dfrac{\partial a_2}{\partial x_3} \\ \dfrac{\partial a_3}{\partial x_1} & \dfrac{\partial a_3}{\partial x_2} & \dfrac{\partial a_3}{\partial x_3} \end{bmatrix}$

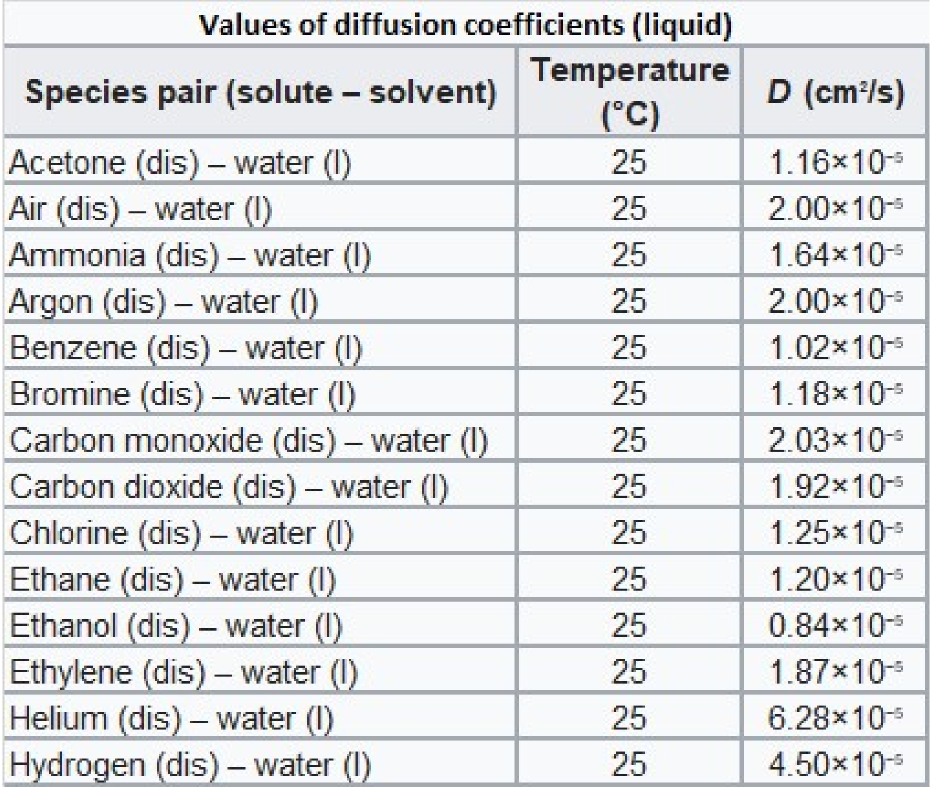
FICK LAW

D is the molecular diffusion coefficient or diffusivity.

$$D = D(T,p) \qquad \text{or} \qquad D = D(T,p,c_s) \qquad [\mathrm{m^2/s}]$$

T is the fluid Temperature → $D \propto T$

p is the fluid pressure → $D \propto 1/p$



Values of diffusion coefficients (liquid)

Species pair (solute – solvent)	Temperature (°C)	D (cm²/s)
Acetone (dis) – water (l)	25	1.16×10^{-5}
Air (dis) – water (l)	25	2.00×10^{-5}
Ammonia (dis) – water (l)	25	1.64×10^{-5}
Argon (dis) – water (l)	25	2.00×10^{-5}
Benzene (dis) – water (l)	25	1.02×10^{-5}
Bromine (dis) – water (l)	25	1.18×10^{-5}
Carbon monoxide (dis) – water (l)	25	2.03×10^{-5}
Carbon dioxide (dis) – water (l)	25	1.92×10^{-5}
Chlorine (dis) – water (l)	25	1.25×10^{-5}
Ethane (dis) – water (l)	25	1.20×10^{-5}
Ethanol (dis) – water (l)	25	0.84×10^{-5}
Ethylene (dis) – water (l)	25	1.87×10^{-5}
Helium (dis) – water (l)	25	6.28×10^{-5}
Hydrogen (dis) – water (l)	25	4.50×10^{-5}

ADVECTION-DIFFUSION EQUATION

A-D equation is based on the mass conservation

$$\begin{cases} M = \int_{\forall} c_s \, \mathrm{d}\forall \\ \dfrac{\mathrm{d}M}{\mathrm{d}t} = 0 \end{cases}$$

∀ is an arbitrary Material Volume

By replacing the first equation into the second one:

$$\frac{\mathrm{d}M}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\int_{\forall} c_s \, \mathrm{d}\forall = 0$$

Transport th.: $\dfrac{\mathrm{d}\Psi}{\mathrm{d}t} = \int_{\forall} \left(\dfrac{\mathrm{d}\psi}{\mathrm{d}t} + \psi \, \nabla \cdot \boldsymbol{u} \right) \mathrm{d}\forall$

$$\frac{\mathrm{d}M}{\mathrm{d}t} = \int_{\forall} \left(\frac{\mathrm{d}c_s}{\mathrm{d}t} + c_s \nabla \cdot \boldsymbol{u_s} \right) \mathrm{d}\forall = 0$$

Definition of velocity divergence ∇ ·: $\nabla \cdot \boldsymbol{u} = \dfrac{\partial u_x}{\partial x} + \dfrac{\partial u_y}{\partial y} + \dfrac{\partial u_z}{\partial z}$

ADVECTION-DIFFUSION EQUATION

The integral is zero for any ∀, that is:

$$\frac{\mathrm{d}c_s}{\mathrm{d}t} + c_s \nabla \cdot \boldsymbol{u_s} = 0$$

$$\frac{\partial c_s}{\partial t} + \boldsymbol{u_s} \cdot \nabla c_s + c_s \nabla \cdot \boldsymbol{u_s} = 0$$

$$\frac{\partial c_s}{\partial t} + \nabla \cdot (c_s\, \boldsymbol{u_s}) = 0$$

If we rearreange the expression by decomposing the absolute velocity of solute, we obtain:

$$\frac{\partial c_s}{\partial t} + \nabla \cdot [c_s(\, \boldsymbol{U} + \boldsymbol{v_s})] = 0$$

$$\frac{\partial c_s}{\partial t} + \nabla \cdot (c_s\, \boldsymbol{U}) = -\nabla \cdot (c_s\, \boldsymbol{v_s})$$

Differential equation of the solute mass balance

7 unknown parameters VS 5 equations (1 solute mass balance, 1 continuity eq., 3 momentum eqs.)

ADVECTION-DIFFUSION EQUATION

The parameters can be reduced through the Fick law. Indeed:

$$\boldsymbol{q}_{\boldsymbol{s}}^{\boldsymbol{r}} = c_s\, \boldsymbol{v}_{\boldsymbol{s}} = -D\, \nabla c_s$$

And then:

$$-\nabla \cdot (c_s\, \boldsymbol{v}_{\boldsymbol{s}}) = \nabla \cdot (D\, \nabla c_s)$$

$$-\nabla \cdot (c_s\, \boldsymbol{v}_{\boldsymbol{s}}) = D\, \nabla \cdot \nabla c_s$$

$$-\nabla \cdot (c_s\, \boldsymbol{v}_{\boldsymbol{s}}) = D\, \nabla^2 c_s$$

By replacing the latter into solute mass balance:

$$\longrightarrow \quad \underbrace{\frac{\partial c_s}{\partial t}}_{\textit{Temporal}} + \underbrace{\nabla \cdot (c_s\, \boldsymbol{U})}_{\textit{Advection}} = \underbrace{D\, \nabla^2 c_s}_{\textit{Diffusion}}$$

<u>Advection-Diffusion Equation</u>

Definition of Laplacian ∇^2*:*

$$\nabla^2 c = \begin{bmatrix} \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \end{bmatrix} \cdot \begin{bmatrix} \frac{\partial c}{\partial x} \\ \frac{\partial c}{\partial y} \\ \frac{\partial c}{\partial z} \end{bmatrix} = \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}$$

CONTINUITY EQUATION

Let’s consider the mass balance equation $c_s = \rho$:

$$\frac{\mathrm{d}M}{\mathrm{d}t} = \int_{\forall} \left(\frac{\mathrm{d}\rho}{\mathrm{d}t} + \rho \nabla \cdot \boldsymbol{u_s} \right) \mathrm{d}\forall = 0$$

Being the Control Volume ∀ arbitrary, the integrating function must be:

$$\frac{\partial \rho}{\partial t} + \boldsymbol{u_s} \cdot \nabla \rho + \rho \nabla \cdot \boldsymbol{u_s} = 0$$

Usually water is assumed to be uncompressible and homogeneous.
It means: $\rho = \rho(\boldsymbol{x}, t) = const$
Then:

$$\cancelto{0}{\frac{\partial \rho}{\partial t}} + \boldsymbol{u} \cdot \cancelto{0}{\nabla \rho} + \rho \nabla \cdot \boldsymbol{u} = 0$$

$$\longrightarrow \qquad \nabla \cdot \boldsymbol{u} = 0$$

3D Continuity Equation

A-D EQUATION FOR INCOMPRESSIBLE FLUID

By replacing continuity equation into advection-diffusion equation, we have:

$$\frac{\partial c_s}{\partial t} + \boldsymbol{U} \cdot \nabla c_s + c_s \cancelto{0}{\nabla \cdot \boldsymbol{U}} = D\, \nabla^2 c_s$$

And finally:

$$\longrightarrow \qquad \frac{\partial c_s}{\partial t} + \boldsymbol{U} \cdot \nabla c_s = D\, \nabla^2 c_s$$

<u>Advection-Diffusion Equation for incompressible fluid</u>

If we consider fluid at rest, i.e. $\boldsymbol{U} = 0$, the latter equation is simplified in the following:

$$\longrightarrow \qquad \frac{\partial c_s}{\partial t} = D\, \nabla^2 c_s$$

<u>Pure Diffusion Equation</u>

DIFFUSION EQUATION

Let’s start from the A-D equation:

$$\frac{\partial c}{\partial t} + \boldsymbol{U} \cdot \nabla C = D\,\nabla^2 C$$

Hp: - non-reactive solute: $\mathrm{d}M/\mathrm{d}t = 0$
- homogeneous and uncompressible fluid: $\rho = 0$

When the fluid is at rest, i.e. $\boldsymbol{U}$=0, then:

$$\longrightarrow \qquad \frac{\partial c_s}{\partial t} = \; D\,\nabla^2 c_s$$

Diffusion Equation

This equation is linear and it can be solved analitycally!

Why do we solve molecular diffusion when this phenomenon is negligible at large scale?

Analitycal solution of molecular diffusivity and turbulent diffusion is the same, hence this solution can be extended to the turbulent case (under certain conditions).

ABOUT BOUNDARY CONDITIONS

To solve the Diffusion equation the initial and the boundary conditions have to be correctly set.

Initial condition: $c(\boldsymbol{x},t) \rightarrow c(\boldsymbol{x},0) = c_0(\boldsymbol{x})$ *Initial distribution of solute concentration*

Boundary condition: $c(\boldsymbol{x},t) \rightarrow c(\boldsymbol{x}_0,t)$ *Evolution with t of c in some sections of the domain*

Three kinds of BCs exist:

- Dirichlet condition: $c = c(t)$ in $\boldsymbol{x}_0$
- Neumann condition: ∇c in $\boldsymbol{x}_0 \rightarrow \boldsymbol{q}^r = c\,\boldsymbol{v_s}$ in $\boldsymbol{x}_0$
- Cauchy condition: Dirichlet condition + Neumann Condition

N.B. In our applications also BCs are linear!

FUNDAMENTAL SOLUTION

Why is it fundamental?

Since the problem is linear, one can use the superimposition of the effects to solve complex problem.

$$\text{complex problem} = \sum \text{elementary problems}$$

→ *We will know their solution*

Let's consider the following **1-D Diffusion problem**:

$$\begin{cases} \dfrac{\partial c}{\partial t} = D\,\dfrac{\partial^2 c}{\partial x^2} \\ c(x,0) = M\delta(x) \quad \text{usually for } x = 0 \quad \longrightarrow \quad \underline{\text{Initial condition}} \\ c(x,t) = 0 \quad \text{for } x \to \pm\infty \quad \longrightarrow \quad \underline{\text{Boundary conditions}} \end{cases}$$

In this case the concentration c is defined as:

$$c = \lim_{\Delta x \to 0} \frac{\Delta M}{\Delta x} \qquad [\text{kg/m}]$$

FUNDAMENTAL SOLUTION

Initial condition $c(x,0) = M\ \delta(x)$ is the injection point.

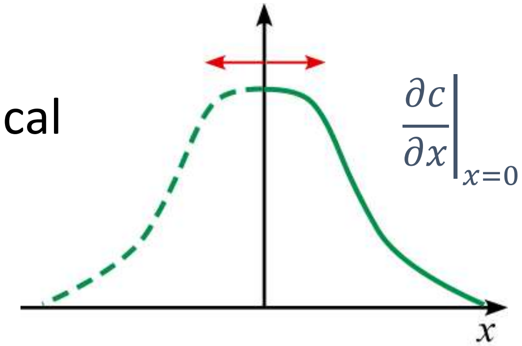
Boundary conditions $c(x,t) = 0$ for $x \rightarrow \pm\infty$ means domain undefinetely extended.

Noting that:

$$\left.\begin{array}{ll} \text{i)} & \text{Actually, } c = c(x,t,M,D) \\ \text{ii)} & \text{Due to linearity, } c \propto M \end{array}\right\} \quad c = M\ f(x,t,D)$$

iii) For the mass conservation, $M = \int_{-\infty}^{+\infty} c(x,t)\ \mathrm{d}x$

iv) For isotropy the concentration distribution is symmetrical



$$\left.\frac{\partial c}{\partial x}\right|_{x=0} = 0 \ \rightarrow \text{max}$$

$\delta(x)$ is Dirac Delta Function, that is defined as following: $\int_{-\infty}^{+\infty} \delta(x)\ \mathrm{d}x = 1$

Dirac Delta Function has the property: $\int_{-\infty}^{+\infty} f(x)\delta(x-x_0)\ \mathrm{d}x = \begin{cases} 0 & x \neq x_0 \\ f(x_0) & x = x_0 \end{cases}$