DIFFUSION

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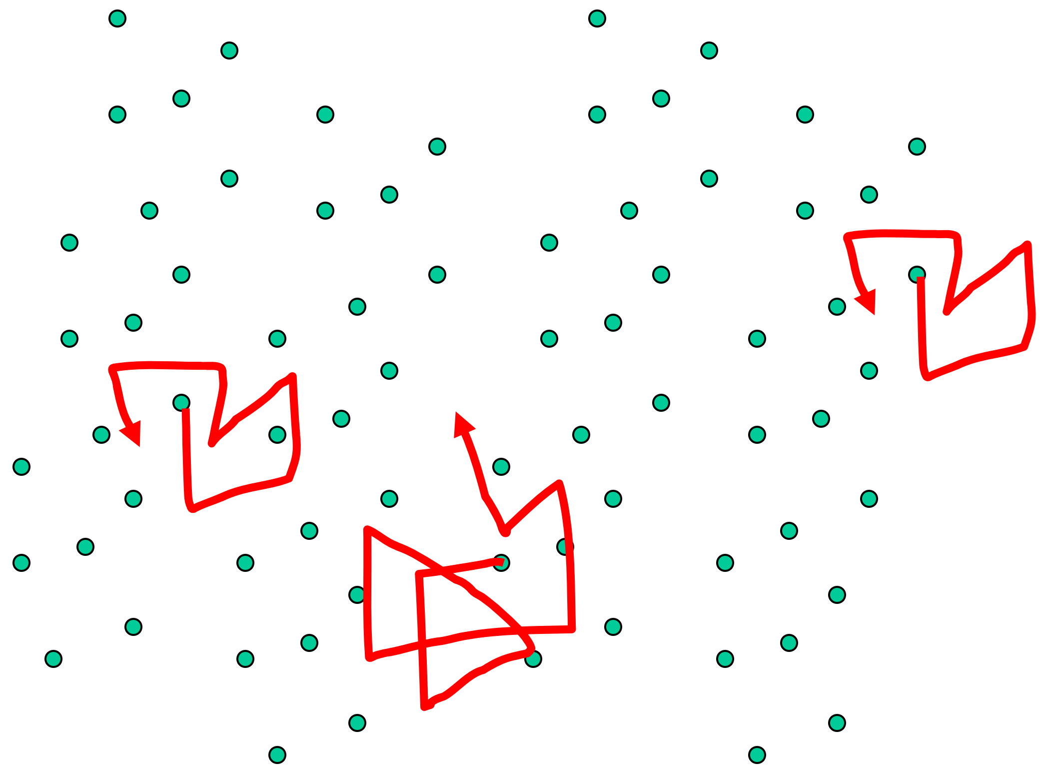
What are the mechanisms for chemical motion?

- Advection
  - Bulk transport by imposed flow. Examples: current in a stream, flow in a pipe.
- Convection
  - Transport due to fluid instability. Examples: air rising over a hot road.
- Diffusion- molecular
  - Scattering of particles (molecules) by random motion due to thermal energy
- Diffusion- turbulent
  - Scattering due to fluid turbuence. Also called eddy diffusion. This type of “diffusion” is much faster than molecular diffusion

Diffusion & Dispersion

- Diffusion is a method by which a chemical is dispersed.
- Dispersion is the “spreading out” of a chemical that can be caused by different mechanisms
- Don’t confuse a molecular diffusion coefficient with a dispersion coefficient (more on dispersion will come later in the course).

Chemical Flux

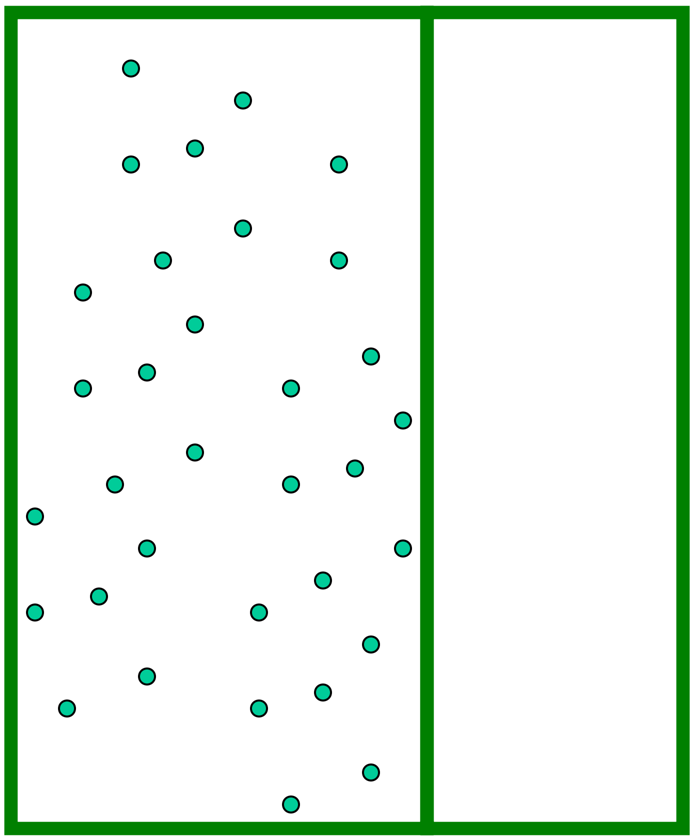


Molecules move in a random direction based on thermal energy

Is there a net flux?

$$Flux \equiv \frac{Total\ \ flow\,rate}{Area} \quad [\frac{moles}{L^2 - t}]$$

Chemical Flux



Net flux occurs when molecules move in a direction where there are no molecules to balance their motion back in the opposite direction.

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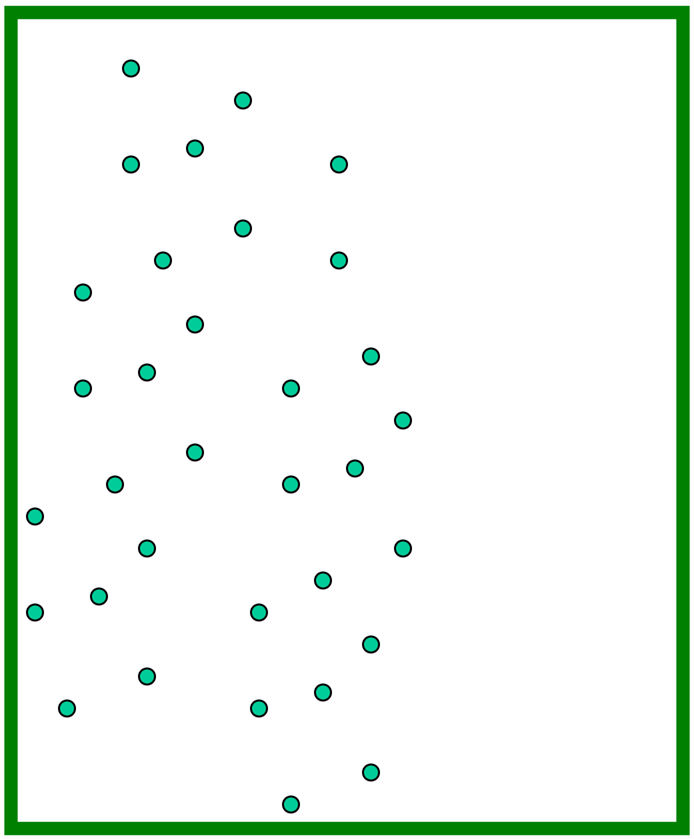

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Direction of net chemical flux

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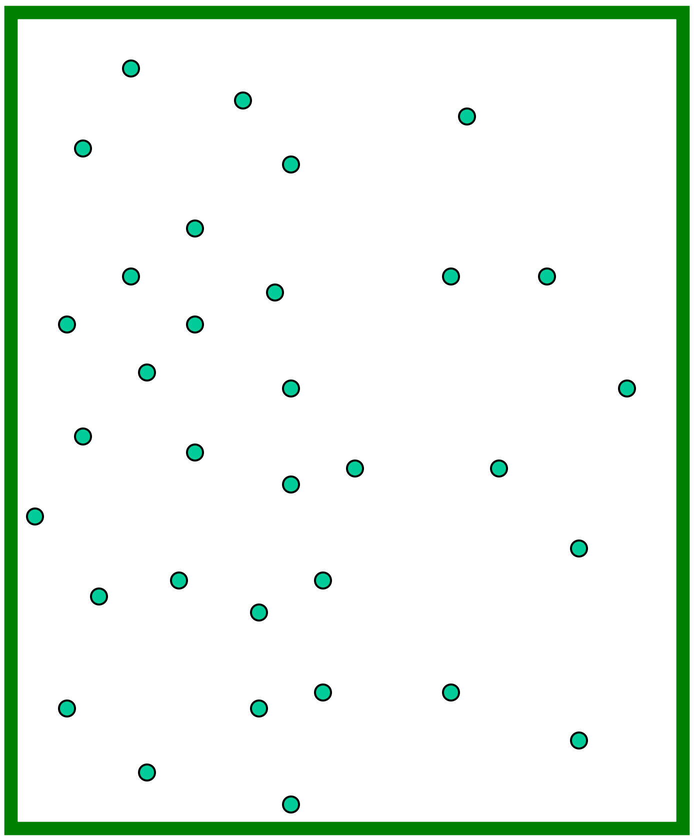

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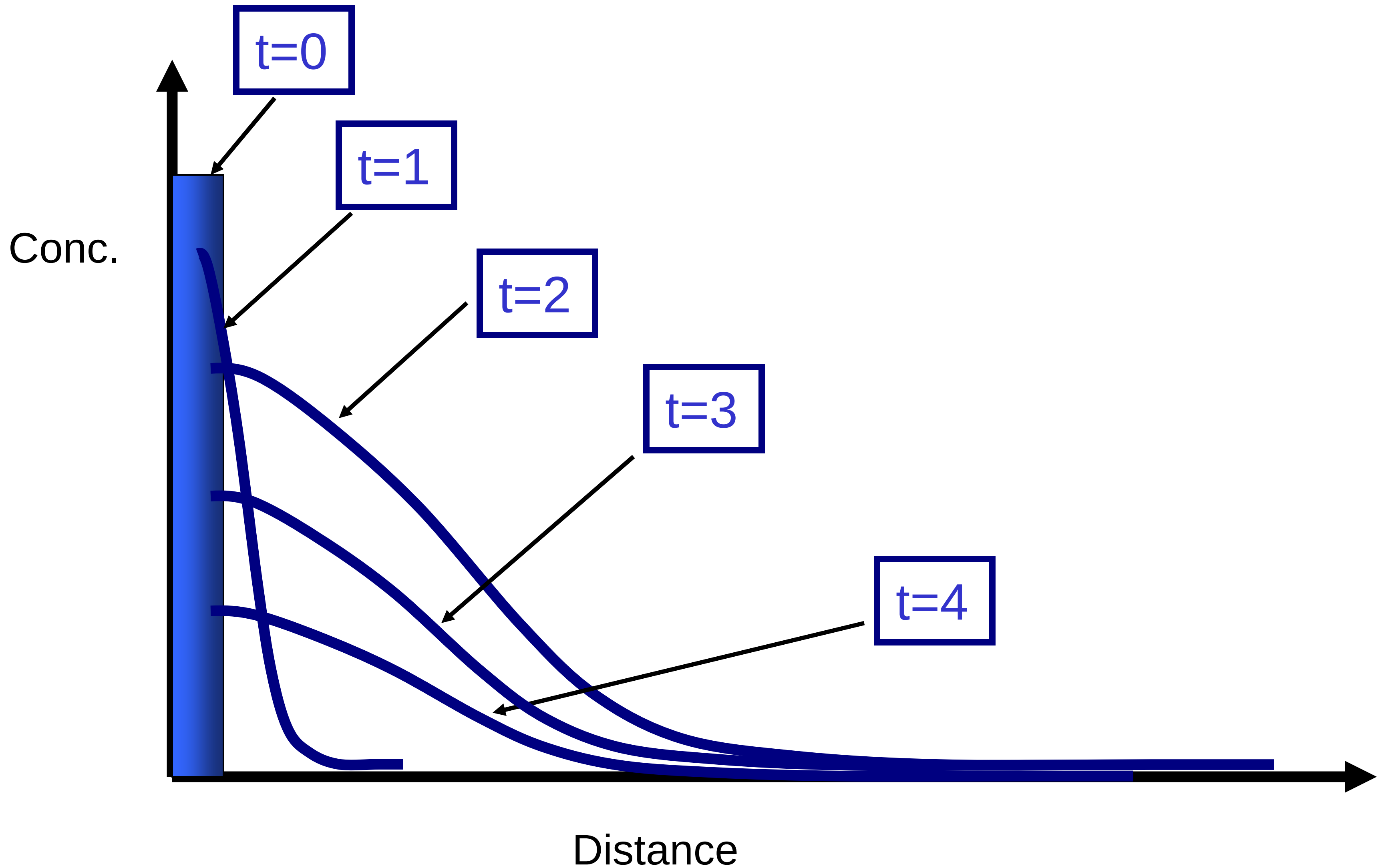
We often show chemical flux graphically as concentration versus time



Fick's First Law

Fick recognized that there must be a difference in concentration to drive the net diffusion of a chemical, and formulated the law:

$$j_{Cw,z} = -c_w D_{Cw} \frac{dx_C}{dz}$$

c_w= molar density of water

dx_C/dz= molar gradient of C in z-direction

$j_{Cw,z}$= molar flux of C in z-direction

D= Diffusion constant (fitted parameter)

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Note negative sign

(flux in direction opposite to gradient)

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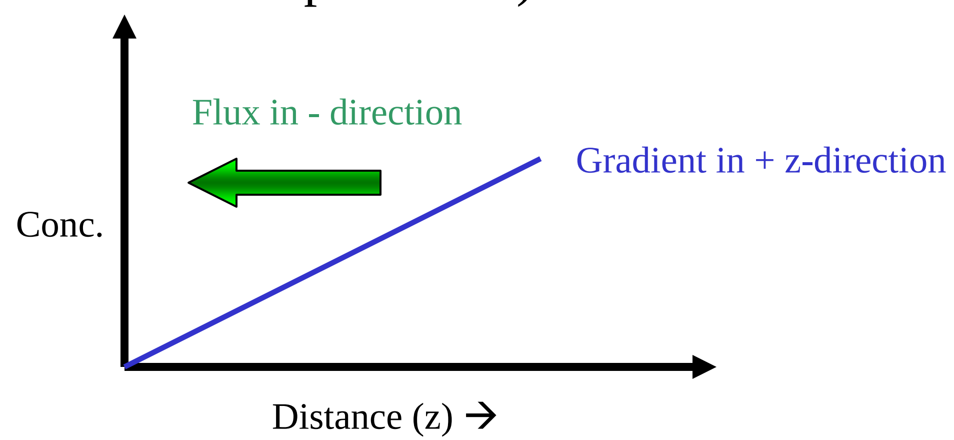

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Under isothermal, isobaric conditions, this can be simplified to:

$$\boxed{j_{Cw,z} = -D_{Cw} \frac{dc_{Cw}}{dz}}$$

Flux in different directions:

$$j_{Cw,x} = -c_w D_{Cw} \frac{dx_C}{dx}$$

$$j_{Cw,y} = -c_w D_{Cw} \frac{dx_C}{dy}$$

$$j_{Cw,z} = -c_w D_{Cw} \frac{dx_C}{dz}$$

$$j_{Cw,r} = -c_w D_{Cw} \frac{dx_C}{dr}$$

Typical values of Diffusion Coefficient

Gas	$D_{Ca} = 10^{-1}$ [cm²/s]
Liquid	$D_{Cw} = 10^{-5}$ [cm²/s]
Solid	$D_{Cw} = 10^{-10}$ [cm²/s]

EXAMPLE CALCULATION

- A jar of phenol contaminates a room with only one cylindrical vent (10 cm diameter, 20 cm deep)
- Neglecting advection, what is the rate of phenol loss through the vent if the room concentration of phenol in air is 0.05%?
- Assume: constant temperature of 20^{o}C; a linear concentration gradient in the vent; $D_{pa}=10^{-1}$ cm^2/s.

Solution…

$$j_{Pa,z} = -c_a D_{Pa} \frac{dy_C}{dz} = -D_{Pa} \frac{dc_{Pa}}{dz} \approx -D_{Pa} \frac{\Delta c_{Pa}}{\Delta z} = -D_{Pa} \frac{(c_{Pa,1} - 0)}{(0 - z_2)}$$

$$Rate: \quad W_{Pa,z} = j_{Pa,z} A = \frac{D_{Pa} c_{Pa,1} A}{z_2}$$

$$c_{Pa,1} = y_P c_a = (0.0005)(\frac{mole}{24.1L}) = 2.1 \times 10^{-5} \frac{mol}{L}$$

$$A = \frac{\pi}{4} d^2 = \frac{\pi}{4} (10\,cm)^2 = 79\,cm^2$$

$$W_{Pa,z} = \frac{(10^{-1}\,cm^2/s)(2.1\times 10^{-5}\,mol/L)(79\,cm^2)}{(20\,cm)} \frac{10^{-3}\,L}{cm^3}$$

$$\boxed{W_{Pa,z} = 8.2\times 10^{-9}\text{ mol/s}}$$

Fick's Second Law

What is the effect of time on the flux? Or… how does the flux change over time?

$$\frac{\text{change in conc}}{\Delta t} \propto \frac{\Delta \text{conc. gradient}}{\Delta \text{ distance}}$$

$$\frac{\Delta c}{\Delta t} = D \frac{\Delta(\Delta c / \Delta z)}{\Delta z}$$

$$\frac{\partial c}{\partial t} = D \frac{\partial(\partial c / \partial z)}{\partial z} = D \frac{\partial^2 c}{\partial z^2}$$

Fick's Second Law

For a chemical in water: $$\frac{\partial c_{Cw}}{\partial t} = D_{Cw}\frac{\partial^2 c_{Cw}}{\partial z^2}$$

At steady state, $$\frac{\partial c_{Cw}}{\partial t} = 0$$

so this becomes $$\frac{\partial c_{Cw}}{\partial t} = 0 = D_{Cw}\frac{\partial^2 c_{Cw}}{\partial z^2}$$

and we have that $$\frac{dc_{Cw}}{dz} = \text{constant}$$

This tells us that at steady state, the flux is constant, i.e.

$$j_{Cw,x} = -c_w D_{Cw}\frac{dx_C}{dx}$$

Fick's First Law

How to calculate Diffusion Coefficients?

- General Approaches
  - Tabulated values- best approach
  - Correlations- many can exist
  - Experimental- can be time consuming
- Air Correlations for D_{Ca}
  - Kinetic theory of gases: many limitations, such as binary mixture.
  - Hirshfelder correlation: requires a lot of constants
  - Fuller correlation: best approach

FULLER CORRELATION: Diffusivities from Structure

Chemical "C" in gas "g"

$$D_{Cg} = \frac{T^{1.75} \times 10^{-3}}{P\,(V_{C,d}^{1/3} + V_{g,d}^{1/3})^2} \left(\frac{1}{M_C} + \frac{1}{M_g} \right)^{1/2}$$

Where: [these units must be used]

D_{Ca}= diffusion coefficient [cm^2/s]

T= temperature [K]

P= pressure [atm]

M_C= molecular weight of chemical [g/mol]

M_g= molecular weight of gas [g/mol]

$V_{C,d}$= atomic diffusion volume (from formula and tabulated values) [cm^3]

For chemicals in air: →

$$D_{Ca} = \frac{T^{1.75} \times 10^{-3}}{P\,(V_{C,d}^{1/3} + 2.73)^2} \left(\frac{1}{M_C} + 0.0345 \right)^{1/2}$$

TABLE 3.1 Atomic Diffusion Volumes for Use in Estimating D_{Cg} by Method of Fuller et al.

Atomic and Structure Diffusion–Volume Increments, v			
C	16.5	Cl	19.5
H	1.98	S	17.0
O	5.48	Aromatic ring	−20.2
N	5.69	Heterocyclic ring	−20.2

Diffusion Volumes for Simple Molecules, v					
H_2	7.07	Ar	16.1	H_2O	12.7
D_2	6.70	Kr	22.8	$CClF_2$	114.8
He	2.88	CO	18.9	SF_6	69.7
N_2	17.9	CO_2	26.9	Cl_2	37.7
O_2	16.6	N_2O	35.9	Br_2	41.1
Air	20.1	NH_3	14.9	SO_2	41.1

Source: Welty et al., 1984.

Table 3.1: Logan, Environmental Transport processes, p. 63.

How to calculate Diffusion Coefficients?

- Water: more on this later
- Solids
  - Less information available
  - Chemical in porous medium is in liquid phase: hindered diffusion
  - Chemical adsorbed to soil is in “solid” phase: surface diffusion
  - For hindered and surface diffusion, need to know diffusion constant in water

Examples: Diffusion constants in/on solids

Hindered diffusion

$$\boxed{D_{Cw,pm} = D_{Cw,h}\frac{\theta}{\tau}}$$

Where:

$D_{Cw,pm}$= diffusion coefficient in porous medium

$D_{Cw,h}$= diffusion coefficient in a single pore

θ= porosity; typically 0.3

τ= tortuosity factor; typically 3

Surface diffusion

$$\boxed{D_{Cw,h+sur} = D_{Cw,h} + \frac{(1-\theta)K^* D_{Cw,sur}}{\theta}}$$

Where:

$D_{Cw,h+sur}$= overall surface diffusion coefficient

$D_{Cw,sur}$= surface diffusion coefficient

K^*= dimensionless adsorption partition coefficient

Diffusion constants: summary

- Tabulated values always best
- For air, simple correlations should be sufficient for level of our calculations
- In a porous medium, porosity and tortuosity factors probably more important than correct value for molecular diffusion in air.
- For water, situation is much more complex… more on that next.