

# Interphase mass transfer I: Diffusion

# Interphase mass transfer

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- **What we will do**
  - Focus on the air-water interphase
  - Discuss factors that affect mass transfer rates
  - Consider the interfacial region
  - Consider models that attempt to predict mass transfer rates
    - Some background
    - Some examples
- **Considerable empiricism involved**
  - Difficult/impossible to directly measure certain parameters of interest
    - Employ models with a fundamental underpinning
    - Get constants from correlations

# Mass transfer is:

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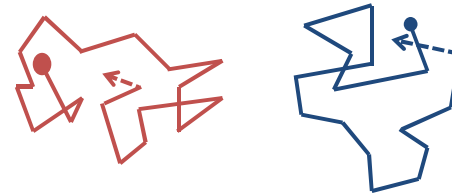
- **Net change in a compound's mass, concentration, and/or fugacity within a specific volume, compartment, phase**
  - Non-equilibrium process
  - Movement is from high to low fugacity
    - Within a single phase, this means from high to low concentration
- **A consequence of random behavior, motion**

# Molecular diffusion

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- **Moles of drunks meandering through space**

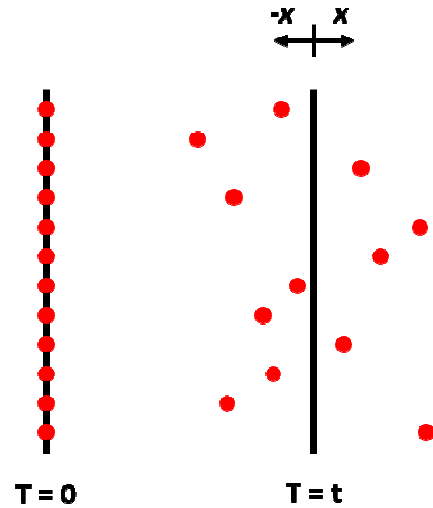
- Random walk (Brownian motion)



- **Consider the (ground level) atmosphere**

- Molecules
  - Take up ~0.1% of available space
  - Zip around at ~450 m/sec (average)
  - Have  $\sim 2 \times 10^{10}$  collisions/sec
    - Mean free path (mfp)  $\sim 20$  nm ( $2 \times 10^{-8}$  m); characteristic travel distance is:
      - » ~6 mm in one second
      - » ~5 cm in one minute
      - » ~40 cm in one hour

# Molecular diffusivity $D_i$ & Flux $J_{x,i}$



$$D_i = \frac{\bar{x}^2}{2t} \quad [L^2/T]$$

**Specific flux (J): net mass (or molecules) crossing unit area of boundary per unit time**

$$J_{x,i} = -D_i \frac{dC_i}{dx} \quad [M/L^2/T] \text{ or } [\text{mole}/L^2/T]$$

Rough estimates of diffusivities in air and water @ 20 °C

	MW	$D_i, m^2/s$	
		Water	Air
Oxygen	32	$2 \times 10^{-9}$	$2 \times 10^{-5}$
Phenol	94	$1 \times 10^{-9}$	$1 \times 10^{-5}$
TCE	131	$1 \times 10^{-9}$	$1 \times 10^{-5}$
Lindane	291	$6 \times 10^{-10}$	$6 \times 10^{-6}$

$$D_i \propto \frac{1}{m^x} \quad \text{or} \quad \frac{1}{V^y}$$

$m$ : molecular weight;  $V$ : molecular volume  
 $x, y$  in the range of 0.6 to 0.8

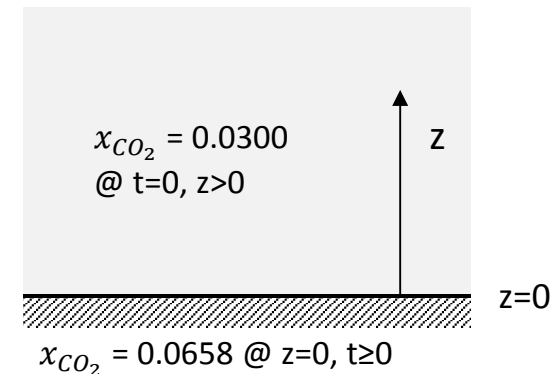
# Molecule transport owing to diffusion only

Source: Thibodeaux et al. (2018)<sup>#1</sup>

CO<sub>2</sub> mole fraction ( $x_{CO_2}$ ) change in stagnant air mass<sup>a</sup>

Time (t)	Penetration distance, z (cm)				
	0.001	0.01	0.10	1.00	10.0
1 s	0.0657	0.0654	0.0606	0.0326	0.0300
1 min	0.0658	0.0657	0.0651	0.0592	0.0307
1 h	0.0658	0.0658	0.0657	0.0649	0.0574

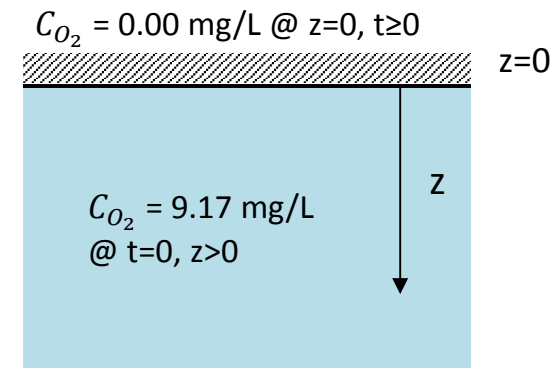
<sup>a</sup> **Simulation** results; used  $D_{CO_2}$  (air) = 0.153 cm<sup>2</sup>/s @ 20 °C, 1 atm.



O<sub>2</sub> concentration ( $C_{O_2}$ ; in mg/L) change in stagnant water<sup>b</sup>

Time (t)	Penetration distance, z (cm)				
	0.001	0.01	0.10	1.00	10.0
5 min	0.069	0.70	6.1	9.17	9.17
10 h	<0.001	0.064	0.64	5.69	9.17
2 d	<0.001	0.028	0.29	2.87	9.17

<sup>b</sup> **Simulation** results; used  $D_{O_2}$  (water) =  $1.80 \times 10^{-5}$  cm<sup>2</sup>/s @ 20 °C.



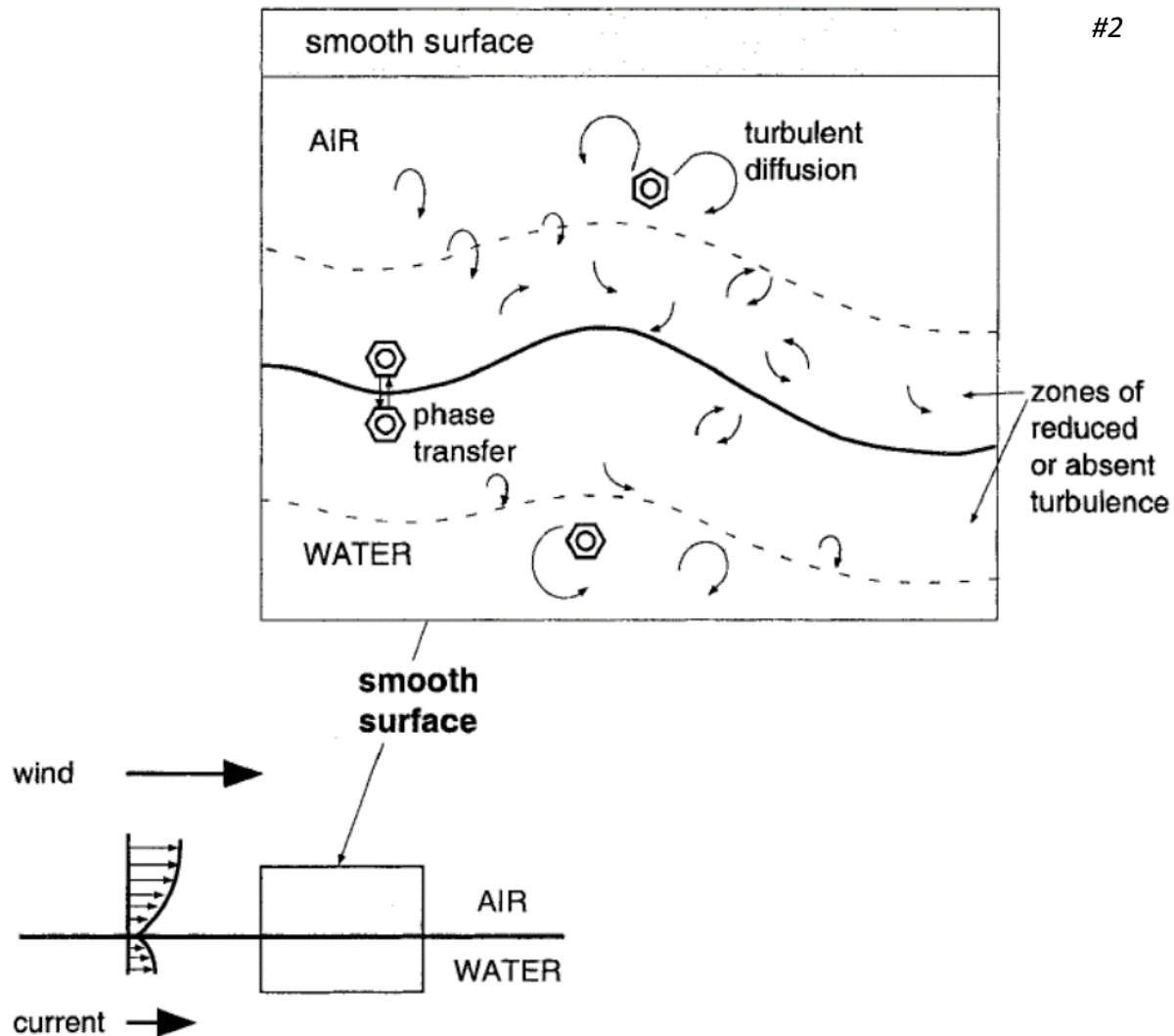
# Interphase mass transfer – $D_i$ is not enough

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- **Observed air/water transfer rates are too fast to be explained by molecular diffusion across a flat interphase from/into a quiescent phase**
  - Regions where diffusion controls are very thin
    - Because of turbulence
  - Actual interfacial areas may be  $\gg$  than nominal
    - Difficult to measure

# Air/water interface: smooth

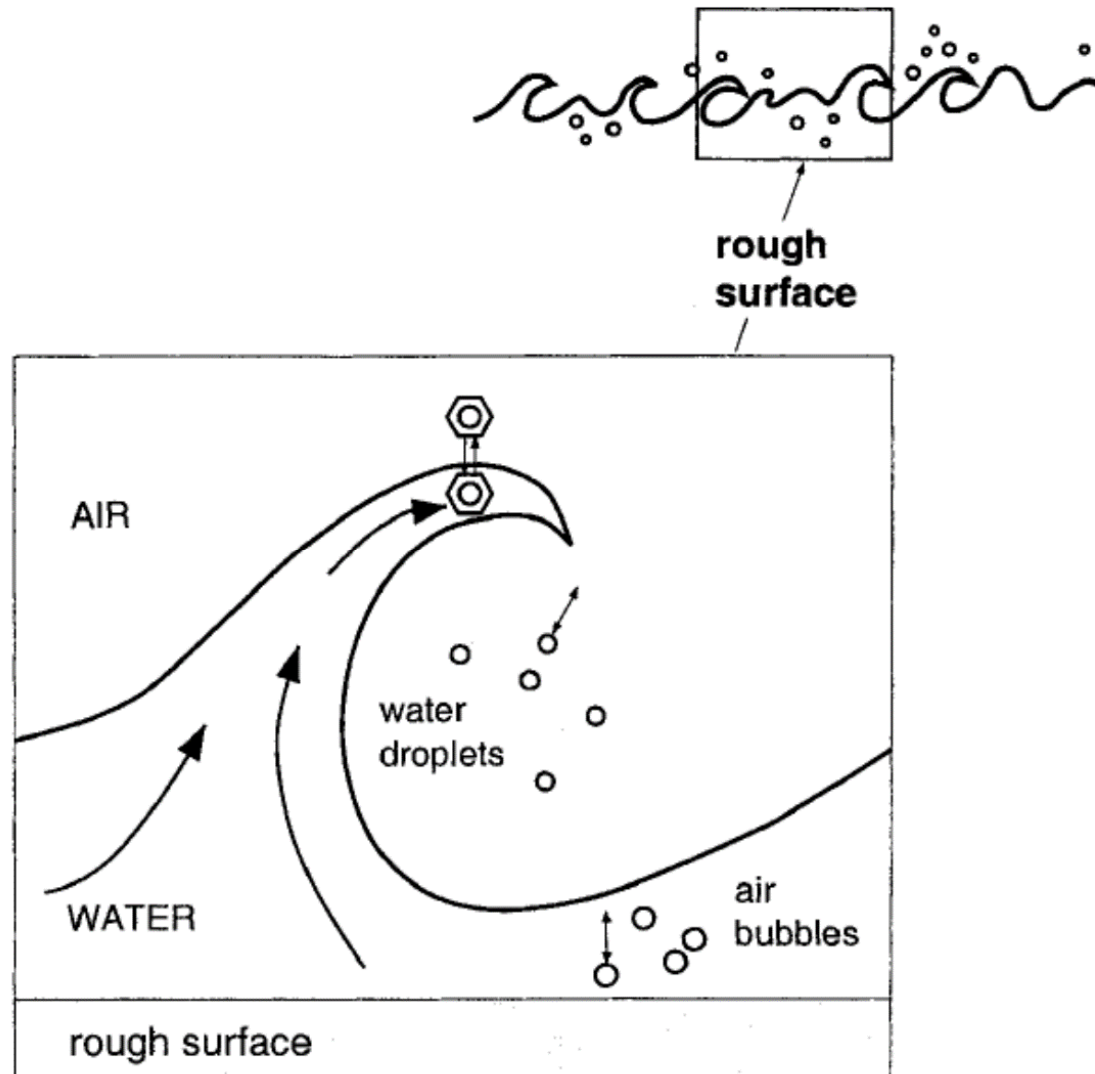
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# Air/water interface: rough

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# Molecular diffusion – example 1

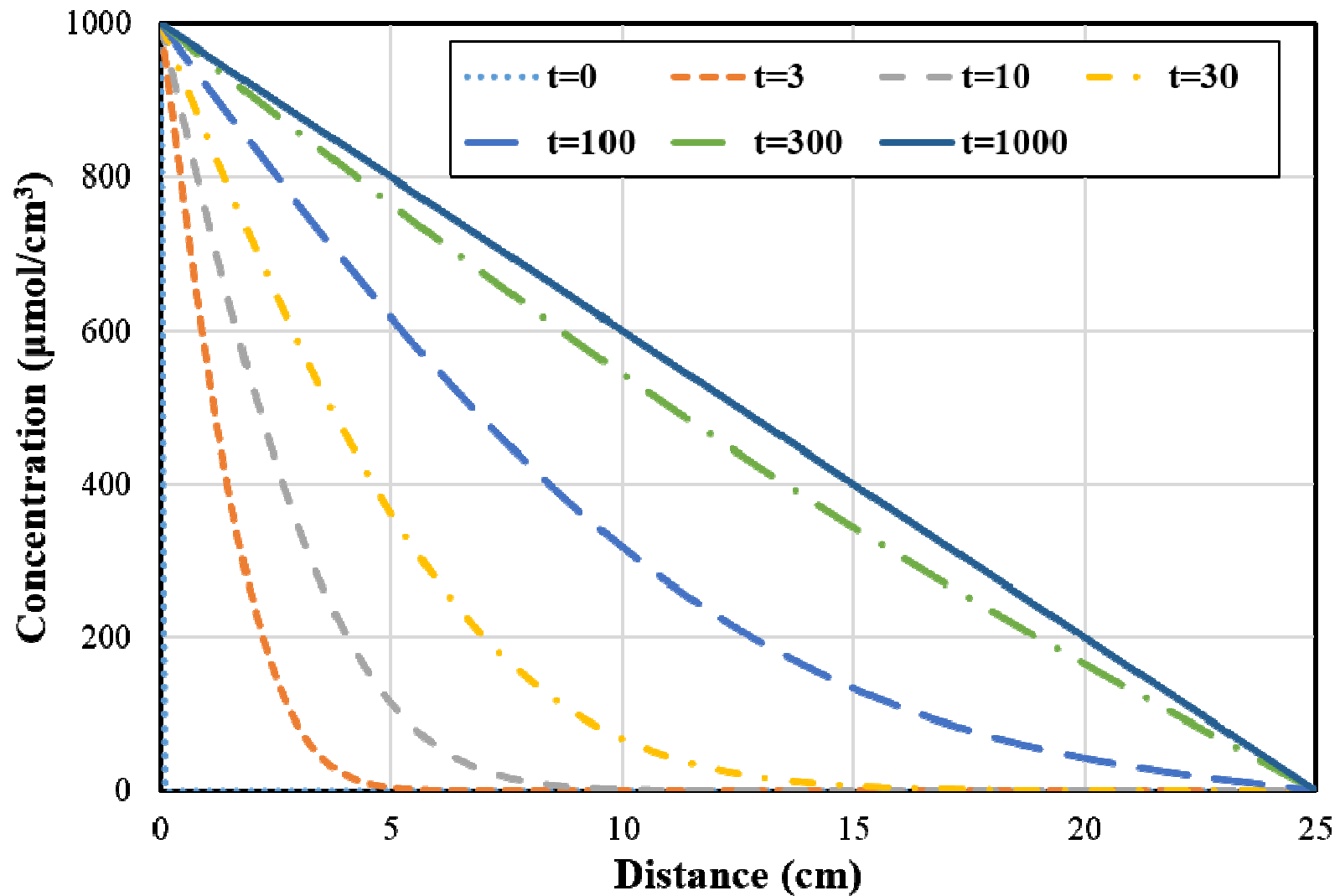
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Let's consider a model system with:

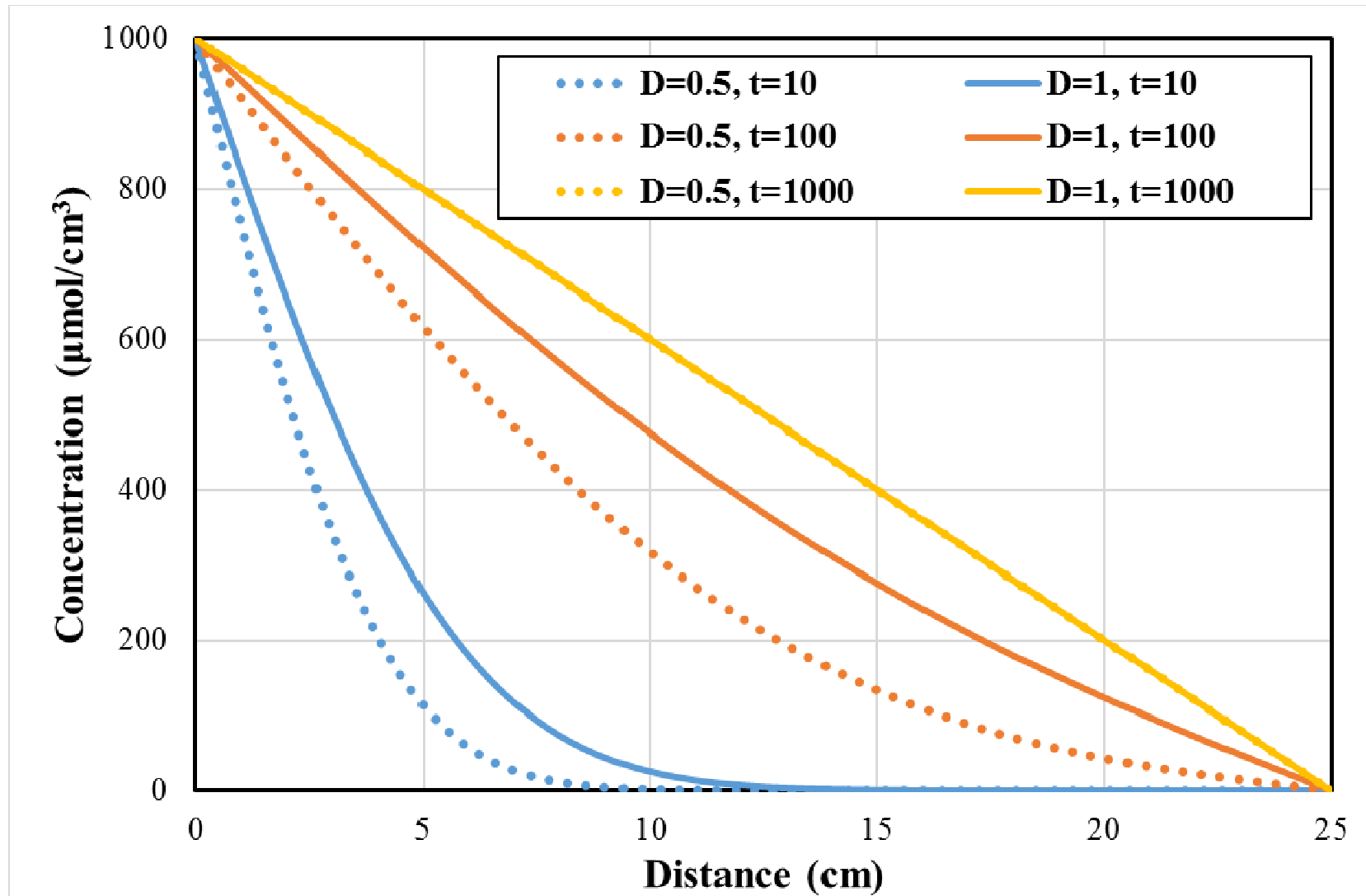
- 1-dimensional movement  $J_{x,i} = -D_i \frac{dC_i}{dx}$
- At  $t = 0$  s
  - For  $0 \text{ cm} < x < 25 \text{ cm}$ ; Concentration ( $C_i$ ) =  $0 \text{ } \mu\text{mol}/\text{cm}^3$
- At any  $t$ 
  - For  $x = 0 \text{ cm}$ ;  $C_i = 1000 \text{ } \mu\text{mol}/\text{cm}^3$
  - For  $x = 25 \text{ cm}$ ;  $C_i = 0 \text{ } \mu\text{mol}/\text{cm}^3$ 
    - At boundaries there is continuous replenishment/scavenging
- For any time step
  - Chemical A:  $D_A = 0.5 \text{ cm}^2/\text{s}$
  - Chemical B:  $D_B = 1 \text{ cm}^2/\text{s}$

# Concentration vs. Distance (1)

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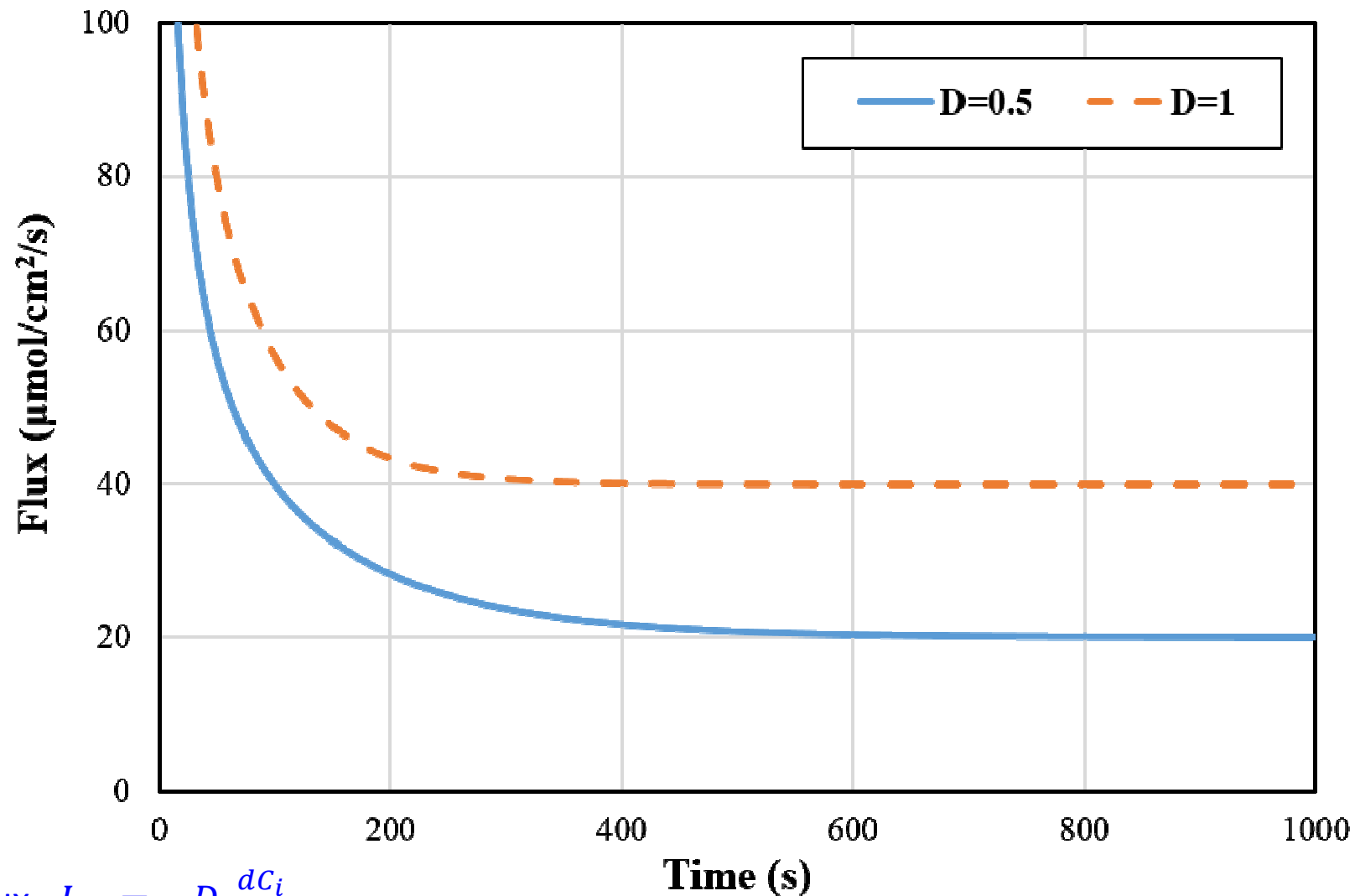


# Concentration vs. Distance (2)



# Flux (@ x = 0 cm) vs. Time

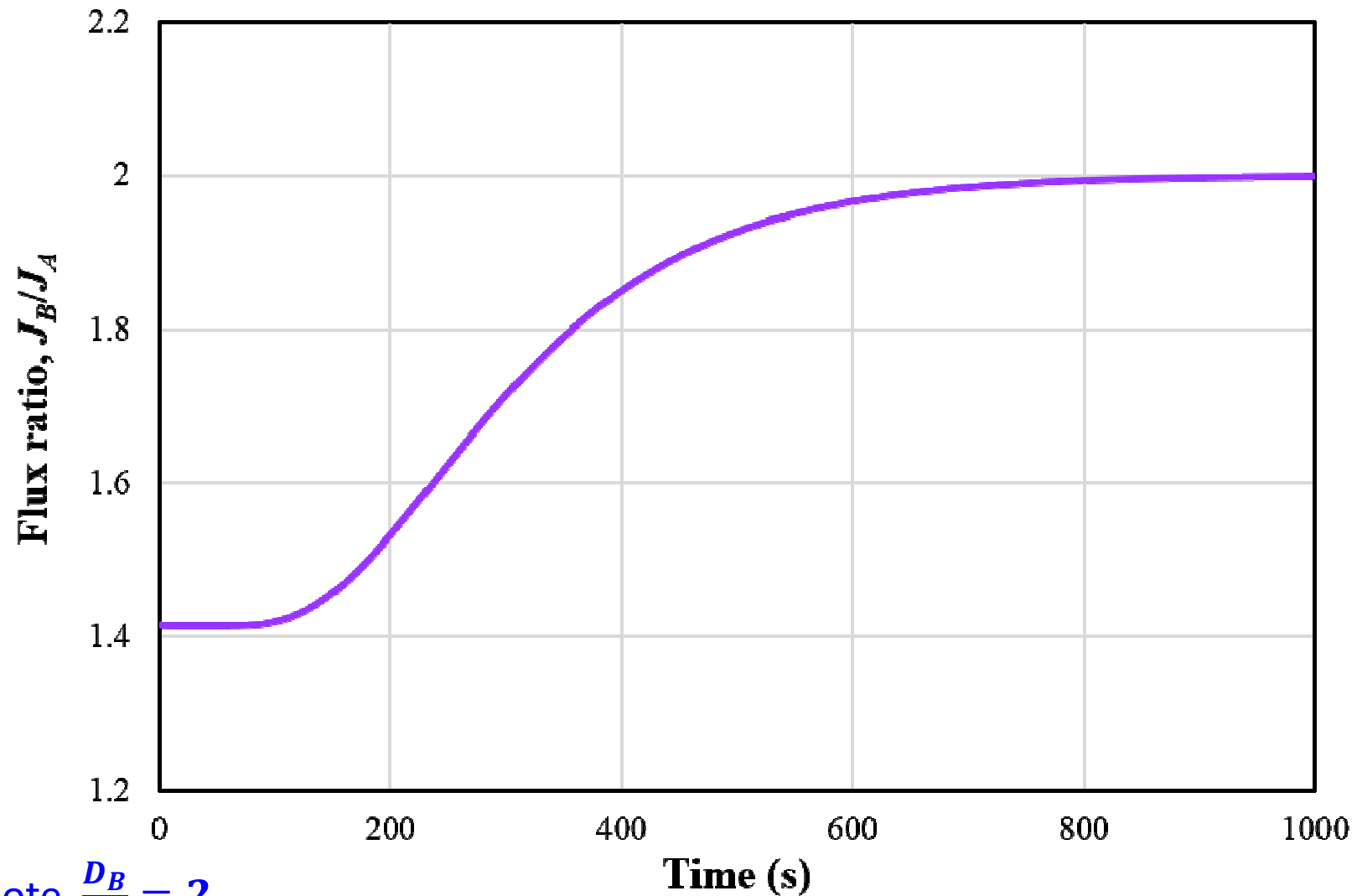
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$$\text{Flux, } J_{x,i} = -D_i \frac{dC_i}{dx}$$

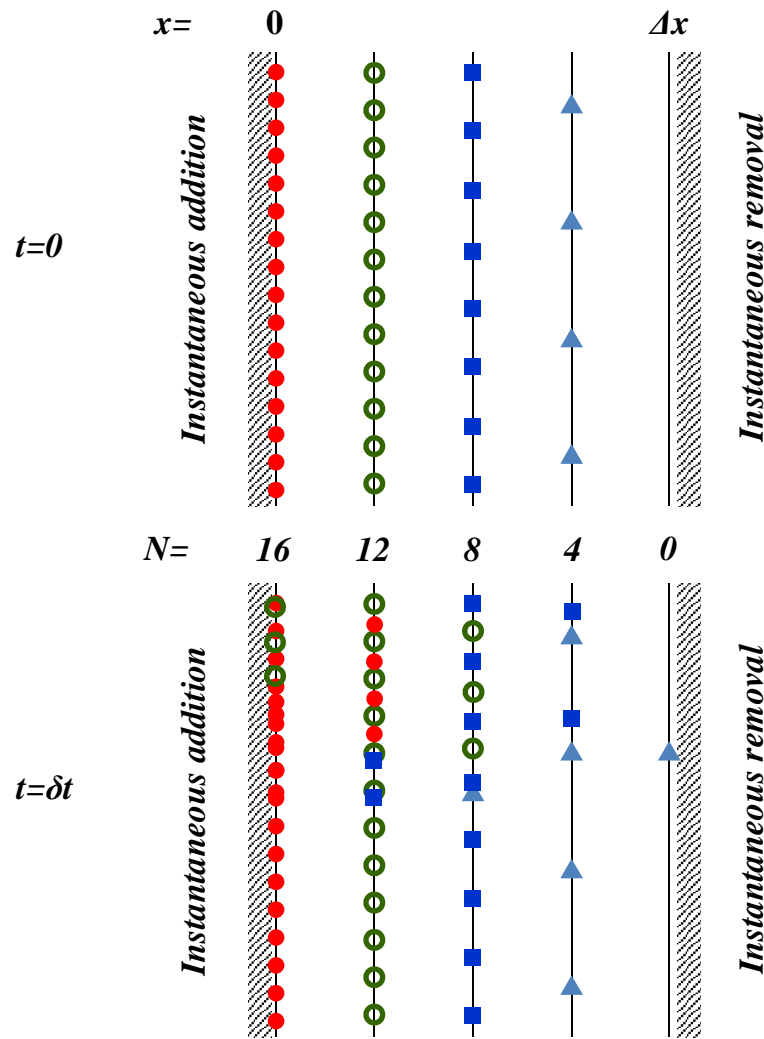
# Flux ratios ( $J_B/J_A$ , @ $x = 0$ cm)

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Note  $\frac{D_B}{D_A} = 2$

# Molecular diffusion – example 2



50% of molecules shift position in time  $\delta t$   
 Equal probability of shifting right or left

$$\left(\frac{\partial N}{\partial t}\right)_x = 0 \quad (\text{the system is at steady state})$$

$$\left(\frac{\partial N}{\partial x}\right)_t = \frac{16}{\Delta x}$$

$$J = \frac{\# \text{ of net movement}}{\text{area } (A) \times \text{time}} = \frac{1}{A \cdot \partial t}$$

# Model system results

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- **Initially**

- Concentration profile changes rapidly
- Flux out changes rapidly
- System with high  $D \rightarrow$  concentration gradient decreases faster at the outlet

$$J_{in} \neq J_{out} \quad \frac{J_B}{J_A} = \sqrt{\frac{D_B}{D_A}}$$

- **After a long time**

- Linear concentration profile

$$J_{in} = J_{out} \quad \frac{J_B}{J_A} = \frac{D_B}{D_A}$$



# References

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- #1) Thibodeaux, L. J., Schnoor, J. L., Zehnder, A. J. B. (2018) *Environmental Chemodynamics: Movement of Chemicals in Air, Water, and Soil*. 3<sup>rd</sup> ed., Science, pp. 100-101.
- #2) Schwarzenbach, R., Gschwend, P. M., Imboden, D. M. (2003) *Environmental Organic Chemistry*, 2nd ed., John Wiley & Sons, p. 907.