Interphase mass transfer

Interphase mass transfer

- **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

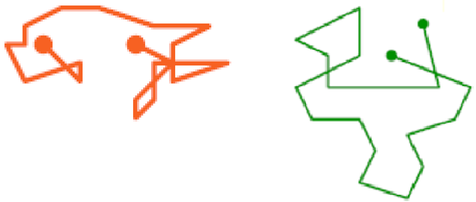
Mass transfer is:

- **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**

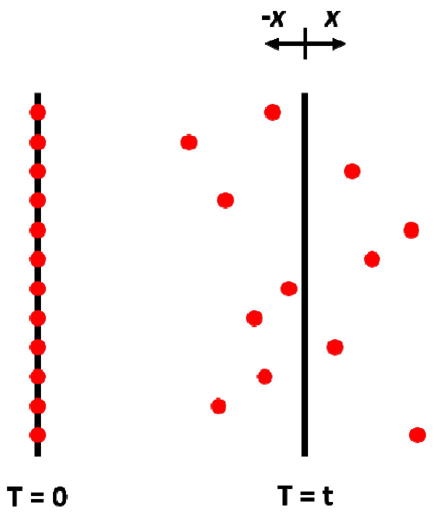
Molecular diffusion

- **Moles of drunks meandering through space**
  - Random walk



- **Consider the (ground level) atmosphere**
  - Molecules
    - Take up ~0.1% of available space
    - Zip around at ~450 m/sec (average)
    - Have ~2 x 10^{10} collisions/sec
      - Mean free path (mfp) ~20 nm (2 x 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

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

Rough estimates of diffusivities in air and water @ 20 ^oC

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

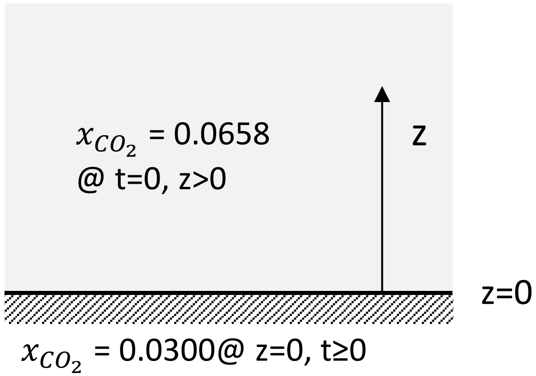
Molecule transport owing to diffusion only

Source: Thibodeaux et al., 1996

CO_2 mole fraction (x_{CO_2}) change in stagnant air mass[a]

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

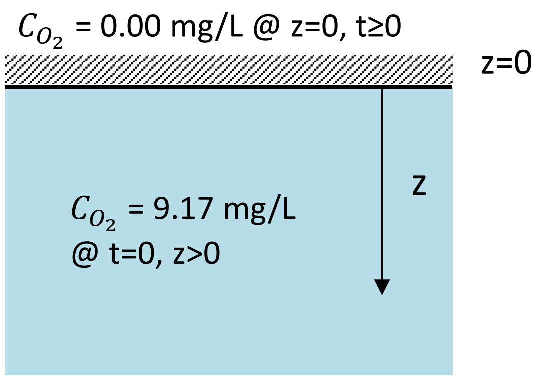
[a] **Simulation** results; used D_{CO_2} (air) = 0.153 cm^2/s @ 20 ^oC, 1 atm.



O_2 concentration (C_{O_2}; in mg/L) change in stagnant water[b]

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	0.0592	9.17
2 d	<0.001	0.028	0.29	0.0649	9.17

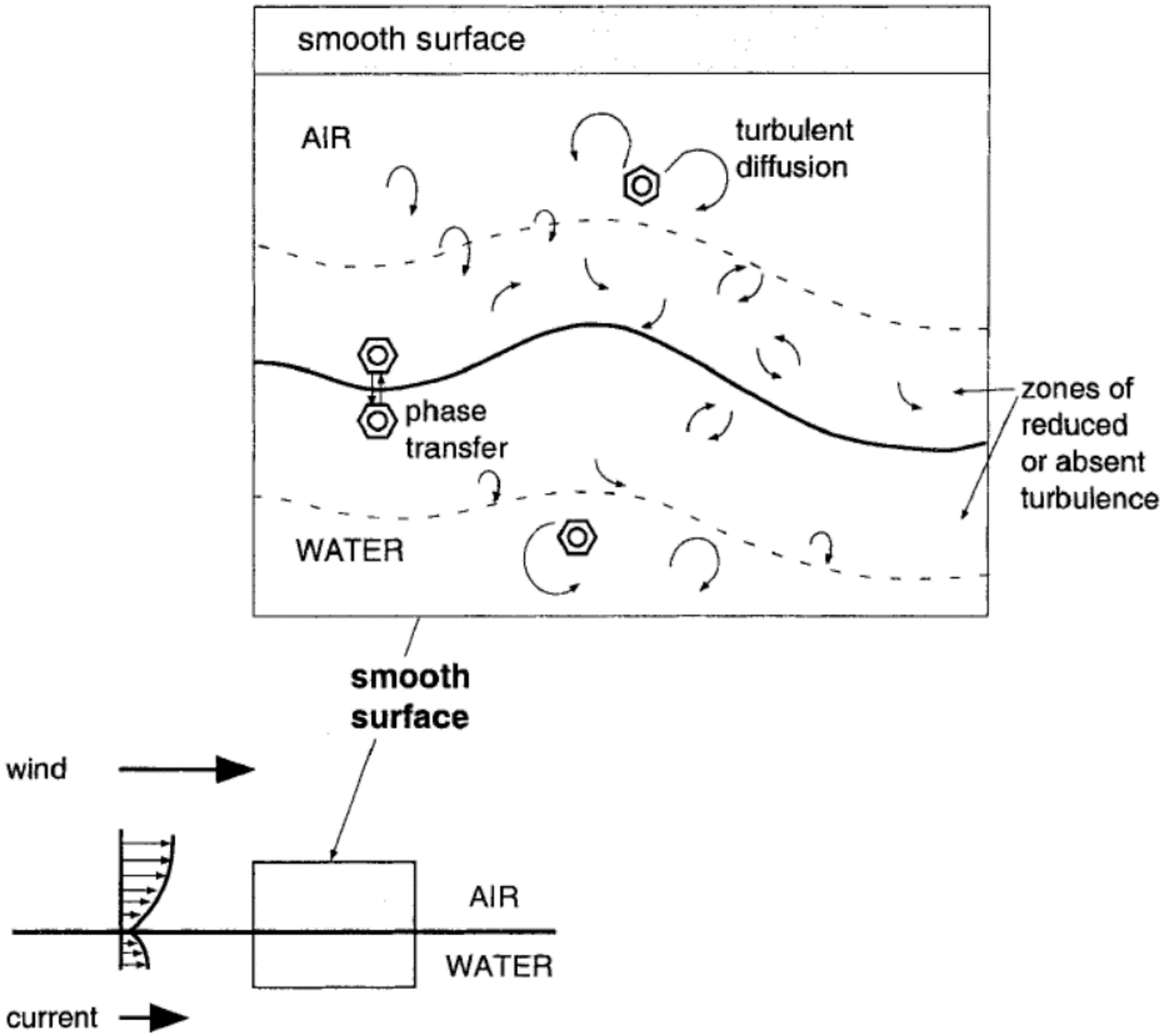
[b] **Simulation** results; used D_{O_2} (water) = 1.80×10^{-5} cm^2/s @ 20 ^oC.



Interphase mass transfer – D_i is not enough

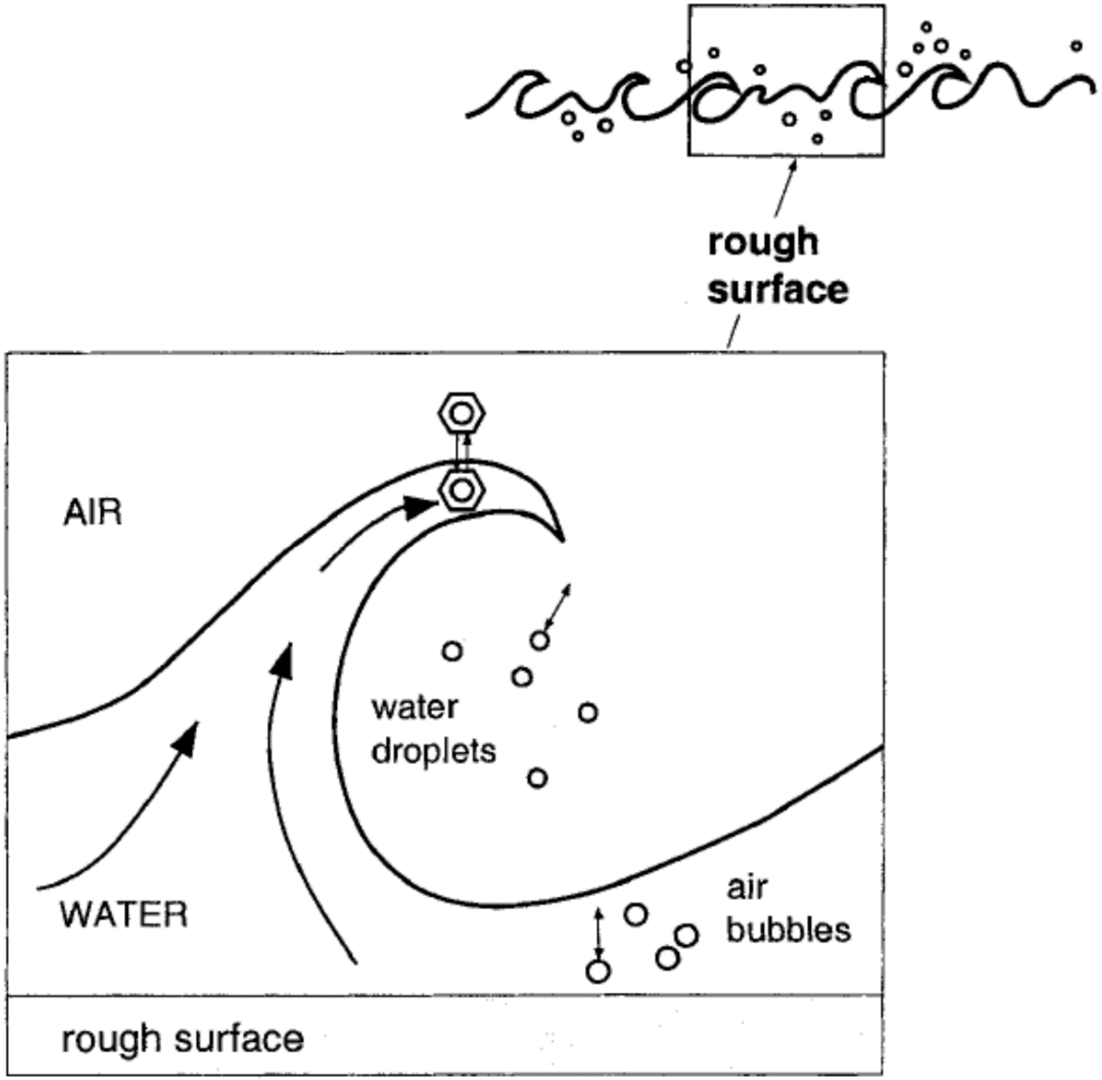
- **Observed air/water transfer rates are too fast to be explained by molecular diffusion across a flat interphase from/into a quiescent phase**
  - Regions where diffusion controls are very thin
    - Because of turbulence
  - Actual interfacial areas may be >> than nominal
    - Difficult to measure

Air/water interface: smooth



Source: EOC textbook, p. 907

Air/water interface: rough



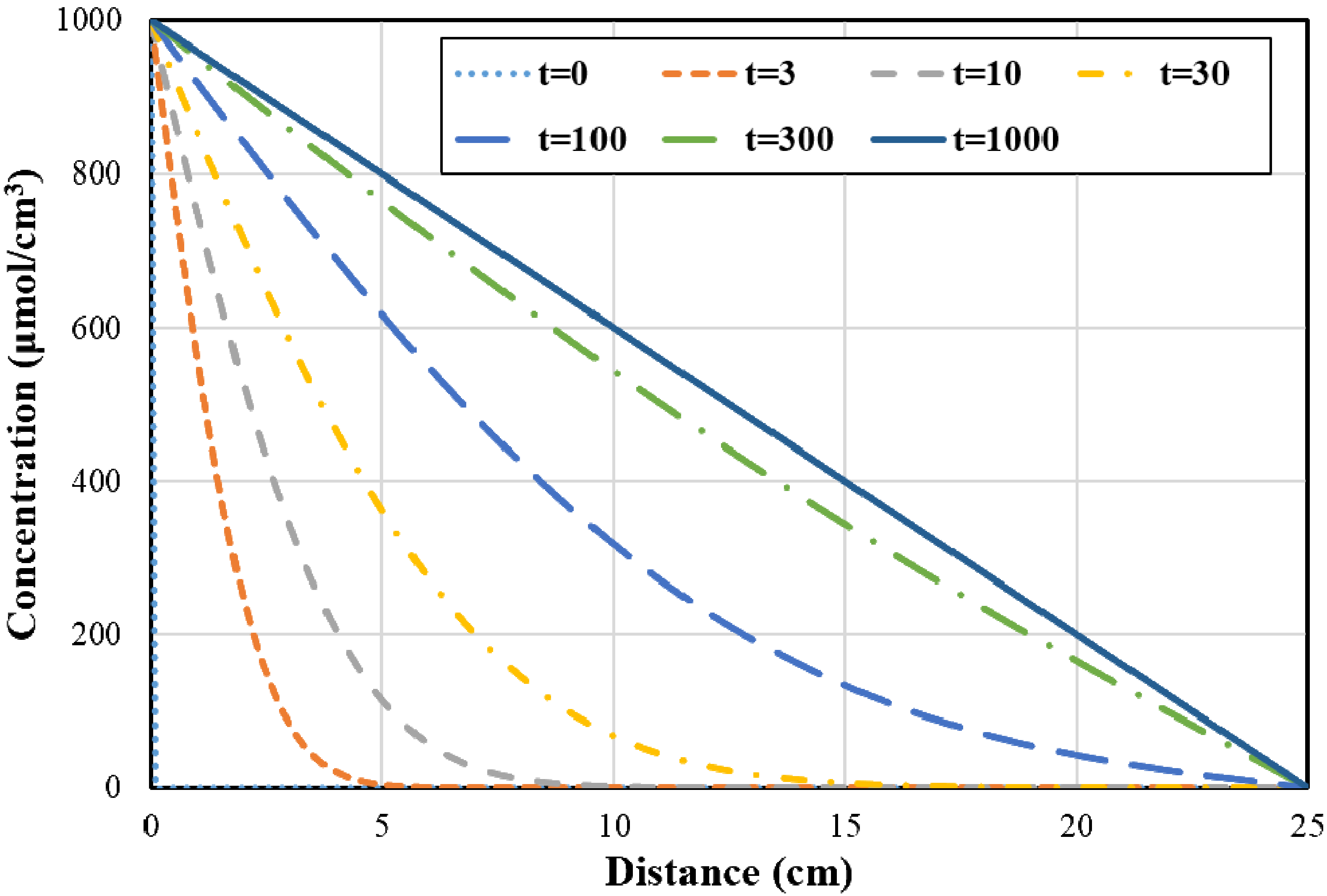
Source: EOC textbook, p. 907

Molecular diffusion – example 1

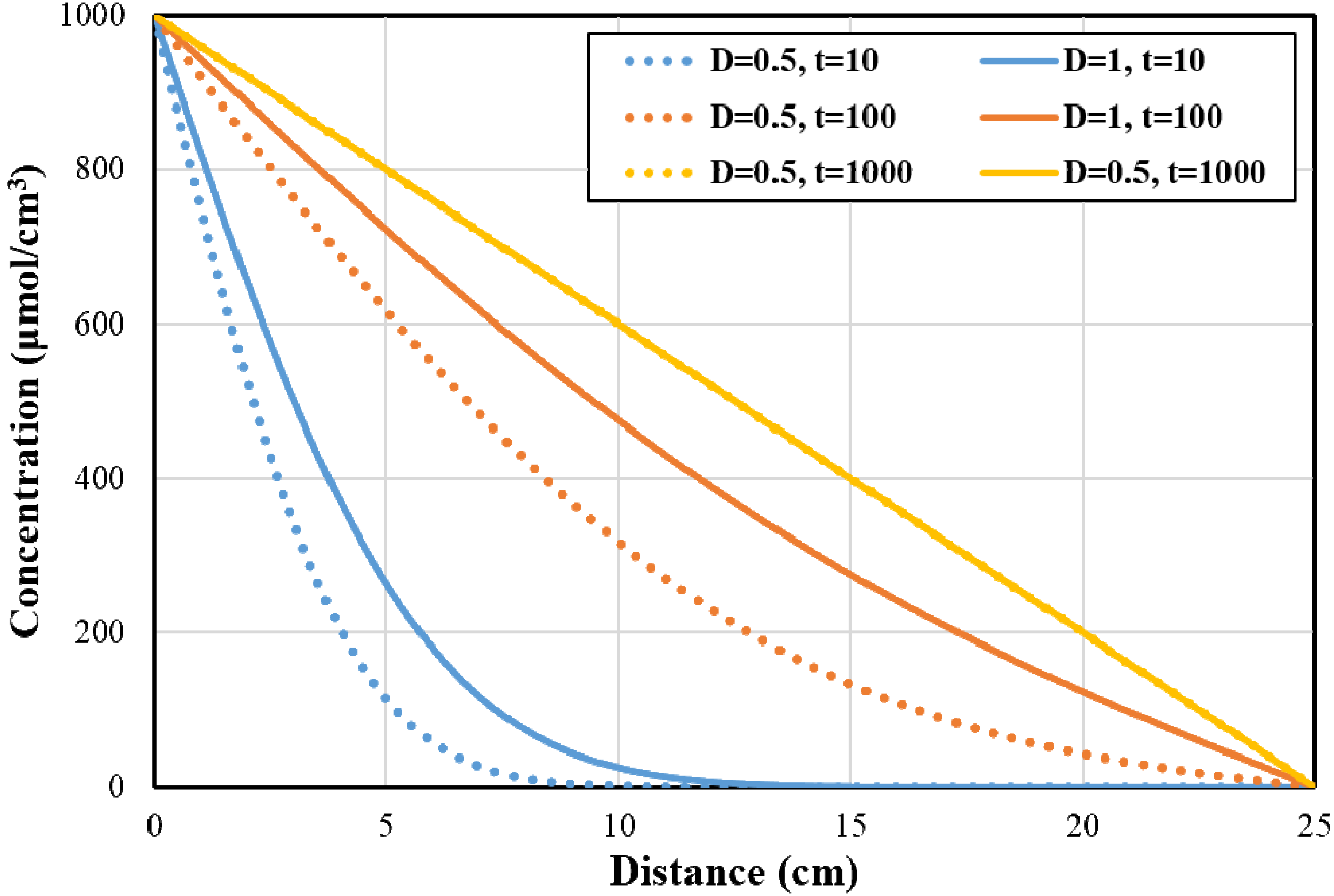
Let's consider model systems with:

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

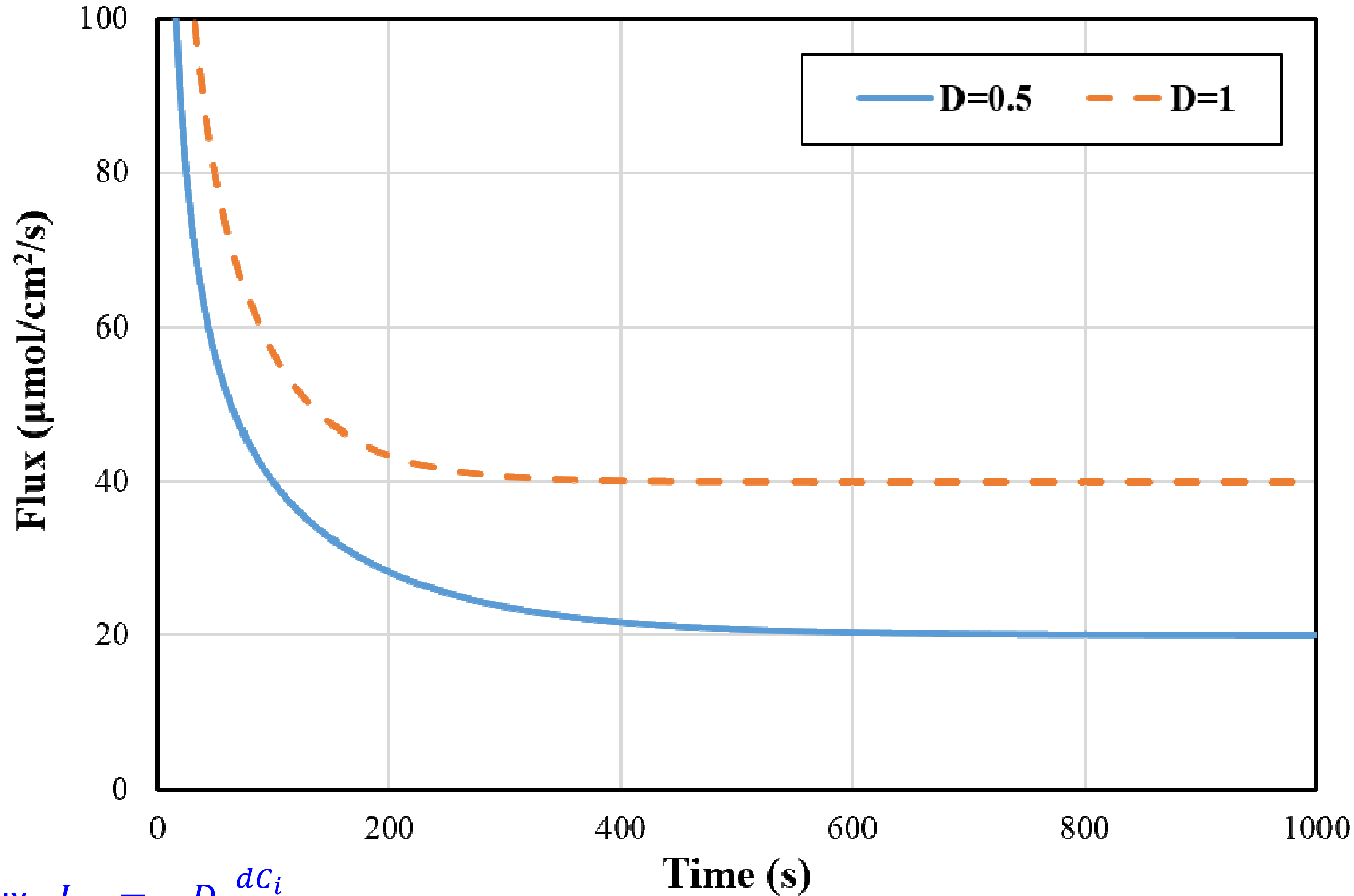
Concentration vs. Distance (1)



Concentration vs. Distance (2)

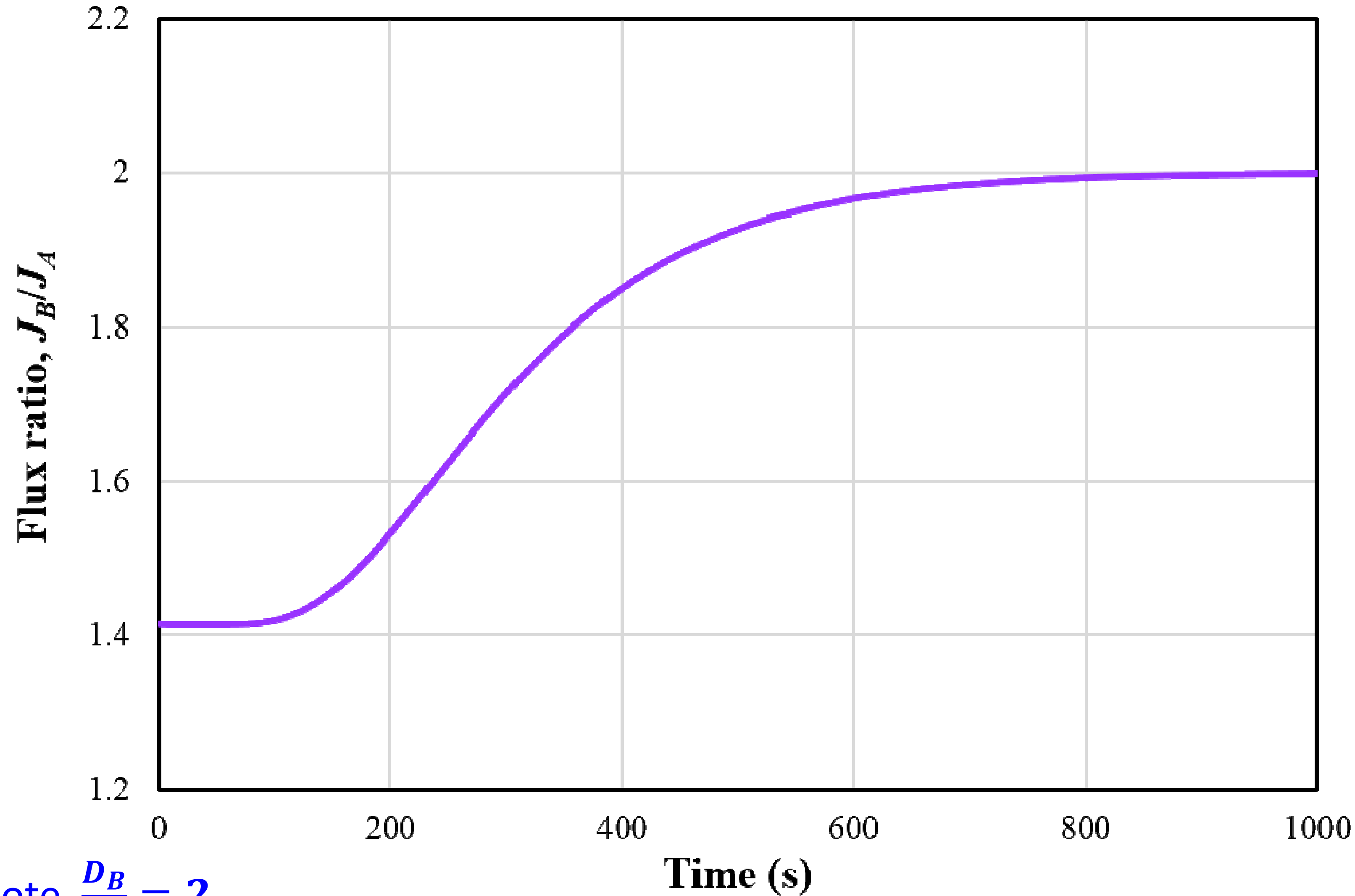


Flux (@ x = 0 cm) vs. Time



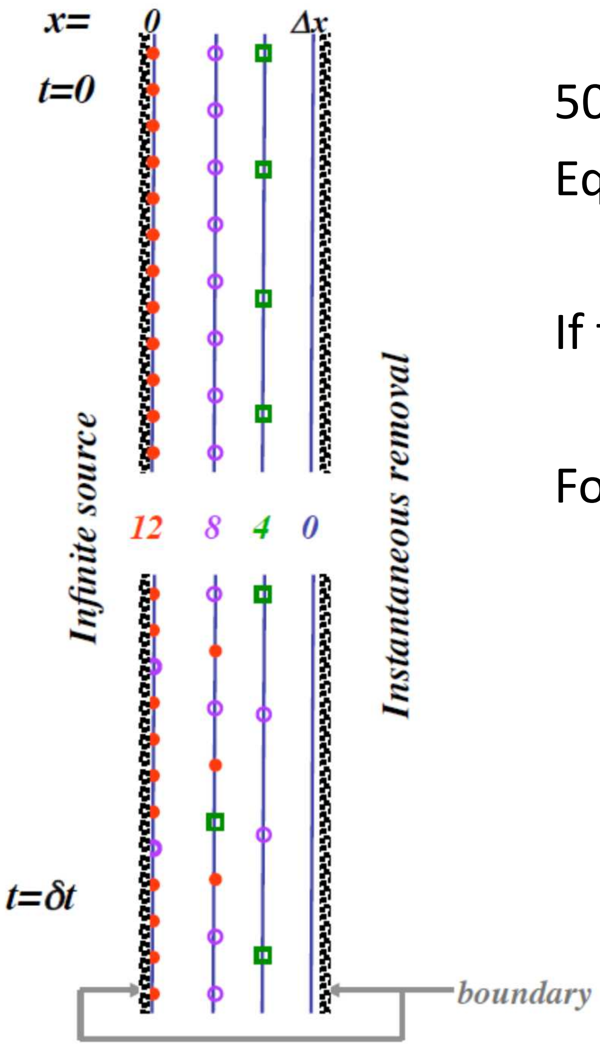
Flux, $J_{x,i} = -D_i \frac{dC_i}{dx}$

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



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

Molecular diffusion – example 2



50% of molecules shift position in time δt

Equal probability of shifting right or left

If this represents a unit area, then flux, J = 1/δt

For this case we are at steady state:

$$\left(\frac{\partial N}{\partial t}\right)_x = 0 \qquad \left(\frac{\partial N}{\partial x}\right)_t = \frac{12}{\Delta x}$$

Model system results

- **Initially**
  - Concentration profile changes rapidly
  - Flux out changes rapidly
  - System with high D → concentration gradient decreases faster at the outlet

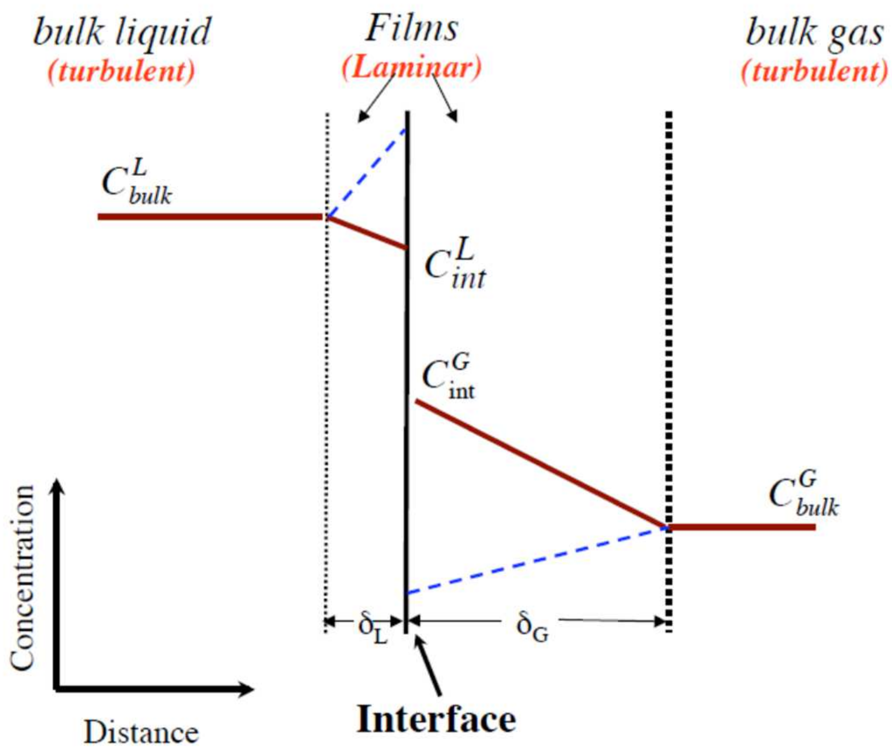
$$J_{in} \neq J_{out} \qquad \frac{J_B}{J_A} = \sqrt{\frac{D_B}{D_A}}$$

- **After a long time**
  - Linear concentration profile

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

Gas/liquid interfaces: film theory

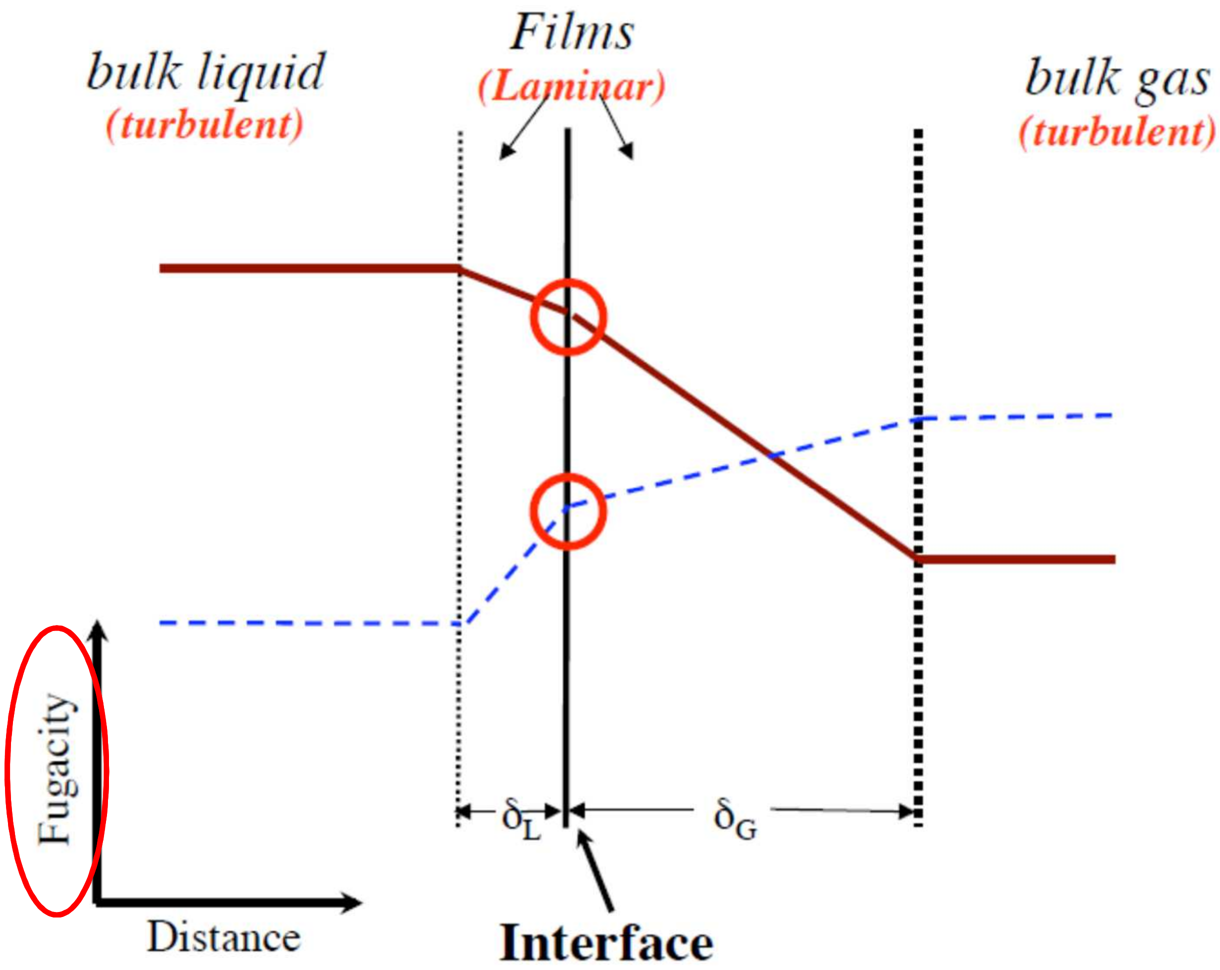
Transport is from high fugacity to low fugacity



Assumptions

- $C_{int}{}^G = H_{cc} \cdot C_{int}{}^L$
  (equilibrium at the interface)
- $|J_G| = |J_L|$
  (No accumulation at the interface)
- "Permanent" films developed
- Sufficient time for linear conc. gradients to develop in each film
- Changes in C_{bulk} are slow compared to gradient response rates

Gas/liquid interfaces: film theory



Gas/liquid interfaces: film theory

Flux in the films for phase *i*:

$$J_i = \frac{D_i}{\delta_i}\left(C_{bulk}{}^{i} - C_{int}{}^{i}\right) = k_i\left(C_{bulk}{}^{i} - C_{int}{}^{i}\right)$$

(+) flux when bulk → interface

$k_i = D_i/\delta_i$, *mass transfer coefficient [L/T]*

Since $|J_G| = |J_L|$,

$$J_{tot} = k_L\left(C_{bulk}{}^{L} - C_{int}{}^{L}\right) = -k_G\left(C_{bulk}{}^{G} - C_{int}{}^{G}\right)$$

set (+) flux when liquid → gas

$$= k_G\left(H_{cc}C_{int}{}^{L} - C_{bulk}{}^{G}\right)$$

$k_L = D_L/\delta_L$, *mass transfer coefficient at the liquid film [L/T]*
$k_G = D_G/\delta_G$, *mass transfer coefficient at the gas film [L/T]*

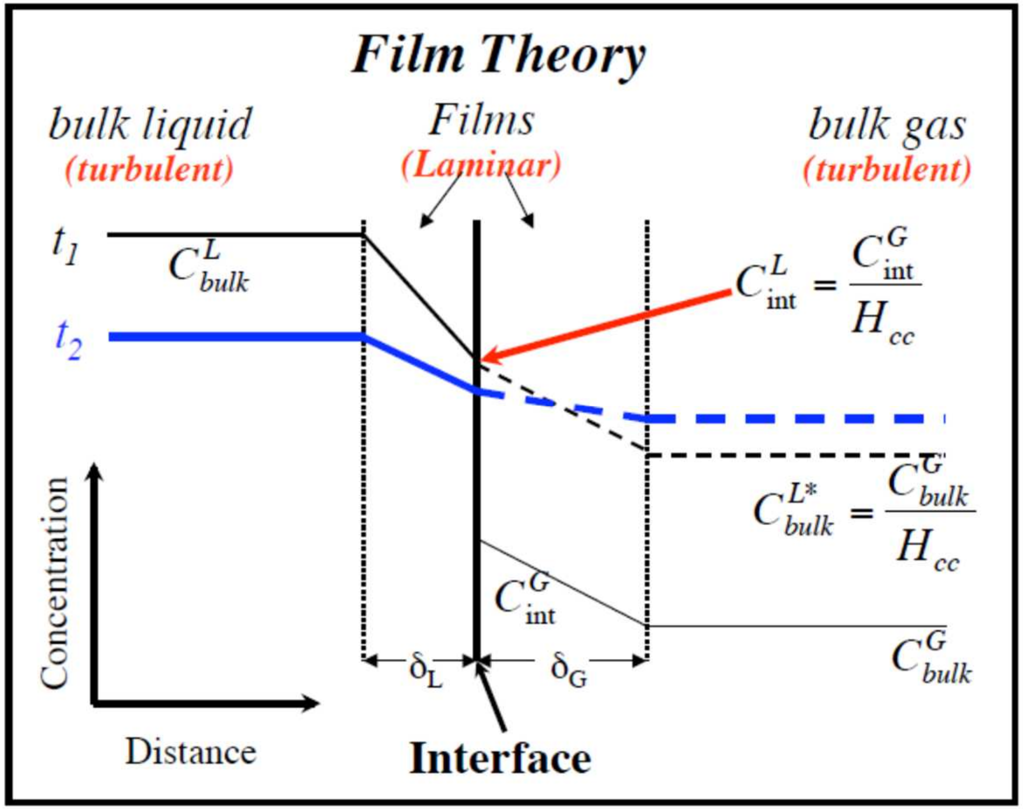
K_L – overall mass transfer coefficient

$$J_{tot} = K_L\left(C_{bulk}{}^{L} - \frac{C_{bulk}{}^{G}}{H_{cc}}\right) = K_L\left(C_{bulk}{}^{L} - C_{bulk}{}^{L*}\right)$$

Liquid phase as a reference

***"As Is"**: the current bulk liquid phase concentration*

***"To Be"**: the liquid phase concentration that would be in equilibrium with the current bulk gas phase concentration*



K_L – overall mass transfer coefficient

$$J_{tot} = K_L\left(C_{bulk}{}^{L} - \frac{C_{bulk}{}^{G}}{H_{cc}}\right)$$

$$= K_L\left\{\left(C_{bulk}{}^{L} - C_{int}{}^{L}\right) + \frac{1}{H_{cc}}\left(C_{int}{}^{G} - C_{bulk}{}^{G}\right)\right\}$$

$$\frac{1}{K_L} = \frac{k_L + k_G H_{cc}}{k_L k_G H_{cc}} = \frac{1}{k_L} + \frac{1}{k_G H_{cc}} = R_L + R_G = R_{tot}$$

The behavior is exactly analogous to having 2 resistors in series in an electric circuit

$$K_L = \frac{k_L k_G H_{cc}}{k_L + k_G H_{cc}}$$

Controlling resistance

$$R_{tot} = R_L + R_G = \frac{1}{k_L} + \frac{1}{k_G H_{cc}}$$

If $k_L \ll k_G H_{cc}$ *then* $R_L \gg R_G$*; liquid phase boundary layer controls flux*

Typically: $$1 < \frac{k_G}{k_L} < 300$$

Gas phase *D* >> liquid (by ~10^4)
Film thickness: $\delta_G > \delta_L$

If assume 95+% resistance equals phase control, & $k_G/k_L = 100$*, then:*

- $H_{cc} > 19$: *liquid phase control*
- $0.06 < H_{cc} \leq 19$: *maybe liquid phase control*
- $H_{cc} < 0.0002$: *gas phase control*
- $0.0002 < H_{cc} < 0.005$: *maybe gas phase control*
- $0.005 < H_{cc} < 5$: *probably affected by both phases*

Controlling resistance

Compound	H_{cc}	R_L/R_G	Controlling resistance
O_2	30	3000	Water
TCE	0.38	38	Water
Arochlor 1212	0.027	2.7	Intermediate
Lindane	1.4×10^{-4}	0.014	Gas
Phenol	3×10^{-5}	0.03	Gas
H_2O	2.2×10^{-5}	N/A	Gas

Assume $k_G/k_L = 100$ *for general estimation*

Film theory, summary, limitations

- **Assumes fully developed, time invariant interfacial regions**
  - Linear concentration gradient within the boundary layer
- **If resistance in one phase dominates, overall mass transfer resistance then**
  - $K_L \propto D_i$, *i = phase of dominant resistance*
- **Experimental studies have shown**
  - $K_L \propto {D_i}^a$
    - $0.5 \leq a \leq 1$
  - Film theory not always consistent with experimental data

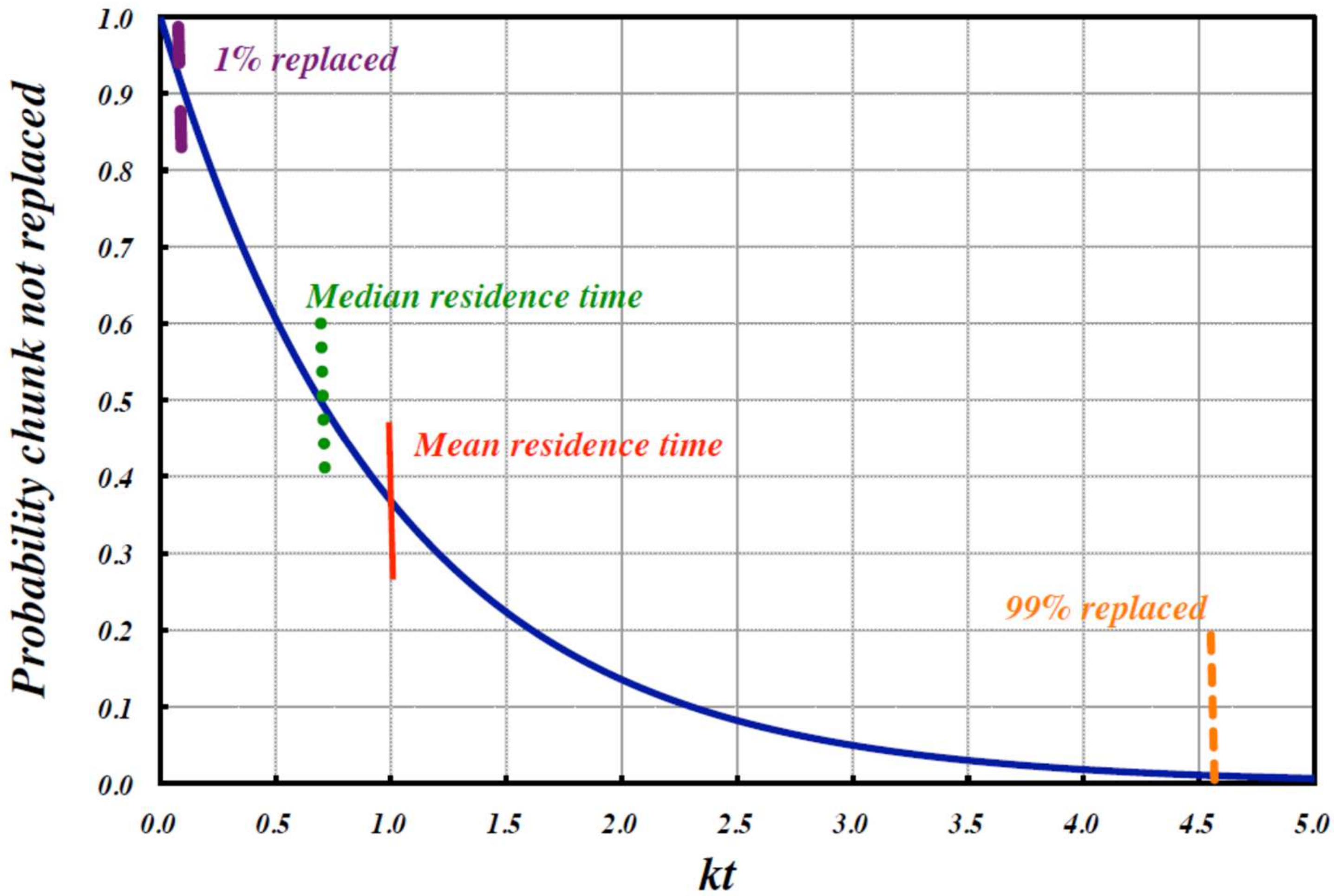
Surface renewal theory

- **Suppose turbulence goes all the way to the interface. Assume:**
  - Some fraction "s" of the N_0 surface "chunks" of water are replaced every unit of time, $\Delta t = 1$
  - The replacement of surface "chunks" is random

$$\frac{dN}{dt} = -sN \quad \Rightarrow \quad N_1 = N_0 e^{-st_1}$$

- N_1 represents the number of surface chunks not replaced at $0 \leq t \leq t_1$

Surface renewal: random replacement



Applying surface renewal theory

- **Flux equations still hold:**

$$J_{tot} = \pm J_i = \pm k_i\left({C_{bulk}}^i - {C_{int}}^i\right)$$

$$J_{tot} = K_L\left({C_{bulk}}^L - \frac{{C_{bulk}}^G}{H_{cc}}\right) = K_L\left({C_{bulk}}^L - {C_{bulk}}^{L*}\right)$$

$$\frac{1}{K_L} = \frac{k_L + k_G H_{cc}}{k_L k_G H_{cc}} = \frac{1}{k_L} + \frac{1}{k_G H_{cc}} = R_L + R_G = R_{tot}$$

- **But** $\boldsymbol{k_i = (D_i s_i)^{0.5}}$

s_i = surface renewal rate, [T^{-1}]

cf. Film theory: $k_i \propto D_i$

Boundary layer theory

- **The Sherwood number:**

$$(Sh)_i = \frac{k_i d}{D_i} = a_1 + a_2 (Re)^{a_3} (Sc)_i^{\,a_4}$$

D_i = molecular diffusion [L^2/T]
k_i = mass transfer coefficient [L/T]
d = characteristic length (particle diameter, stream depth, etc.)
a_j = constants, often empirical

Dimensionless numbers:

Re = Reynolds #, ratio of inertial force to viscous forces

Sc = Schmidt #, ratio of momentum diffusivity to mass diffusivity

Sh = Sherwood #, ratio of mass transport to mass diffusivity

- Mathematical form analogous to momentum and heat transfer models
- Incorporates effects of mixing on mass transfer

Dimensionless numbers

- **Used in fluid mechanics to predict system behavior**
  - Re: Reynolds #, ratio of inertial force to viscous force

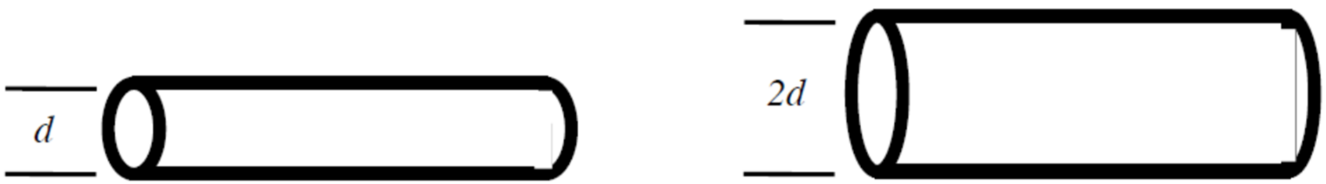
$$Re = \frac{d \times u}{\nu} = \frac{d \times u \times \rho}{\mu}$$

velocity x density = inertial force

viscosity

d = characteristic length
u = velocity [L/T]
ν = kinematic viscosity [L^2/T]
μ = dynamic viscosity [M/L-T]

  - Low Re: laminar flow; High Re: turbulent flow
- For pipe flow
  - $Re_{2d} = Re_d$ if $u_d = 2u_{2d}$



Boundary layer theory: coefficients

$$\frac{k_i d}{D_i} = (Sh)_i = a_1 + a_2 (Re)^{a_3} (Sc)_i^{a_4}$$

$$Re = \frac{d \times u}{\nu} = \frac{d \times u \times \rho}{\mu}$$

$$(Sc)_i = \frac{\nu}{D_i} = \frac{\mu}{D_i \rho}$$

If a_1 = 0, then:

$$k_i = \frac{(Sh)_i D_i}{d} = \frac{a_2 (Re)^{a_3} (\nu)^{a_4} D_i^{1-a_4}}{d} = a_2 d^{(a_3-1)} u^{a_3} \nu^{(a_4-a_3)} D_i^{(1-a_4)}$$

a_2: 0.01 to 1.0

a_3: 0.33 (laminar flow) to 0.8 (turbulent flow)

a_4: 0 to 0.5 (~0.33 is common)

a_3 = 0.33; a_4 = 0.5

$$k_i = a_2 d^{-0.67} u^{0.33} \nu^{0.17} D_i^{0.5}$$

a_3 = 0.8; a_4 = 0.33

$$k_i = a_2 d^{-0.2} u^{0.8} \nu^{-0.47} D_i^{0.67}$$

Flux to concentration change (in water)

$$J_{tot} = -K_L\left(C_{bulk}{}^{L} - C_{bulk}{}^{L*}\right)$$

Flux rate per unit area

$$A \cdot J_{tot} = -K_L \cdot A\left(C_{bulk}{}^{L} - C_{bulk}{}^{L*}\right)$$

Total flux (A is area of air-water interface)

$$\frac{dC_{bulk}{}^{L}}{dt} = \left(\frac{A}{V}\right)J_{tot} = -K_L\left(\frac{A}{V}\right)\left(C_{bulk}{}^{L} - C_{bulk}{}^{L*}\right) = -K_L a\left(C_{bulk}{}^{L} - C_{bulk}{}^{L*}\right)$$

This is the rate of change in concentration in water

a = interfacial area for mass transfer per unit volume, A/V [L^{-1}]

V = volume in which concentration is changing [L^{3}]

$K_L a$ = volumetric mass transfer coefficient [T^{-1}]

Mass transfer example: change in stream DO

Studies of **oxygen reaeration in streams** have been reasonably fit by the following:
(O'Connor & Dobbins, 1958)

$$K_L = \left(\frac{D_L u}{H}\right)^{0.5} = k_L$$

$$K_L a = \frac{(D_L u)^{0.5}}{H^{1.5}}$$

u = stream velocity, m/s

$H = 1/a$ = average stream depth, m

D_L = liquid phase diffusivity, m^2/s

Mass transfer example: change in stream DO

- Applying surface renewal model:
  - O'Connor and Dobbins hypothesized that

$$s_L = \frac{Avg.\,vertical\ velocity\ by\ turbulence}{Avg.\,mixing\ length} = \frac{0.1u}{0.1H} = \frac{u}{H}$$

  - Therefore,

$$K_L \approx k_L = (D_L s_L)^{1/2} = \left(\frac{D_L u}{H}\right)^{1/2}$$

Mass transfer example: change in stream DO

- Applying boundary layer theory:

$$k_L = \frac{(Sh)_L D_L}{d} = \frac{a_2 (Re)^{a_3} (\nu)^{a_4} {D_L}^{1-a_4}}{d} = a_2 d^{(a_3-1)} u^{a_3} \nu^{(a_4-a_3)} {D_L}^{(1-a_4)}$$

If a_2 = 1.0; a_3 & a_4 = 0.5:

$$K_L \approx k_L = \left(\frac{D_L u}{d}\right)^{0.5}$$

Boundary layer theory: applications

Transfer to particle surface in stagnant fluid:

$$\frac{k_L d}{D_L}(Sh)_L = a_1 + a_2(Re)^{a_3}(Sc)_L{}^{a_4}$$

$$Re = \frac{d \times u}{\nu} = \frac{d \times u \times \rho}{\mu}$$

$$(Sc)_L{}^{a_4} = \frac{\nu}{D_L} = \frac{\mu}{D_L \rho}$$

Here, $a_1 = 2$

$$k_L = \frac{2D_L}{d_p} = \frac{D_L}{r_p} \approx \frac{1 \times 10^{-9}}{r_p}\ m/sec$$

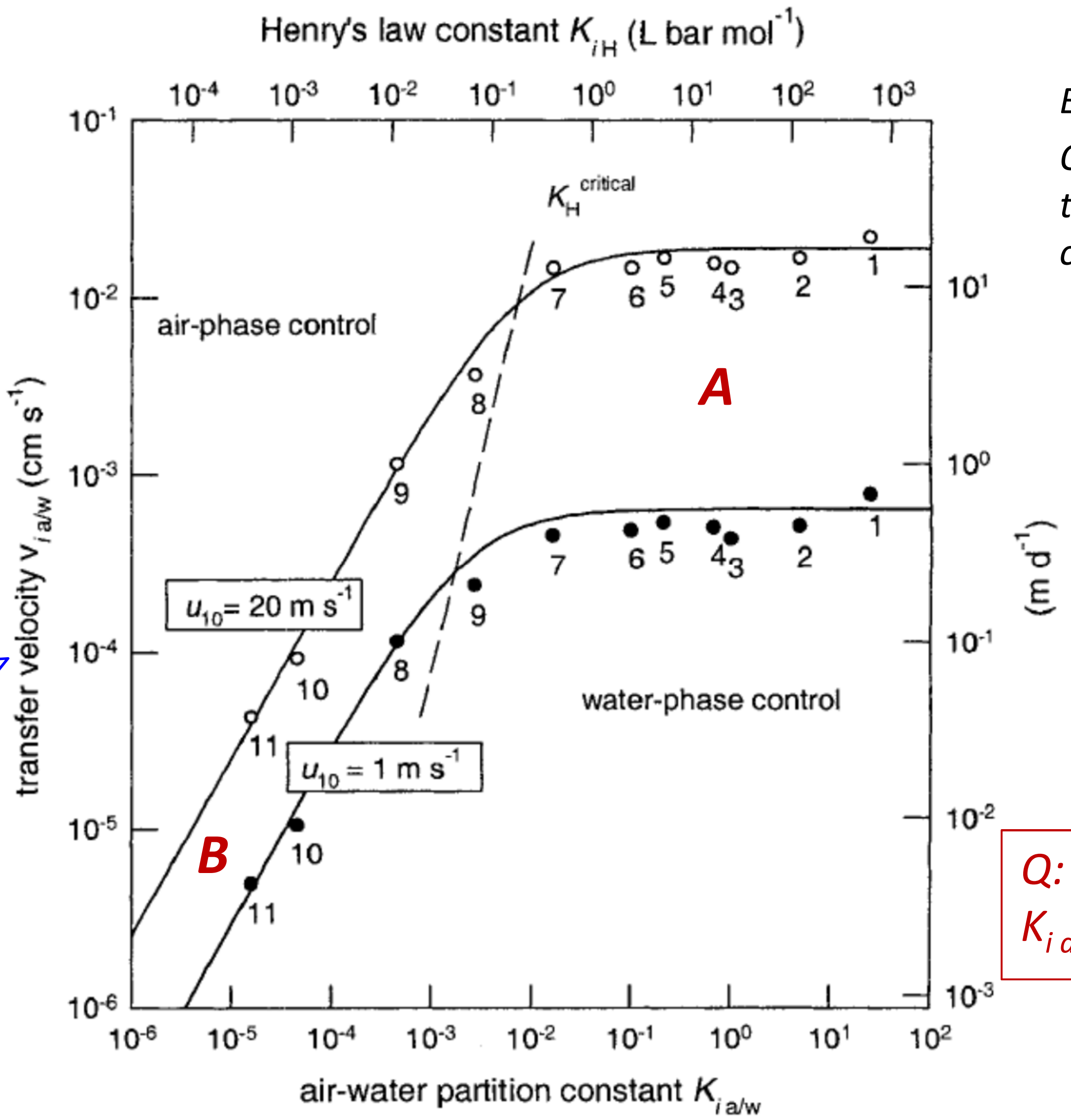
$$a = \frac{area}{volume} = \frac{6}{d_p}\ m^{-1}$$

If resistance is dominant at liquid phase,

$$K_L a \approx k_L a \approx \frac{10^{-8}}{d_p{}^2}\ sec^{-1}$$

Equilibration time can be characterized by $1/k_L a$

Wind effects on mass transfer



mass transfer coeff. has unit of [L/T]; sometimes called as velocity

EOC text Fig. 20.7

Overall mass transfer coeff. gor two very different wind conditions

Q: Why is $v_{i\,a/w}$ a function of $K_{i\,a/w}$ (=H_{cc}) at B but not at A?

Mass transfer summary

- **Molecular diffusion important over short lengths**
  - Thin, stagnant regions at interphases
  - Turbulence critical at macroscopic levels
    - Mixing within phase
    - Generating interfacial surfaces
- **Three models**
  - Differing versions of the interfacial region
    - Difficult/impossible to directly measure region
    - Infer interfacial region properties from experimental data
    - Models differ in molecular diffusion's impact on overall mass transfer
- **For many compounds mass transfer resistance in one phase controls overall mass transfer rate**