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

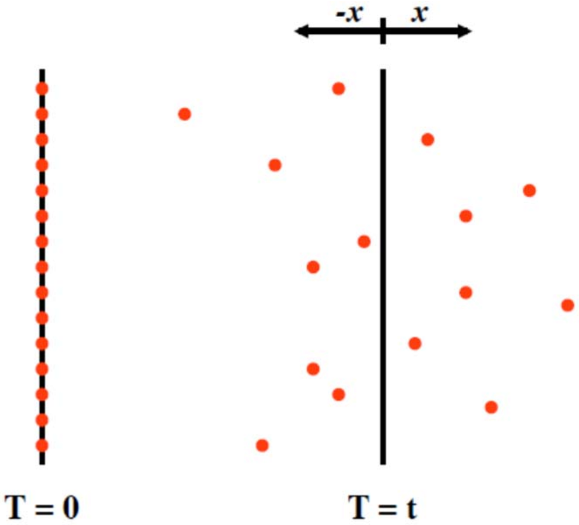
- **A consequence of random behavior, motion**

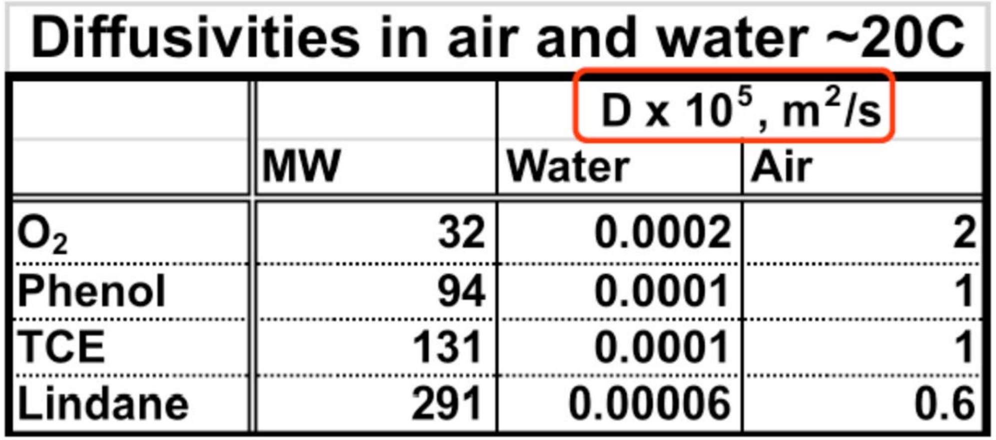
Molecular diffusion

- **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 $J_{x,i}$





Diffusivities in air and water ~20C

		D x 10^5, m^2/s	
	MW	Water	Air
O_2	32	0.0002	2
Phenol	94	0.0001	1
TCE	131	0.0001	1
Lindane	291	0.00006	0.6

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

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

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

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

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

Carbon dioxide diffusion; water into air

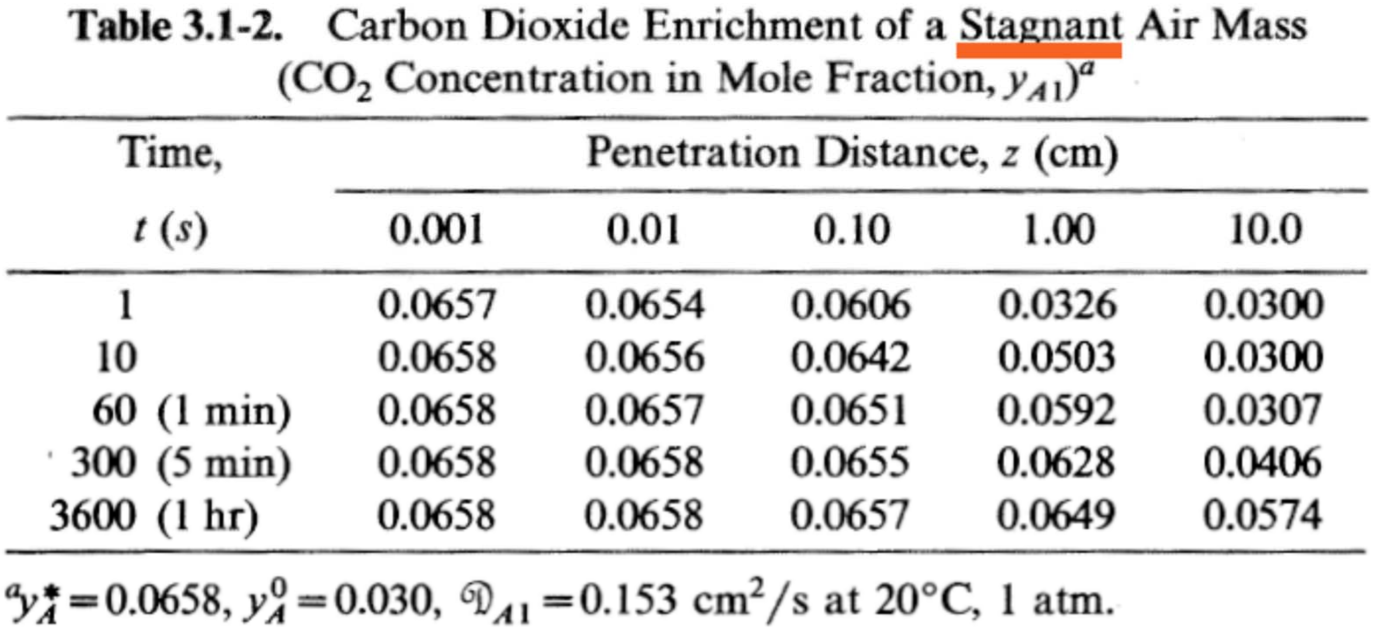


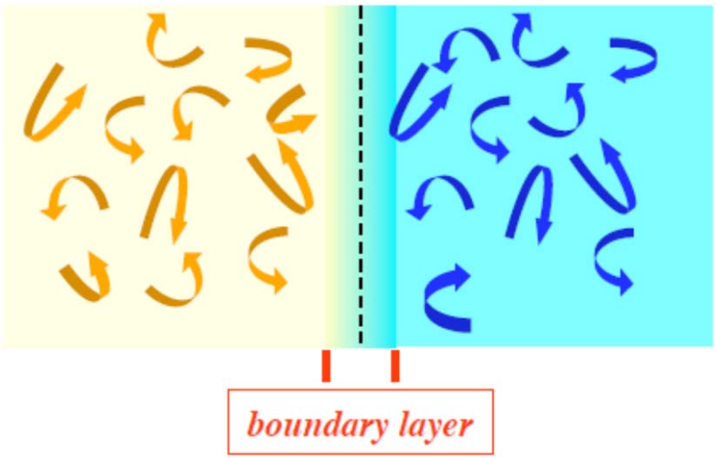
Table 3.1-2. Carbon Dioxide Enrichment of a Stagnant Air Mass (CO_2 Concentration in Mole Fraction, y_{A1})[a]

Time, t (s)	Penetration Distance, z (cm) 0.001	0.01	0.10	1.00	10.0
1	0.0657	0.0654	0.0606	0.0326	0.0300
10	0.0658	0.0656	0.0642	0.0503	0.0300
60 (1 min)	0.0658	0.0657	0.0651	0.0592	0.0307
300 (5 min)	0.0658	0.0658	0.0655	0.0628	0.0406
3600 (1 hr)	0.0658	0.0658	0.0657	0.0649	0.0574

[a] $y_A^* = 0.0658$, $y_A^0 = 0.030$, $\mathcal{D}_{A1} = 0.153\ \text{cm}^2/\text{s}$ at 20°C, 1 atm.

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
    - Turbulence
  - Actual interfacial areas may be >> than nominal
    - Difficult to measure



Air/water interface

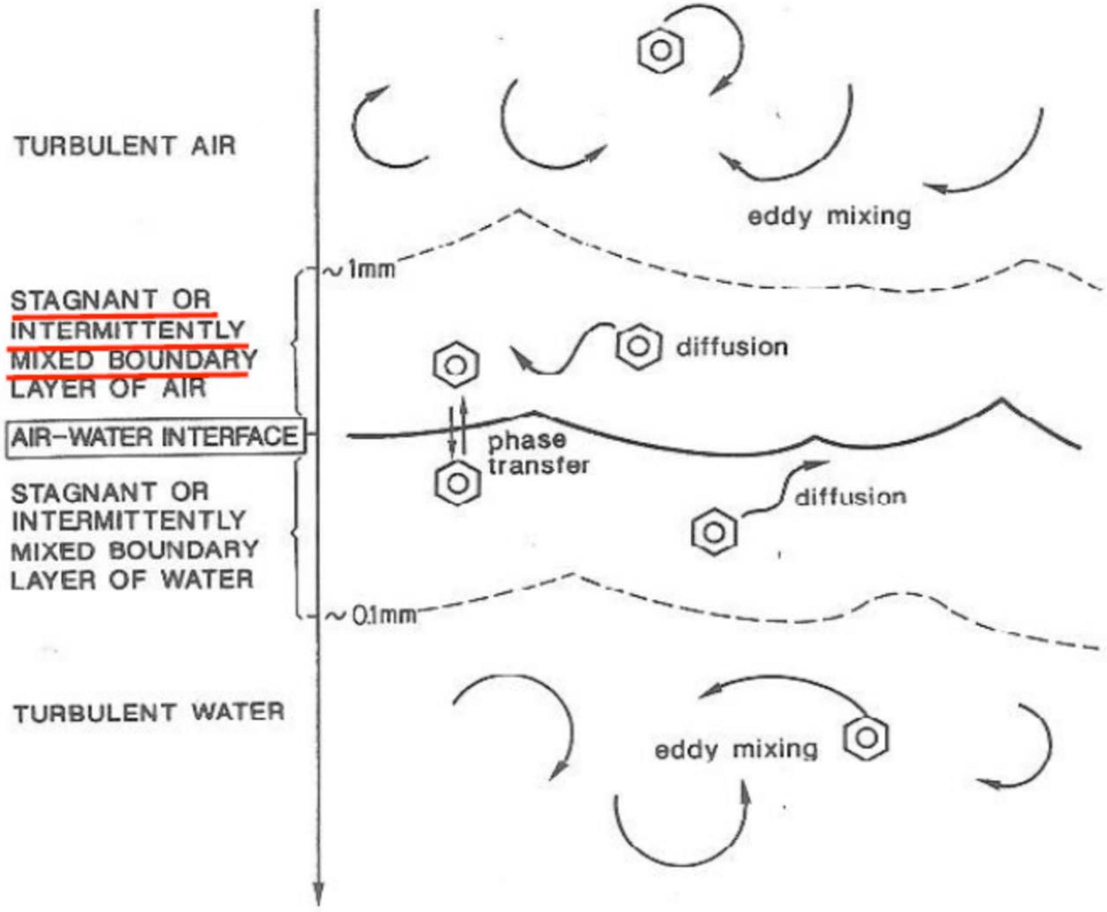


Figure 10.1 Depiction of the physical processes responsible for the movement of chemicals through four zones spanning an "intact" air–water interface (i.e., no bubbles or aerosols).

1 to 10 mm

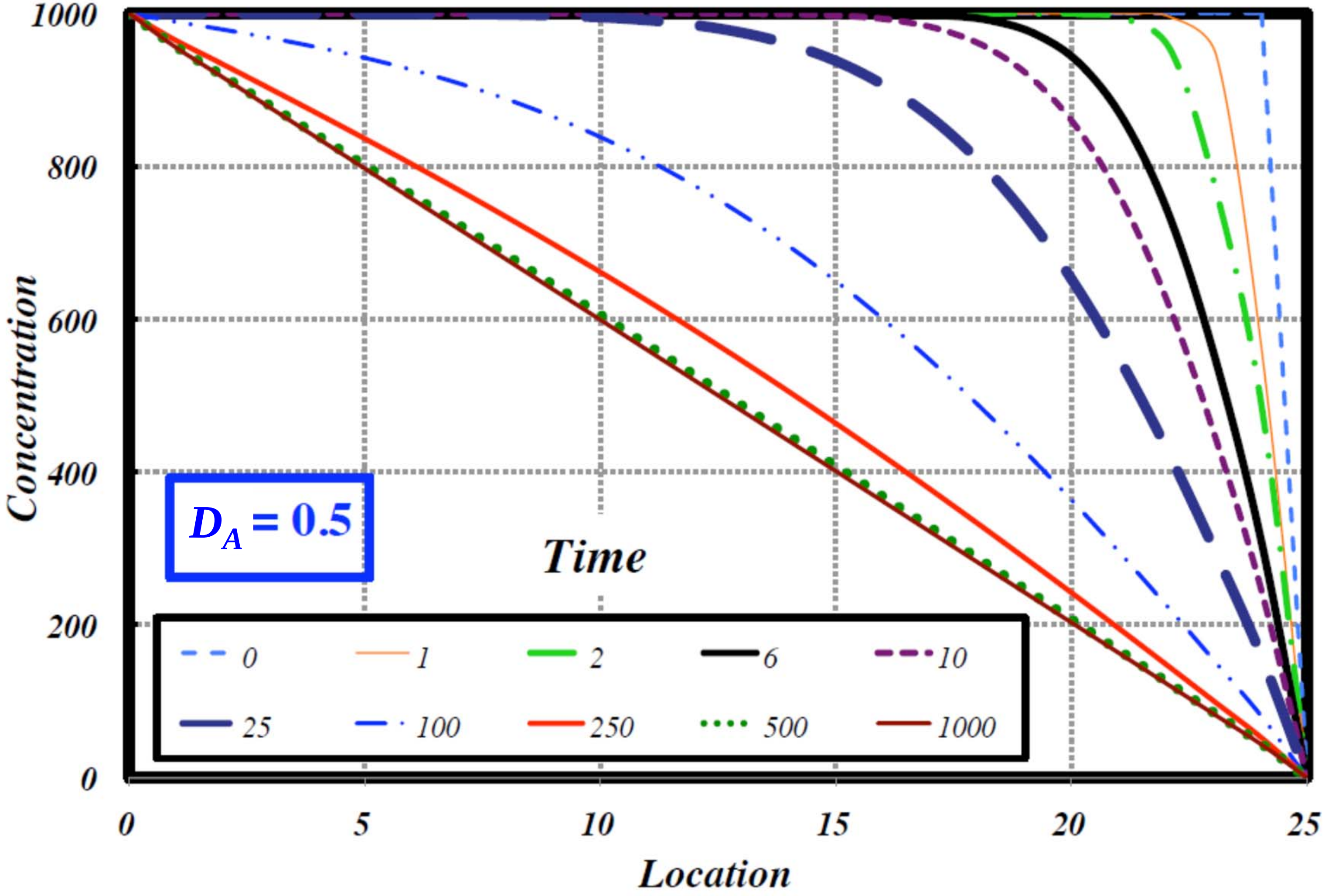
0.01 to 0.1 mm

Molecular diffusion – example 1

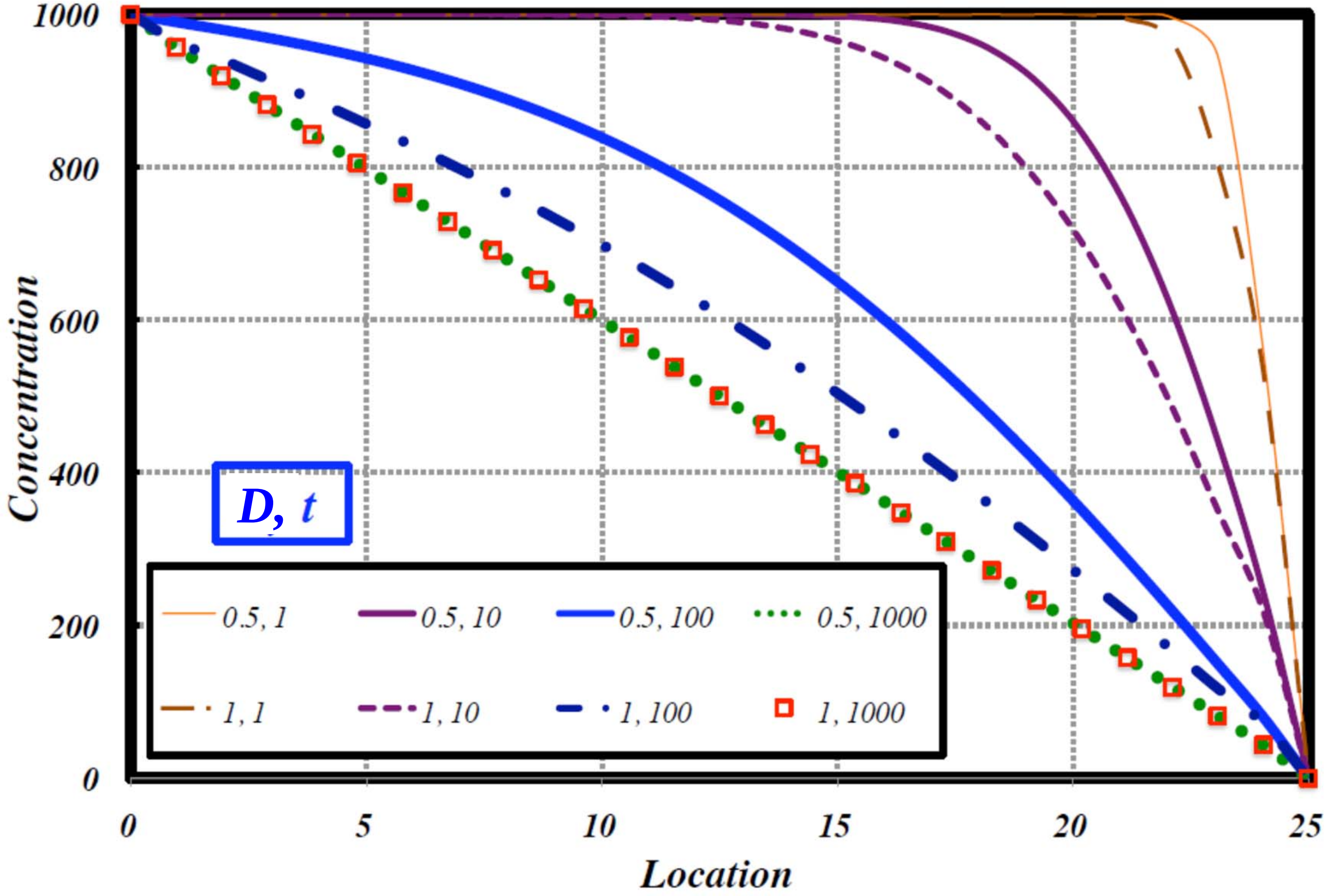
Let’s consider model systems with:

- 1-dimensional movement
- At t = 0
  - For $0 < x < 25$; Concentration (C) = 1000/unit volume
- At any t
  - For $x = 0$; $C = 1000$
  - For $x = 25$; $C = 0$
    - At boundaries there is continuous replenishment/scavenging
- For any time step
  - System A: $D_A = 0.5$
  - System B: $D_B = 1$

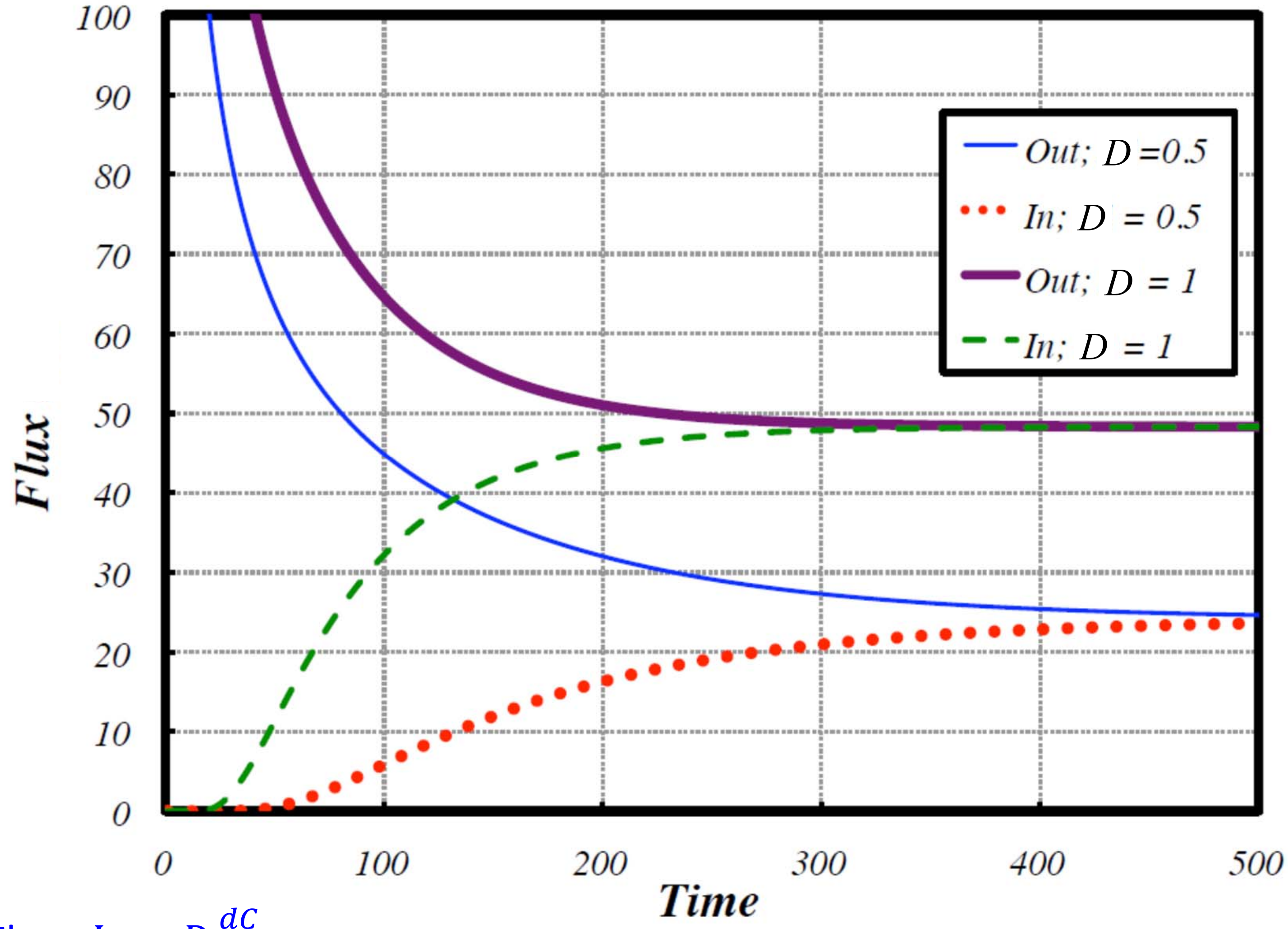
Entity distribution vs. time



Entity distribution vs. time & D

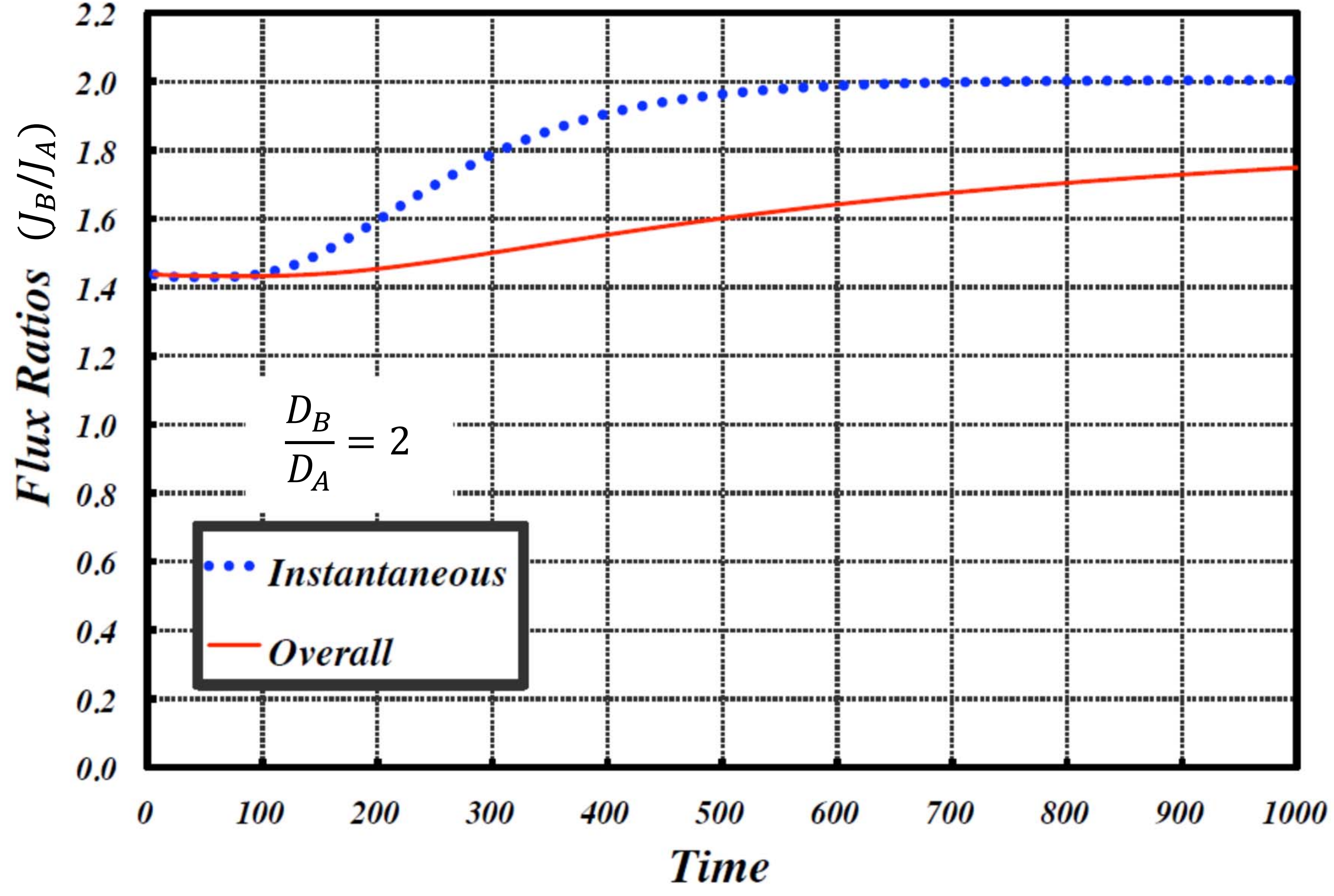


Flux vs. time

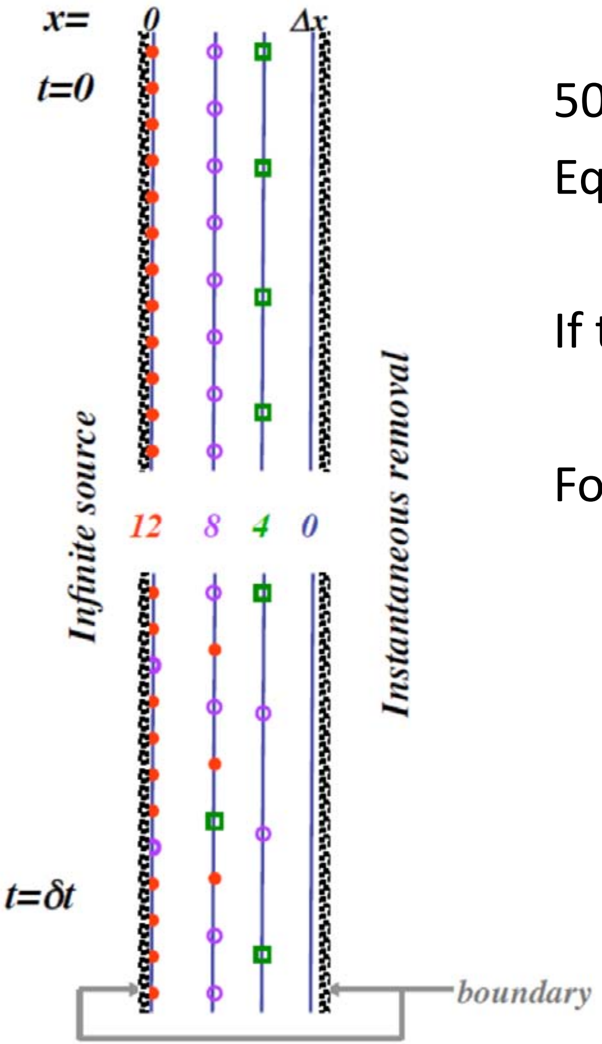


Flux, $J_x = D\frac{dC}{dx}$

Flux ratios at the outlet



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

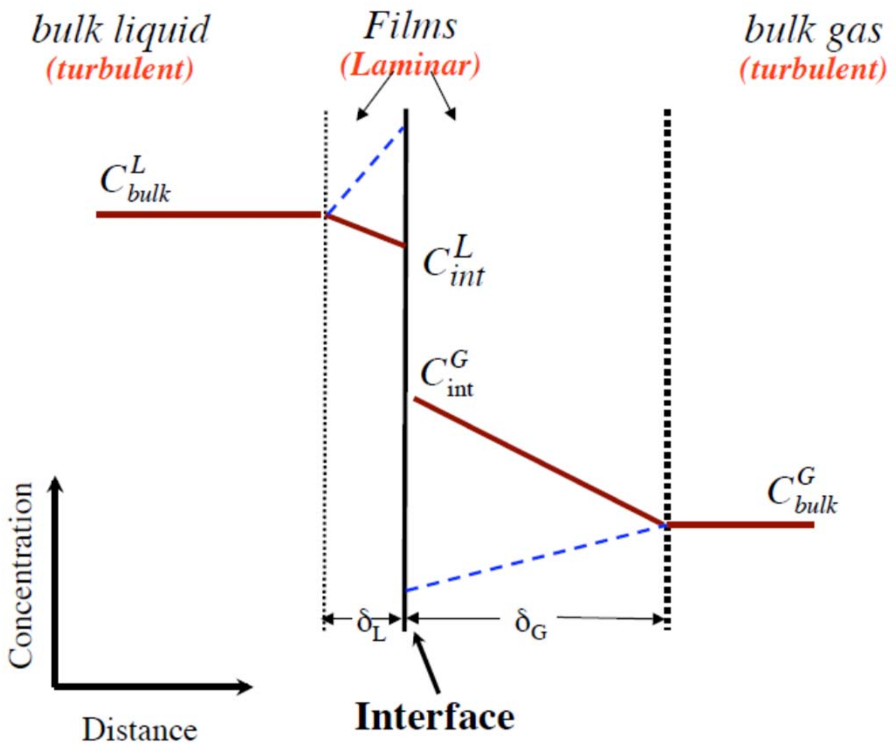
$$J_{in} \neq J_{out} \qquad \frac{J_B}{J_A} = \sqrt{\frac{D_B}{D_A}}$$

- **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



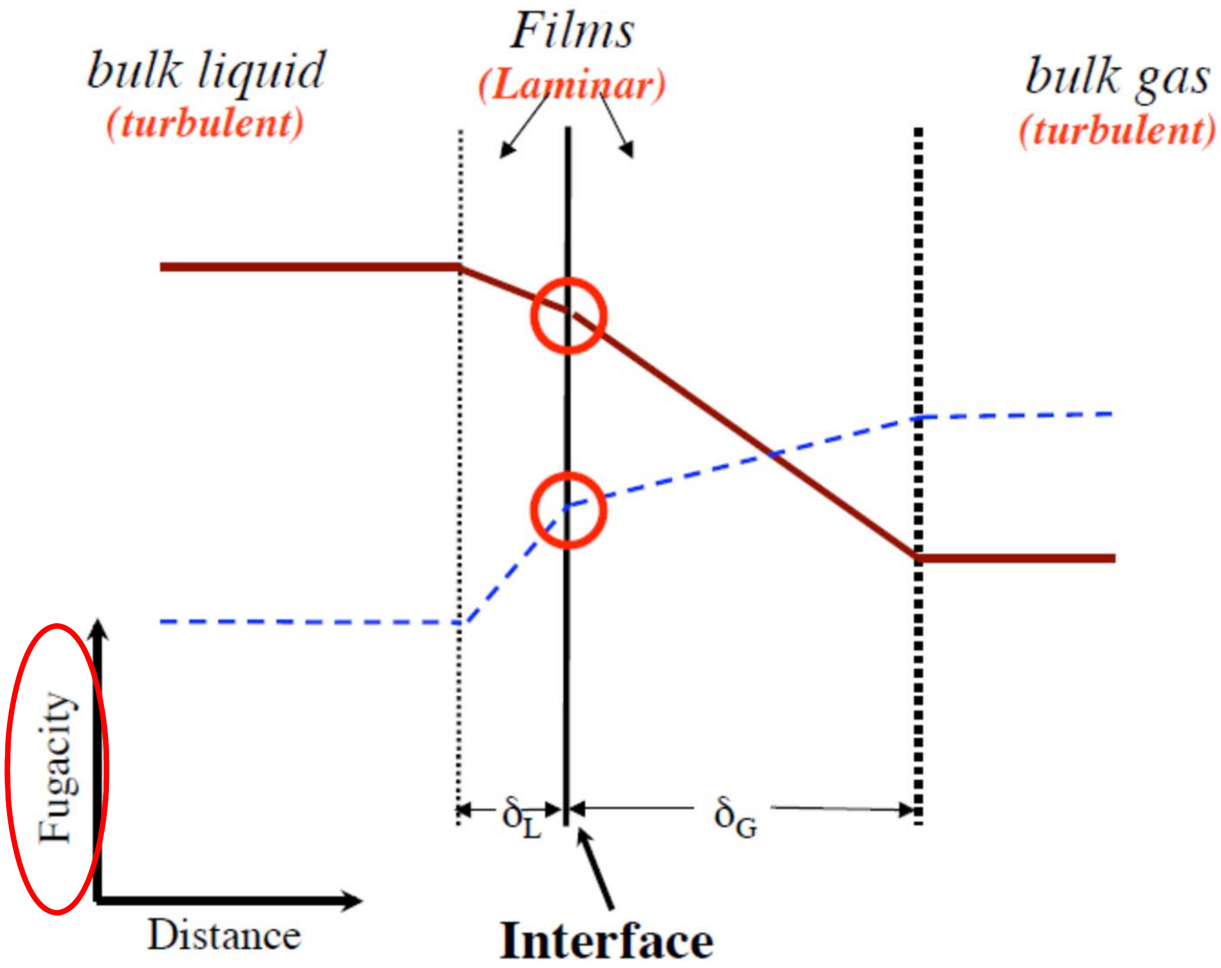
Assumptions

- $C_{int}{}^G = H_{cc} \cdot C_{int}{}^L$

  (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

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

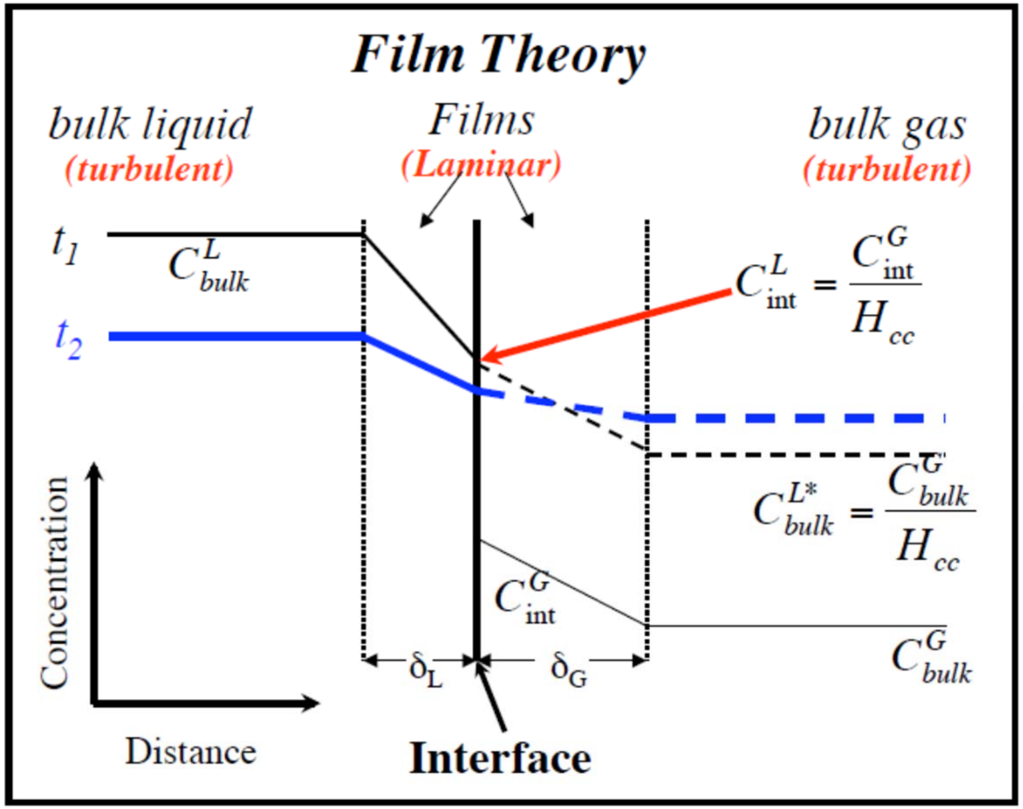
$k_L = D_L/\delta_L$, *mass transfer coefficient at the liquid film [L/T]*
$k_G = D_G/\delta_G$, *mass transfer coefficient at the gas film [L/T]*

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

This is the liquid phase concentration that would be in equilibrium with the actual 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

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

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*

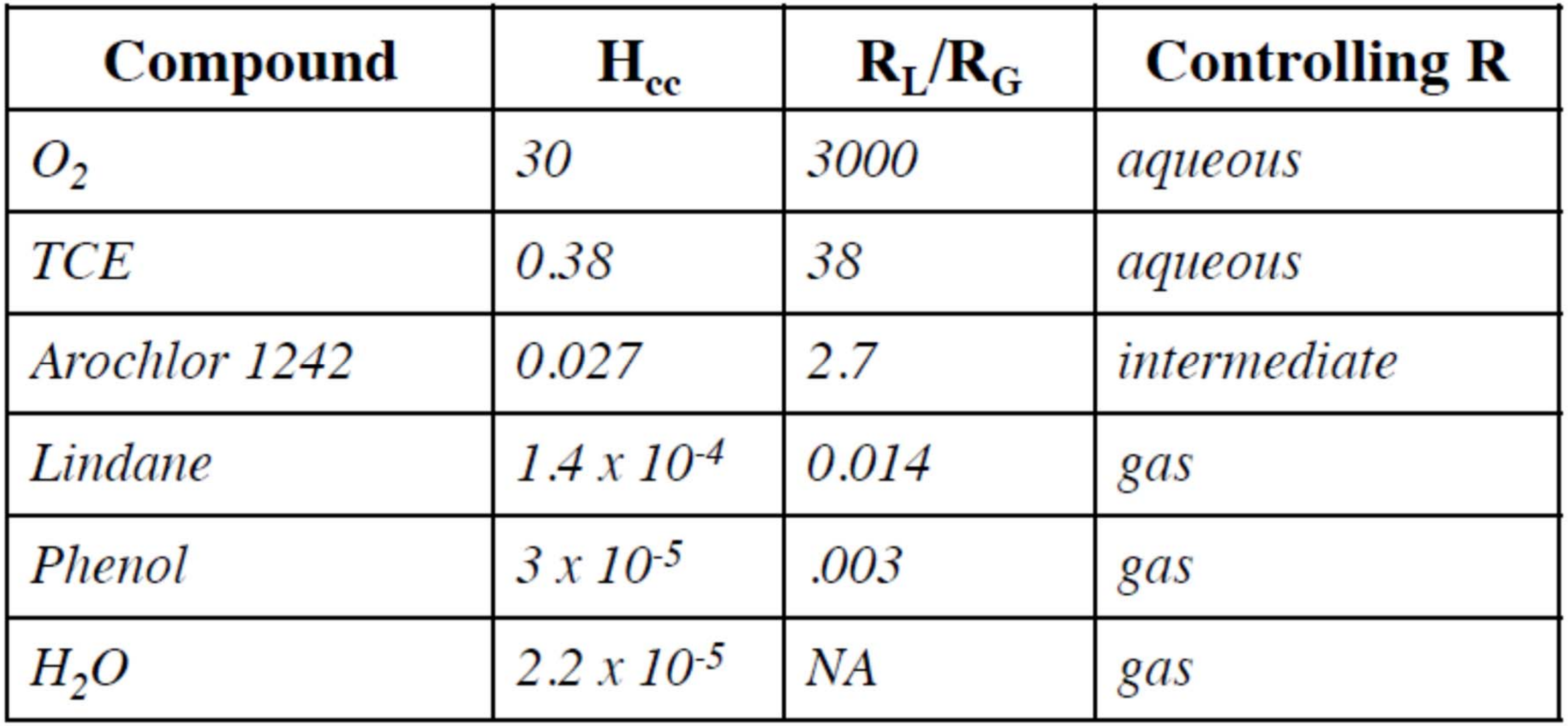
Typically: $1 < \frac{k_G}{k_L} < 300$

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 R
O_2	30	3000	aqueous
TCE	0.38	38	aqueous
Arochlor 1242	0.027	2.7	intermediate
Lindane	1.4×10^{-4}	0.014	gas
Phenol	3×10^{-5}	.003	gas
H_2O	2.2×10^{-5}	NA	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

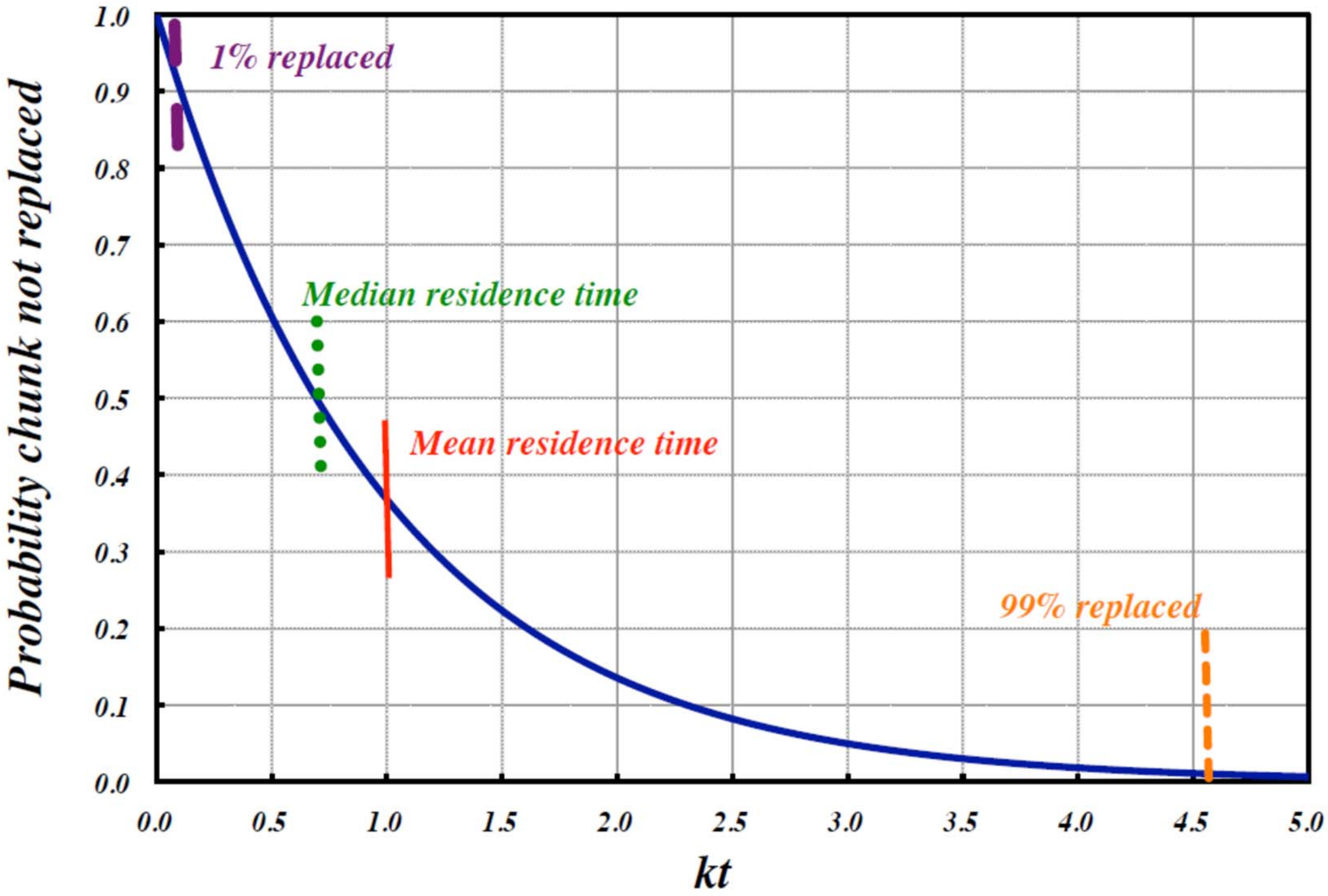
Surface renewal theory

- **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



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

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

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

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

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

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

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

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

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)

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

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)*

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

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

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:

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

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

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

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

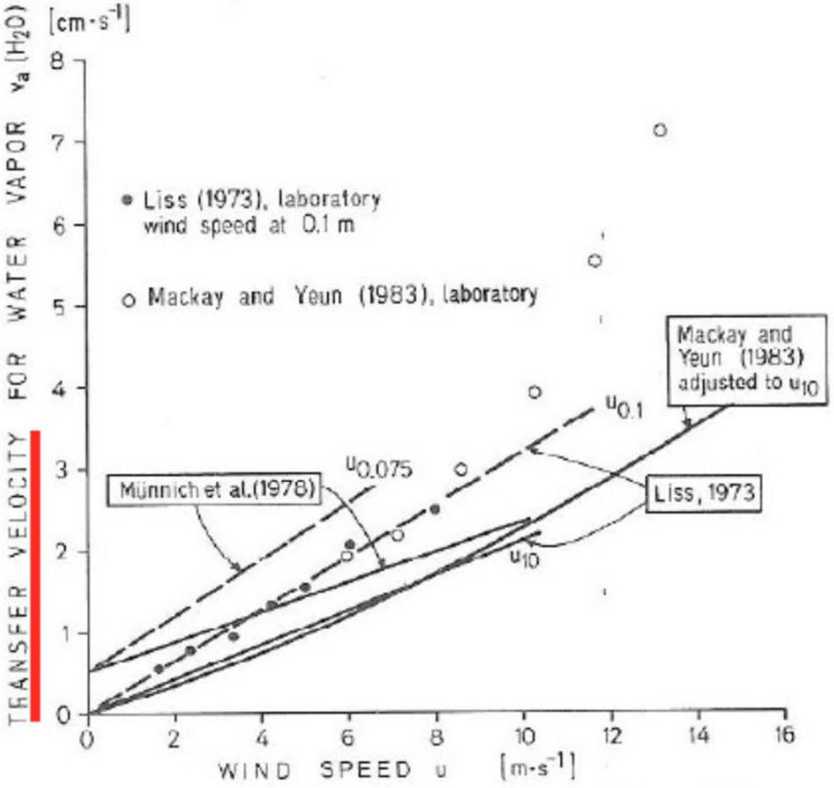
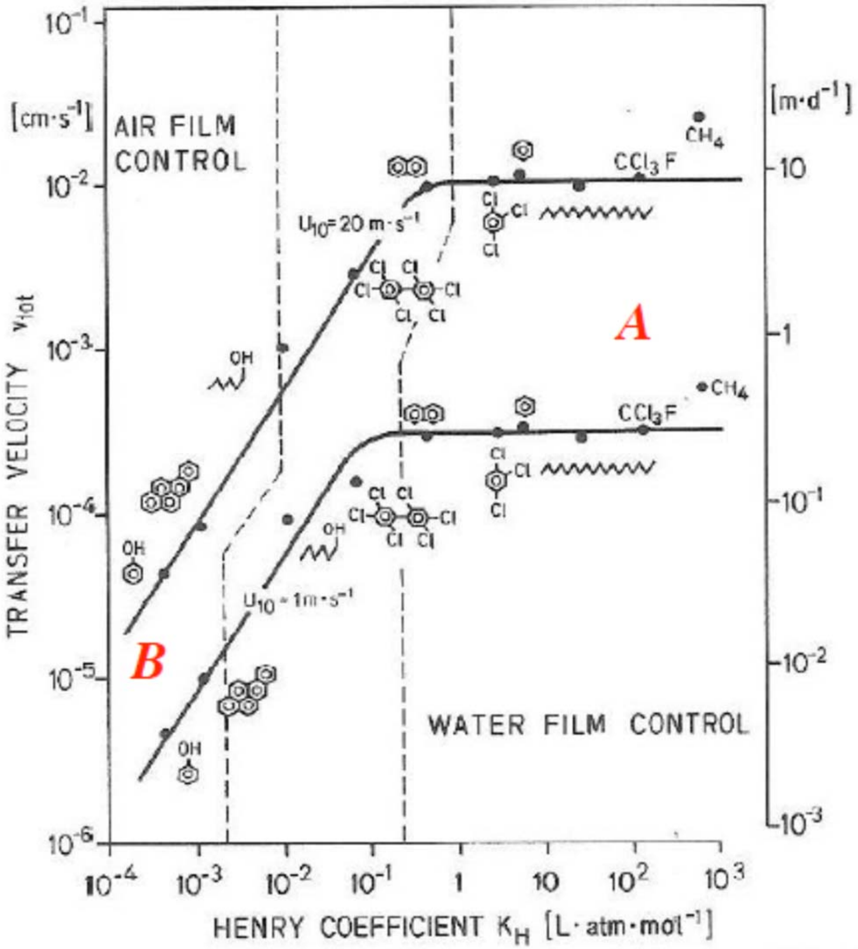


Figure 10.5 Impact of wind speed u_z on the air-side mass transfer coefficient v_a, as observed by the evaporation of water in laboratory experiments and as predicted using various correlation expressions (see Table 10.1). Note that the wind speeds refer to different heights above the water surface. This explains the higher v_a values for wind measurements made at small height z. In Table 10.1, values are also adjusted to wind speeds at 10 m using Eq. 10-24.

k_i: mass transfer coefficient has unit of [L/T]; velocity

Wind, stirring, H_{PC} effects on mass transfer



Total air-water transfer velocity v_{tot} as a function of Henry's coefficient K_H for two different wind speeds, u_{10}.

Q: Why is v_{tot} a function of K_H (=H_{PC}) at B but not at A?

Summary: mass transfer

- **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**