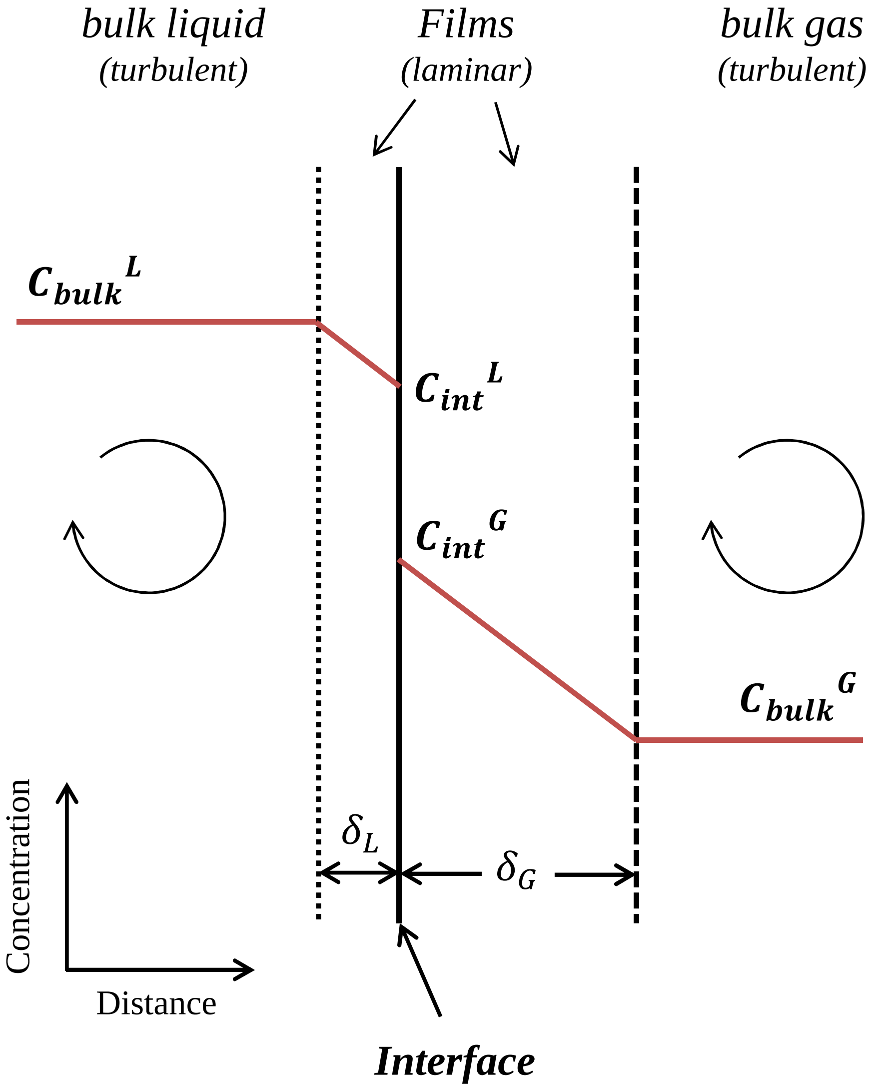
Interphase mass transfer II:

Theories on gas/liquid interface

Gas/liquid interfaces: film theory



Assumptions

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

  (equilibrium at the interface)

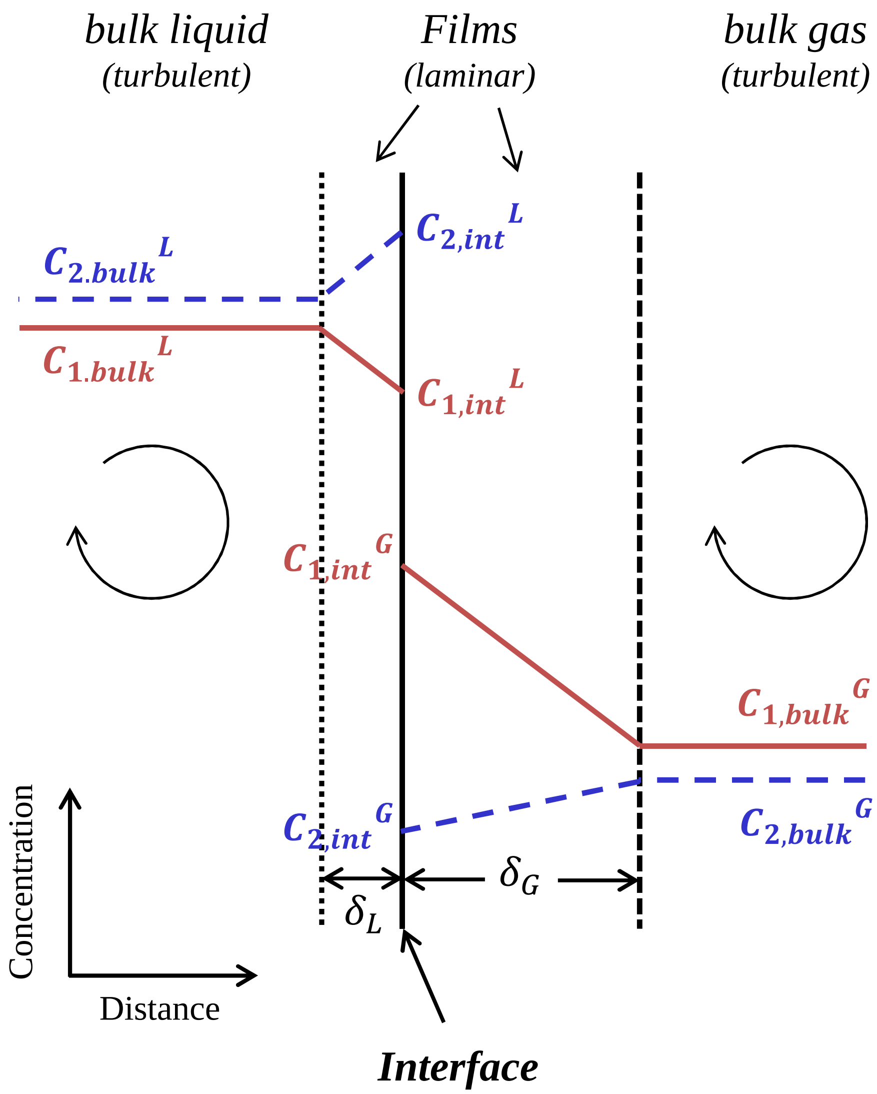
- $|J_G| = |J_L|$

  (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

Caution!!

For interphase mass transfer, molecule movement is **<u>from high fugacity to low fugacity</u>**; not necessarily from high concentration to low concentration



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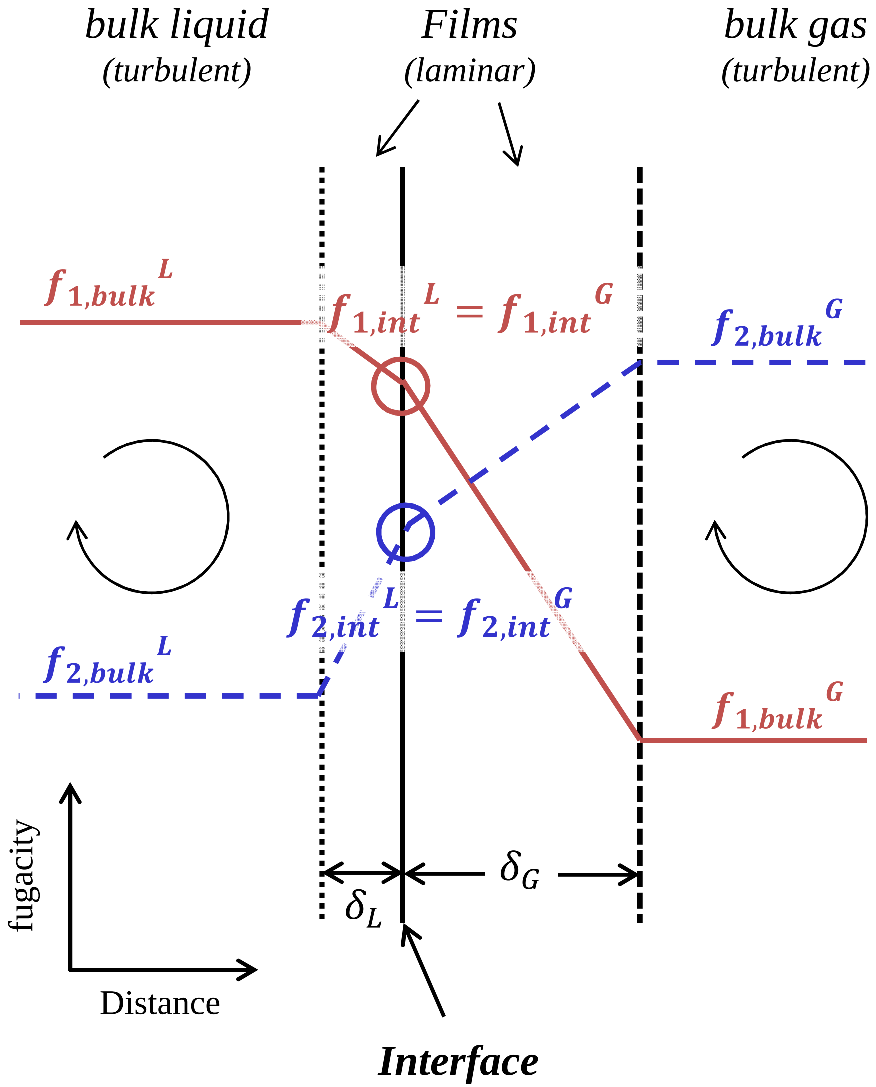


Gas/liquid interfaces: film theory

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*

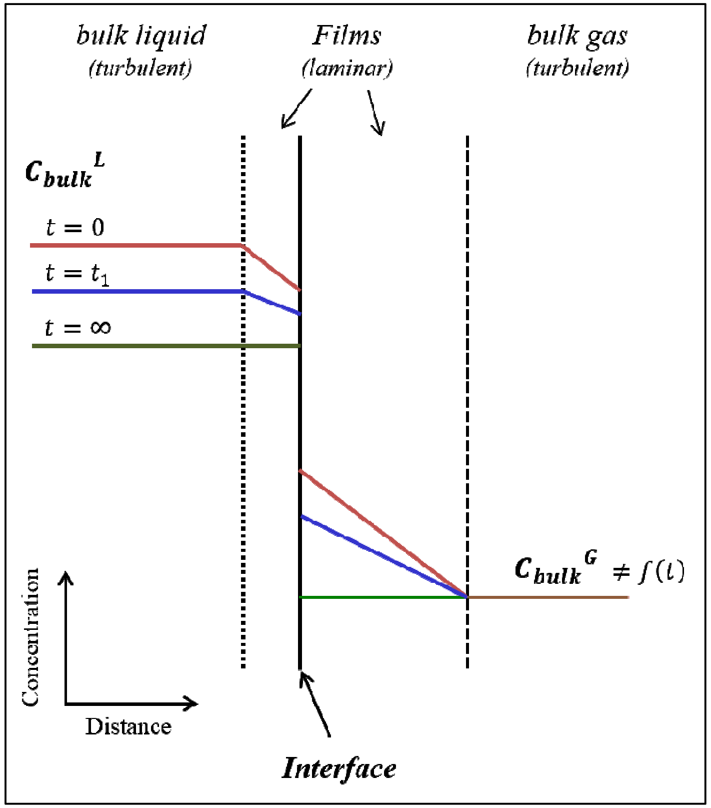
“To Be”*: the liquid phase concentration that would be in equilibrium with the current bulk gas phase concentration*

How to set a reference phase?

If $V_{bulk}{}^{L} \ll V_{bulk}{}^{G}$*:* $C_{bulk}{}^{G*} \approx C_{bulk}{}^{G}(t=0)$ *while* $C_{bulk}{}^{L*}$ *is significantly different from* $C_{bulk}{}^{L}(t=0)$

Then, our interest is the change in $C_{bulk}{}^{L}$ *over time*

➡ *Use* ***liquid phase*** *as a reference*



cf)

If $V_{bulk}{}^{G} \ll V_{bulk}{}^{L}$*:* $C_{bulk}{}^{L*} \approx C_{bulk}{}^{L}(t=0)$ *while* $C_{bulk}{}^{G*}$ *is significantly different from* $C_{bulk}{}^{G}(t=0)$

Then, our interest is the change in $C_{bulk}{}^{G}$ *over time*

➡ *Use* ***gas phase*** *as a reference*

k_L & k_G to K_L; resistance concept

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

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

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

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 refers to phase control & $k_G/k_L = 100$*, then:*

$H_{cc} > 0.19$*: liquid phase controls*
$H_{cc} < 0.0005$*: gas phase controls*
$0.0005 < H_{cc} < 0.19$*: both phases are significant*

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

* $k_G/k_L=100$ *assumed*

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 coefficient 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:

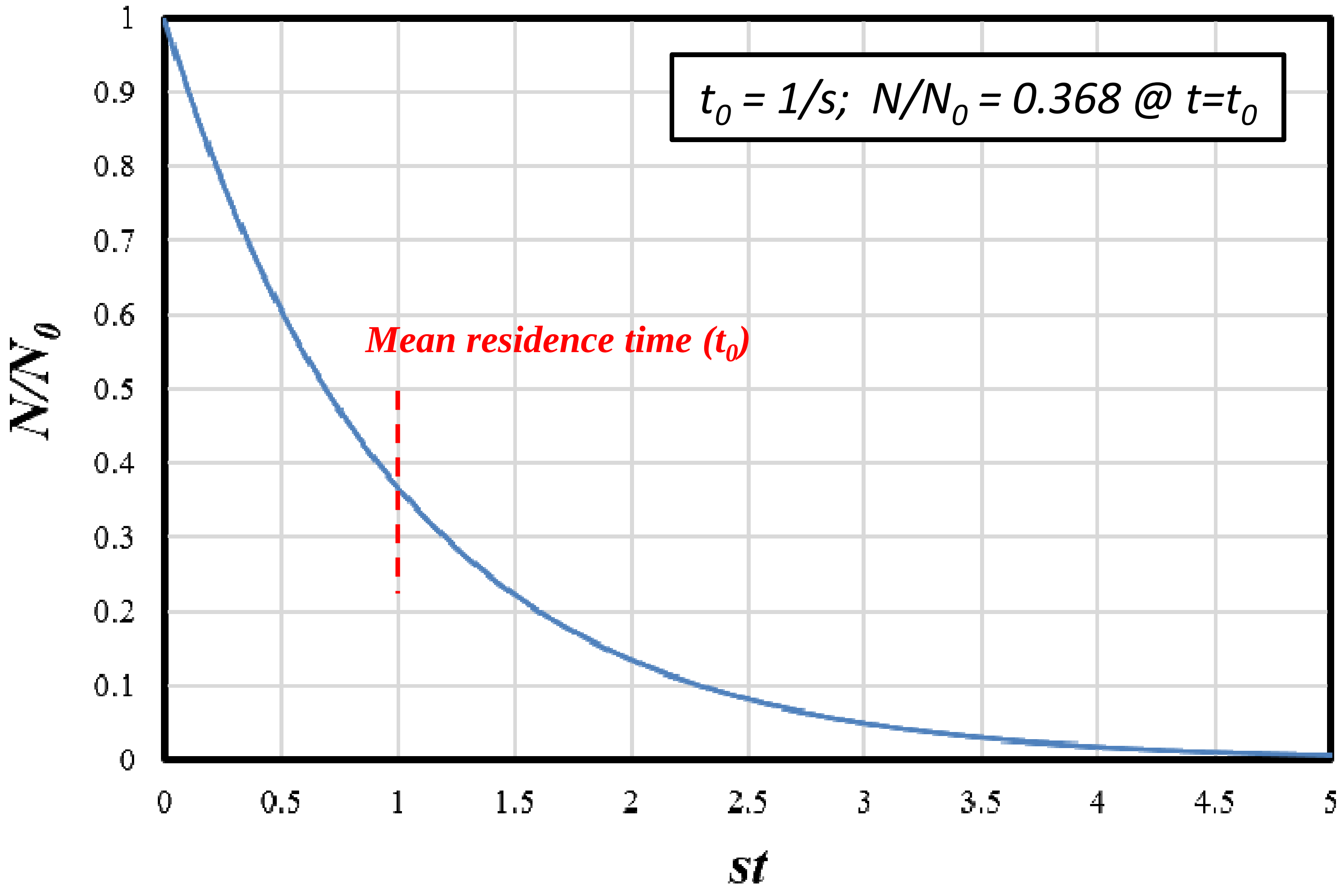
- Some fraction “*s*” of the fluid elements in the interfacial region (“surface chunks”) is replaced with the bulk fluid during a unit period of time
- The replacement of “surface chunks” is random

In mathematical terms:

$$\frac{dN}{dt} = -sN \quad \Rightarrow \quad N = N_0 e^{-st}$$

N = number of surface chunks that remains not to be replaced at time t

Surface renewal: random replacement



Applying surface renewal theory

- **It has been shown that:** $\boldsymbol{k_i = (D_i s_i)^{0.5}}$

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

cf) film theory: $k_i = D_i/\delta_i$

- **Other relationships still hold:**

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

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

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

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

Boundary layer theory: coefficients

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

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

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

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)

$\boxed{\boldsymbol{a_3 = 0.33;\ a_4 = 0}}$ $\quad k_i = a_2 d^{-0.67} u^{0.33} \nu^{-0.33} \times \boxed{{D_i}^{1.0}}$

$\boxed{\boldsymbol{a_3 = 0.8;\ a_4 = 0.5}}$ $\quad k_i = a_2 d^{-0.2} u^{0.8} \nu^{-0.3} \times \boxed{{D_i}^{0.5}}$

Interphase mass transfer III:

Applications

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)

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

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)*$^{\#1}$*:*

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

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

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, $a_1 = 2$

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

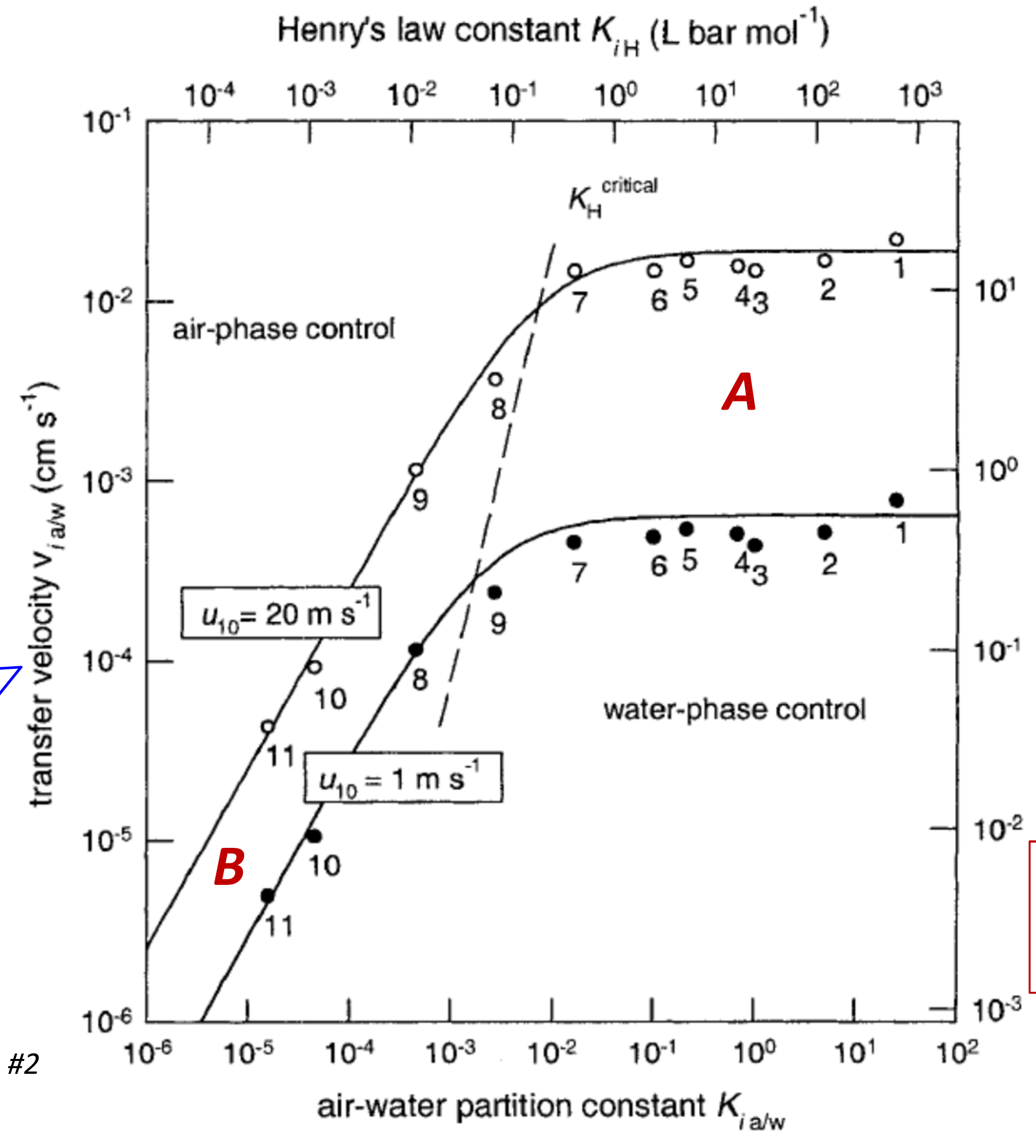
$$a = \frac{area}{volume} = \frac{6}{d_p}\ m^{-1}$$

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



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

EOC text Fig. 20.7

Overall mass transfer coeff. for 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**

References

#1) O'Connor, D. J., Dobbins, W. E. (1958) Mechanism of reaeration in natural systems. Transactions of the American Society of Civil Engineers, 23(1): 641-666.

#2) Schwarzenbach, R., Gschwend, P. M., Imboden, D. M. (2003) Environmental Organic Chemistry, 2nd ed., John Wiley & Sons, p. 918.

Interphase mass transfer IV:

Exercise

Controlling resistance

Q: You set an experiment to determine the overall mass transfer coefficient with liquid phase as a reference, K_L, for gas-liquid transfer of oxygen and ethanol in a well-mixed reactor. You also need to estimate the K_L for nitrogen, which was not determined by the experiment. The results of the experiment, the Henry's law constants, and the diffusion coefficients in water are as follows:

Compounds	K_L **(m/s)**	H_{cc}	D_{aq} **(m²/s)**
Nitrogen, N_2	-	65	1.9×10^{-9}
Oxygen, O_2	2.0×10^{-5}	30	2.1×10^{-9}
Ethanol, C_2H_5OH	4.1×10^{-7}	2.7×10^{-4}	1.2×10^{-9}

1) Determine which phase controls the mass transfer for each compound. Assume k_G/k_L of 100. Show your reasoning.

Controlling resistance

For N_2:

$$\frac{R_L}{R_G} = \frac{k_G H_{cc}}{k_L} = 100 \times 65 \gg 1$$

liquid phase controls

For O_2:

$$\frac{R_L}{R_G} = \frac{k_G H_{cc}}{k_L} = 100 \times 30 = 3000 \gg 1$$

liquid phase controls

For C_2H_5OH:

$$\frac{R_L}{R_G} = \frac{k_G H_{cc}}{k_L} = 100 \times (2.7 \times 10^{-4}) = 0.027 \ll 1$$

gas phase controls

Film theory

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2) Assuming that film theory is applicable, predict the K_L for nitrogen.

Film theory

If film theory is valid, then

$$k_L \propto D_L$$

$$\frac{k_{L,N_2}}{k_{L,O_2}} = \frac{D_{L,N_2}}{D_{L,O_2}}$$

For both N$_2$ & O$_2$, liquid phase controls the mass transfer. Therefore:

$$K_L \approx k_L$$

We conclude:

$$K_{L,N_2} = k_{L,N_2} = k_{L,O_2} \times \frac{D_{L,N_2}}{D_{L,O_2}}$$

$$= (2.0 \times 10^{-5}\ m/s) \times \frac{1.9 \times 10^{-9}\ m^2/s}{2.1 \times 10^{-9}\ m^2/s} = \mathbf{1.8 \times 10^{-5}\ \boldsymbol{m/s}}$$

Predicting conc. change in water

Q: You bought a bottle of “super oxygen water” from a market, which is highly supersaturated with oxygen (dissolved oxygen concentration (DO) = 60 mg/L). You poured 200 cm^3 of the drink to a cup in a cylindrical shape with an inner diameter of 8 cm and left it for 3 hours. What will be the DO of the drink then? Use an overall mass transfer coefficient (K_L) of 1.00×10^{-2} m/h and the saturation DO of 8.3 mg/L.

$\boxed{C^{L*}_{bulk}}$

Predicting conc. change in water

$$a = \frac{A}{V} = \frac{\pi d^2}{V} = \frac{\pi \cdot (8\ cm)^2}{200\ cm^3} = 0.251\ cm^{-1}$$

$$K_L a = (1.00 \times 10^{-2}\ m/h) \times (100\ cm/m) \times (0.251\ cm^{-1}) = 0.251\ h^{-1}$$

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

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

$$\int_{C_{bulk}{}^{L}\,(t=0)}^{C_{bulk}{}^{L}\,(t=t)} \frac{dC_{bulk}{}^{L}}{\left(C_{bulk}{}^{L} - C_{bulk}{}^{L*}\right)} = -K_L a \cdot \int_0^t dt$$

$$ln\left\{C_{bulk}{}^{L} - C_{bulk}{}^{L*}\right\}\Big|_{C_{bulk}{}^{L}\,(t=0)}^{C_{bulk}{}^{L}\,(t=t)} = -K_L a \cdot t\Big|_0^t$$

$$ln\frac{\left\{{C_{bulk}}^{L}\ (t=t)\right\}-{C_{bulk}}^{L*}}{\left\{{C_{bulk}}^{L}\ (t=0)\right\}-{C_{bulk}}^{L*}}=-K_L a\cdot t$$

$$\left\{{C_{bulk}}^{L}\ (t=t)\right\}=\left\{{C_{bulk}}^{L}\ (t=0)\right\}\cdot e^{-K_L a\cdot t}\ +{C_{bulk}}^{L*}\cdot(1-e^{-K_L a\cdot t}\ )$$

$$=60\ mg/L\cdot e^{-0.251\ h^{-1}\cdot 3\ h}+8.3\ mg/L\cdot\left(1-e^{-0.251\ h^{-1}\cdot 3\ h}\right)$$

$$=\mathbf{32.6\ mg/L}$$