Interphase mass transfer I: Diffusion

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 (Brownian motion)



- Consider the (ground level) atmosphere
 - Molecules
 - Take up ~0.1% of available space
 - Zip around at ~450 m/sec (average)
 - Have ~2 x 10¹⁰ 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 $J_{x,i}$



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

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

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

Rough estimates of diffusivities in air and water @ 20 $^{\rm o}{\rm C}$

		D_i , m²/s	
	MW	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

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

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)

Time	Penetration distance, z (cm)				
(t)	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

CO_2 mole fraction (x_{CO_2}) change in <u>stagnant</u> air mass^a



^a Simulation results; used D_{CO_2} (air) = 0.153 cm²/s @ 20 °C, 1 atm.

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

Time	Penetration distance, z (cm)				
(t)	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

^b <u>Simulation</u> results; used D_{O_2} (water) = 1.80×10⁻⁵ cm²/s @ 20 °C.

$$C_{O_2} = 0.00 \text{ mg/L} @ z=0, t \ge 0$$

 $z=0$
 $C_{O_2} = 9.17 \text{ mg/L}$
@ t=0, z>0

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



Air/water interface: rough



Molecular diffusion – example 1

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 cm < x < 25 cm; Concentration (C_i) = 0 μ mol/cm³
- At any t
 - For x = 0 cm; $C_i = 1000 \,\mu mol/cm^3$
 - For x = 25 cm; $C_i = 0 \mu mol/cm^3$
 - 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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Flux ratios $(J_B/J_A, @ x = 0 cm)$



Molecular diffusion – example 2



Model system results

• Initially

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

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

- After a long time
 - Linear concentration profile

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

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</u> <u>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*:

$$J_{i} = \frac{D_{i}}{\delta_{i}} \left(C_{bulk}{}^{i} - C_{int}{}^{i} \right) = k_{i} \left(C_{bulk}{}^{i} - C_{int}{}^{i} \right)$$

$$(+) flux when bulk \rightarrow interface$$

$$k_{i} = coep$$

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

Since $|J_G| = |J_L|$,

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

set (+) flux when liquid \rightarrow gas $= k_G (H_{cc} C_{int}{}^L - C_{bulk}{}^G)$

 $k_L = D_L/\delta_L$, 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



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 \bigvee Use <u>liquid phase</u> as a reference



cf)

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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

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

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 ~104)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*
0 ₂	30	3000	Water
TCE	0.38	38	Water
Arochlor 1212	0.027	2.7	Intermediate
Lindane	$1.4 imes 10^{-4}$	0.014	Gas
Phenol	3 × 10 ⁻⁵	0.03	Gas
H ₂ O	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
 - $-K_L \propto D_i^a$
 - $0.5 \le a \le 1$
 - 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:

$$\frac{dN}{dt} = -sN \qquad \Longrightarrow \qquad N = N_0 e^{-st}$$

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: $k_i = (D_i s_i)^{0.5}$

s_i = surface renewal rate, [T⁻¹]

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

• Other relationships still hold:

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

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

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

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

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

$$Re = \frac{d \times u}{v} = \frac{d \times u \times \rho}{\mu}$$
$$(Sc)_i = \frac{v}{D_i} = \frac{\mu}{D_i\rho}$$

If
$$a_1 = 0$$
, then:
 $k_i = \frac{(Sh)_i D_i}{d} = \frac{a_2 (Re)^{a_3} (v)^{a_4} D_i^{1-a_4}}{d} = a_2 d^{(a_3-1)} u^{a_3} v^{(a_4-a_3)} D_i^{(1-a_4)}$
 $a_2: 0.01 \text{ to } 1.0$
 $a_3: 0.33 \text{ (laminar flow) to } 0.8 \text{ (turbulent flow)}$
 $a_4: 0 \text{ to } 0.5 (\sim 0.33 \text{ is common})$
 $\boxed{a_3 = 0.33; a_4 = 0}$
 $k_i = a_2 d^{-0.67} u^{0.33} v^{-0.33} \times \boxed{D_i^{1.0}}$
 $k_i = a_2 d^{-0.2} u^{0.8} v^{-0.3} \times \boxed{D_i^{0.5}}$