

# Physical unit processes III

# Mass transfer processes

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- **Phase partitioning:** in multi-phase systems, materials are distributed with some ratio between the phases at equilibrium

– Recall Henry's law (gas-liquid partitioning):  $C_g/C_s = H_u$

ex) At 1 atm, 20°C, the saturation concentration of dissolved oxygen in pure water is 9.08 mg/L (0.208 atm partial pressure of O<sub>2</sub> in gas phase ↔ 9.08 mg/L O<sub>2</sub> in aqueous solution)

# Mass transfer processes

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- Transfer of material from one homogeneous phase to another
- Interphase mass transfer occurs **towards equilibrium**
- **Time as a factor**: it takes some time for the mass transfer processes to occur such that equilibrium is established

ex) Drying clothes

phase partitioning: moisture wetting the clothes vs. moisture in the ambient air

equilibrium: almost no moisture in the clothes because the amount of ambient air is almost infinite

time as a factor: it takes some time (~1 day) for the clothes to dry

# Application of mass transfer in WW treatment

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Type of reactor	Phase equilibria	Application
Absorption	Gas → liquid	Addition of gases to water (e.g., O <sub>2</sub> ), NH <sub>3</sub> scrubbing in acid
Adsorption	Gas → solid	Removal of organics with activated carbon
	Liquid → solid	Removal of organics with activated carbon, dechlorination
Desorption	Solid → liquid	Sediment scrubbing
	Solid → gas	Reactivation of spent activated carbon
Drying (evaporation)	Liquid → gas	Drying of sludge
Gas stripping	Liquid → gas	Removal of gases (e.g., CO <sub>2</sub> , H <sub>2</sub> S, NH <sub>3</sub> , VOCs)
Ion exchange	Liquid → solid	Selective removal of chemical constituents, demineralization

# Basic principle of mass transfer

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- **Fundamental mechanism: molecular diffusion**

Fick's 1<sup>st</sup> law of diffusion

$$r = -D_m \frac{\partial C}{\partial x}$$

*r = mass flux; rate of mass transfer per unit area per unit time [ML<sup>-2</sup>T<sup>-1</sup>]*

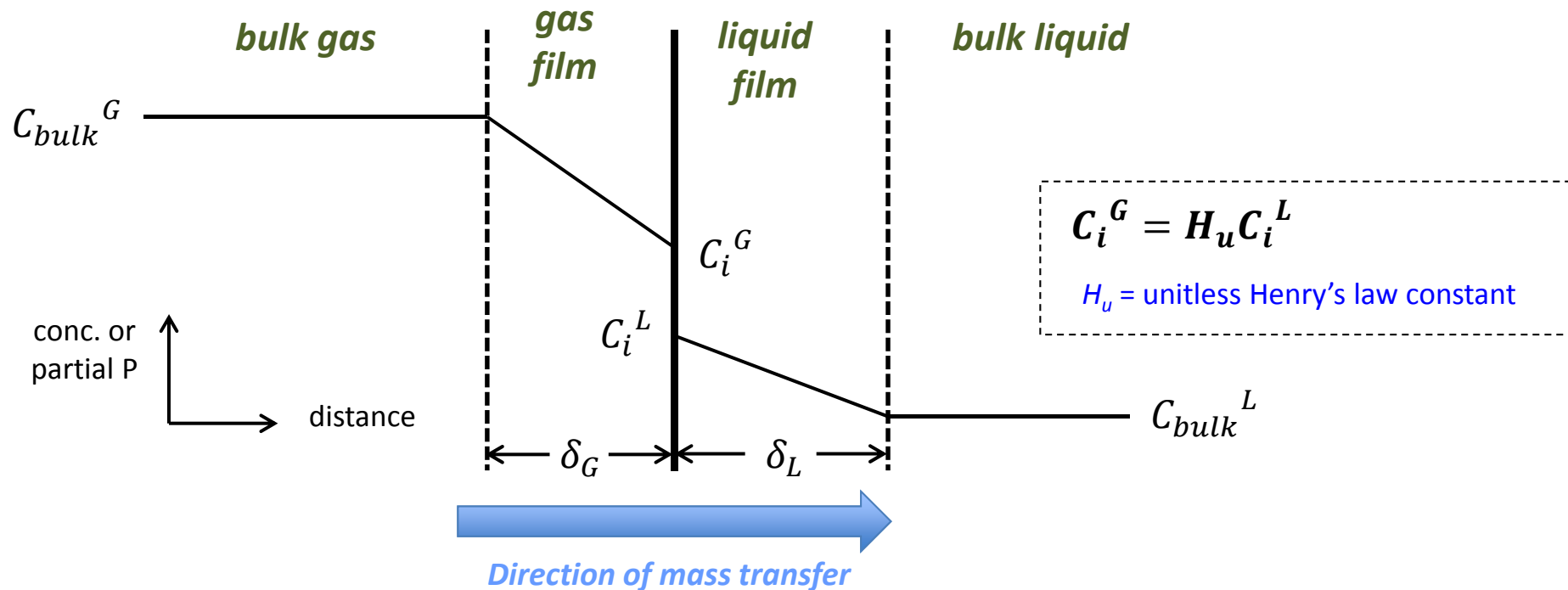
*D<sub>m</sub> = molecular diffusion coefficient [L<sup>2</sup>T<sup>-1</sup>]*

*C = concentration [ML<sup>-3</sup>]*

*x = distance [L]*

➡ Driving force: concentration gradient

# Gas-liquid mass transfer: Two-film theory



## Assumptions

- 1) Resistance to interphase mass transfer in stagnant films
- 2) Equilibrium obtained at the interphase
- 3) Uniform concentration in bulk fluids
- 4) Linear concentration gradients in the stagnant film (steady state diffusion)

# Two-film theory

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- For steady-state diffusion,  
***(rate of mass transfer at the gas film)***  
***= (rate of mass transfer at the liquid film)***

- The mass flux for each phase is written as

$$r = k_G(C_{bulk}^G - C_i^G) = k_L(C_i^L - C_{bulk}^L)$$

*r = mass flux [ML<sup>-2</sup>T<sup>-1</sup>]*

*k<sub>G</sub> = gas film mass transfer coefficient [LT<sup>-1</sup>] (= D<sub>m</sub><sup>G</sup>/δ<sub>G</sub>)*

*k<sub>L</sub> = liquid film mass transfer coefficient [LT<sup>-1</sup>] (= D<sub>m</sub><sup>L</sup>/δ<sub>L</sub>)*

- ✘ The film thickness (δ) depends on the conditions at the interphase  
high turbulence at the interphase → smaller δ → greater k  
calm interphase → greater δ → smaller k

# Two-film theory

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- **Overall mass transfer coefficient**

The film thickness ( $\delta_G$  or  $\delta_L$ ) and the interphase concentration ( $C_i^G$  or  $C_i^L$ ) are not easy to determine

➡ Use overall mass transfer coefficient with easily measurable values

Using liquid phase as a reference, the mass flux is written as

$$r = K_L (C_s^L - C_{bulk}^L)$$

*$r$  = mass flux [ $ML^{-2}T^{-1}$ ]*

*$K_L$  = overall liquid mass transfer coefficient [ $LT^{-1}$ ]*

*$C_s^L$  = liquid concentration of the constituent in equilibrium with the gas concentration of the constituent in the bulk phase [ $ML^{-3}$ ] ( $=C_{bulk}^G/H_u$ )*



# Two-film theory

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- Overall mass transfer coefficient

$$r = K_L(C_s^L - C_{bulk}^L) = k_G(C_{bulk}^G - C_i^G) = k_L(C_i^L - C_{bulk}^L)$$

$$\Rightarrow \frac{r}{K_L} = \frac{r}{k_L} + \frac{r}{H_u k_G}$$

or

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{H_u k_G}$$

# Two-film theory

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$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{H_u k_G}$$

- In most cases,  $1 < (k_G/k_L) < 300$
- For volatile, less water soluble compounds (high  $H_u$ ), water-air mass transfer is usually controlled by liquid film (ex:  $O_2$ ,  $H_u \approx 30$ )
- For less volatile, highly water soluble compounds (low  $H_u$ ), water-air mass transfer is usually controlled by gas film (ex: phenol,  $H_u \approx 0.00003$ )

# Gas-liquid mass transfer

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- **Modeling concentration change by mass transfer**

- Flux = (mass transferred) / (area) / (time)

$$r = K_L(C_S^L - C_{bulk}^L)$$

- When the bulk gas concentration is constant, change in bulk liquid concentration is represented as:

$$r_v = \left. \frac{dC}{dt} \right|_{mass\ transfer} = K_L \frac{A}{V} (C_S - C) = K_L a (C_S - C)$$

*$r_v$  = rate of mass transfer [ML<sup>-3</sup>T<sup>-1</sup>]*

*A = area through which mass is transferred [L<sup>2</sup>]*

*V = bulk liquid volume [L<sup>3</sup>]*

*C<sub>s</sub> = liquid concentration in equilibrium with bulk gas concentration [ML<sup>-3</sup>]*

*C = liquid concentration at time t*

*K<sub>L</sub>a = volumetric mass transfer coefficient [T<sup>-1</sup>]*

# Gas-liquid mass transfer

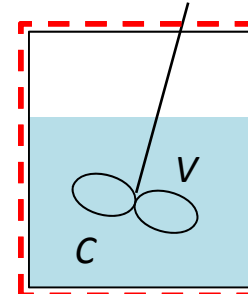
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- **Absorption of gas in a batch reactor**

*(rate of accumulation)*

*= (rate of inflow) – (rate of outflow) + (rate of generation)*

$$\frac{dC}{dt} = K_L a (C_s - C_t) \quad \Rightarrow \quad \frac{C_s - C_t}{C_s - C_0} = e^{-(K_L a)t}$$



- **Desorption of gas in a batch reactor**

$$\frac{dC}{dt} = -K_L a (C_s - C) \quad \Rightarrow \quad \frac{C_t - C_s}{C_0 - C_s} = e^{-(K_L a)t}$$

# Gas-liquid mass transfer

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**Q:** Secondary effluent is placed in a storage basin for reuse. If the initial DO concentration is 1.5 mg/L, estimate the time required for the DO concentration to increase to 8.5 mg/L due to surface reaeration. The surface area of the storage basin is 400 m<sup>2</sup> and the depth is 3 m. Assume the  $K_L$  value for oxygen is 0.03 m/hr. Use the saturation DO concentration of 9.09 mg/L at 20°C.

# Chemical unit processes I

# Chemical processes in wastewater treatment

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- Usually applied as a unit process for tertiary treatment or for supplementary processes
- **Biological vs. chemical processes**
  - Biological processes as a major unit for the current wastewater treatment
    - Biological processes – less reliable but more cost-effective, benign products
    - Chemical processes – more reliable but concern with chemical cost & sludge disposal
    - Biological processes may be more suitable for concentrated treatment systems
  - Wastewater management in the next generation – decentralized treatment??
    - Reconsideration of chemical processes needed as significant limitations of biological processes are expected because of.
      - Significant variations in flowrates & loadings at small scale
      - Small-scale facilities cannot be maintained by trained personnel & in a continuous manner

# Chemical unit processes

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Processes	Application
Advanced oxidation	Removal of refractory organic compounds
Chemical coagulation	Chemical destabilization of particles in wastewater to bring about their aggregation during flocculation
Chemical disinfection	Disinfection with chlorine, chlorine compounds, bromine, and ozone Control of odors
Chemical neutralization	Control of pH
Chemical oxidation	Removal of BOD, grease, etc. Removal of ammonium Destruction of microorganisms Control of odors in sewers, pump stations, and treatment plants Removal of resistant organic compounds



# Chemical unit processes

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Processes	Application
Chemical precipitation	Enhanced removal of TSS and BOD in primary sedimentation facilities Removal of phosphorous Removal of ammonium Removal of heavy metals Physical-chemical treatment Corrosion control in sewers due to H <sub>2</sub> S
Chemical scale control	Control of scaling due to calcium carbonate and related compounds
Chemical stabilization	Stabilization of treated effluents
Ion exchange	Removal of ammonium, heavy metals, total dissolved solids Removal of organic compounds

# Considerations in chemical processes

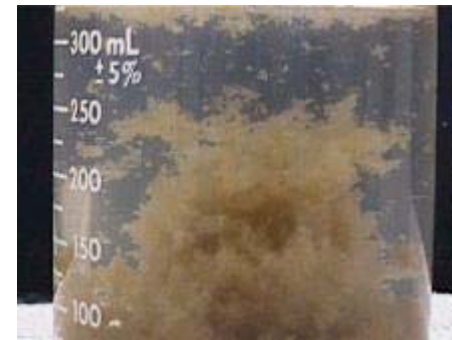
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- **External substances are often added**
  - There is often a net increase in certain dissolved wastewater constituents
    - ex1) addition of coagulants → increase in wastewater TDS
    - ex2) addition of chlorine for disinfection: increase in TDS and generation of disinfection byproducts
- **Generation of chemical precipitation sludge**
  - Handling, treatment, and disposal of the chemical sludge requires additional cautions
- **Cost of chemicals & sustainability**

# Chemical coagulation

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- Colloidal particles in wastewater typically have a net negative charge and thus, at stabilized condition
- **Coagulation vs. flocculation**
  - Coagulation
    - A chemical process to destabilize the particles by changing the surface properties so that particles can stick together when they collide
    - But quite often used as a term that includes mechanisms involved both in chemical destabilization of particles and growth in particle size
  - Flocculation
    - A physical process to create conditions (by gentle mixing) that allow particles to grow in size



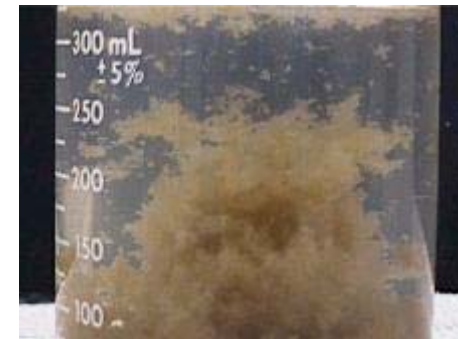
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# Chemical coagulation

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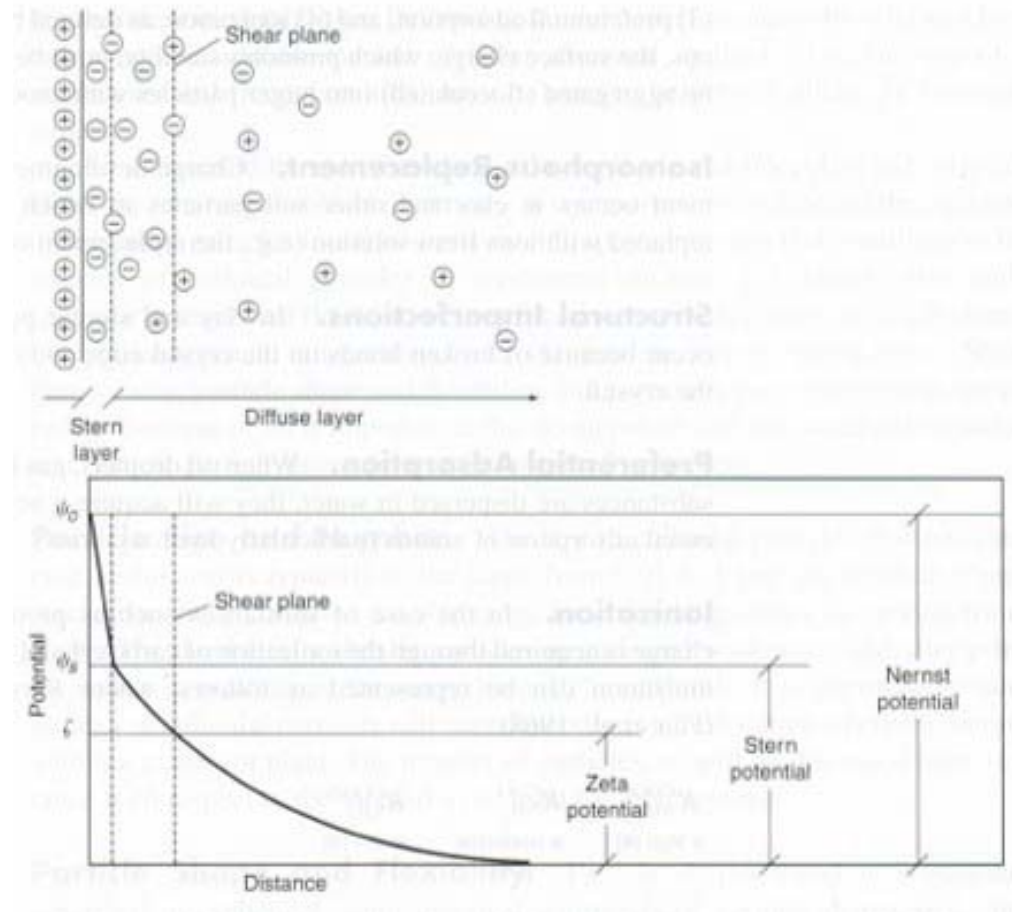
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# Nature of particles

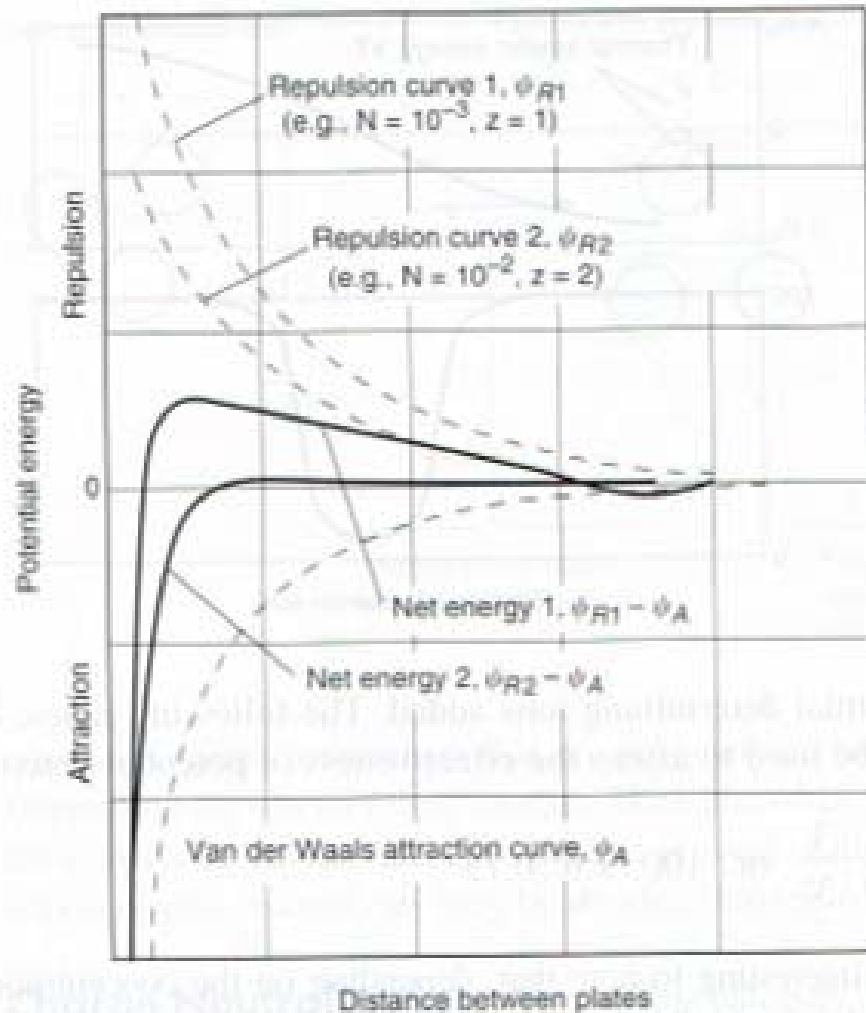
- The electrical double layer
  - Charged particles in water are surrounded by ions of opposite charge
  - A compact layer (Stern layer) + a diffuse layer



*Stern model of electrical double layer*

# Nature of particles

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*Definition sketch for particle-particle interactions based on the repulsion due to particle surface charge and van der Waals forces of attraction.  $N$  = concentration;  $z$  = charge.*

# Nature of particles

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- **Forces between particles**
  - Electrical force (repulsion; when the particles are of the same charge)
  - van der Waals force (attraction)
  - Net energy = electrical force + van der Waals force
  - The energy barrier (maximum repulsive force of the net energy) has to be overcome for particles to be attached to each other
- **How to reduce the energy barrier?**
  - Reduce the particle surface charge by attachment of ions of opposite charge
    - Charge neutralization
  - Add electrolytes to reduce the electrical double layer thickness
    - Ionic strength  $\uparrow$   $\rightarrow$  Compression of electrical double layer

# Chemical coagulation

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- **Mechanisms of particle removal by coagulation**
  - Charge neutralization
  - Compression of electrical double layer
  - Inter-particle bridging
  - Enmeshment in sweep floc
- **Use of polyelectrolytes**
  - Ions of multiple charge are good at charge neutralization & electrical double layer compression (+1 << +2 << +3)
  - Commonly used coagulants: Al<sup>3+</sup> or Fe<sup>3+</sup> salts  
(Alum, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·14H<sub>2</sub>O: most common)