LECTURE TEN: Gas Liquid Mass Transfer in bio-reactors

This lecture covers: Applications of gas-liquid transport with reaction, Effective diffusivity, internal and overall effectiveness factor, Thiele modulus and apparent reaction rates

Gas-liquid mass transfer in bioreactors

Microbial cells often grown aerobically in stirred tank reactors

-oxygen supply is often limiting

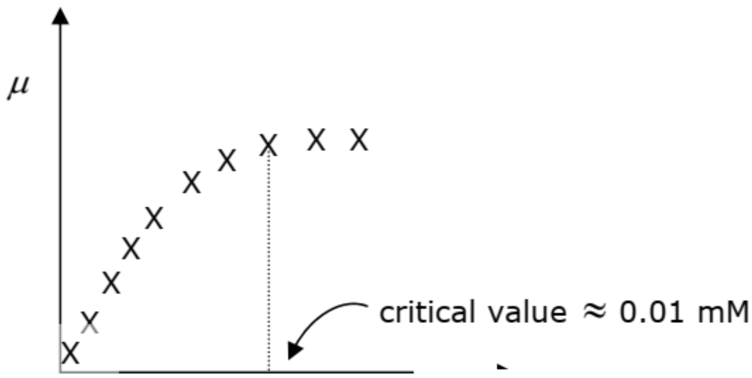


Figure 1. μ vs dissolved oxygen.

D.O. = dissolved oxygen

Equilibrium solubility of O_2 ≈ 1 mM

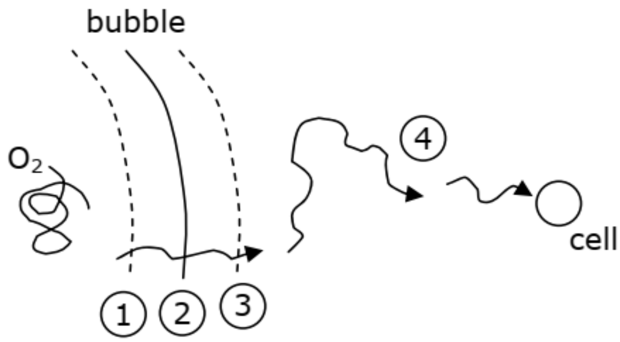


Figure 2. Oxygen pathway.

1) Diffusion across stagnate gas film
2) Absorption
3) Stagnate liquid layer (rate-limiting step)
4) Diffusion and convection

at equilibrium

3) O_2 flux $= k_l(C^*_{O_2} - C_{O_2})$ [=] $\frac{\text{mol}}{\text{area time}}$

mass transfer coefficient (k_l); bulk liquid concentration (C_{O_2})

What is the value for the interfacial area?

Important system parameters:

- liquid physical properties (surface tension, viscosity)
- power input/volume (stirring, propeller size)
- superficial gas velocity

empirical correlations (TIB 1:113 '83)

$$k_l a = constant\, U_s^{\alpha} \left(\frac{P}{V}\right)^{\beta}$$ where U_s is the superficial gas velocity

$$k_l a [=] \left(\frac{\text{length}}{\text{time}}\right)\left(\frac{\text{area}}{\text{volume}}\right) = \text{time}^{-1} \qquad (s^{-1})$$

$$U_S [=] \frac{\text{length}}{\text{time}} \qquad (m/s)$$

$$\frac{P}{V} = \frac{\text{power}}{\text{volume}} \qquad (W/m^3)$$

const. = 0.002
α = 0.2
β = 0.7

@ SS, O_2 transport = O_2 uptake by biomass

$$k_l a(C^*_{O_2} - C_{O_2}) = \frac{\mu X}{Y_{X/O_2}}$$

μX: biomass growth rate or $\frac{dX}{dt}$

Y_{X/O_2}: yield coefficient $\approx$ .4-.9 $\frac{\text{g cell dry wt.}}{\text{g } O_2}$

Crude limit: $\frac{dX}{dt} < k_l a C^*_{O_2} Y_{X/O_2}$

O_2 transport in tissues

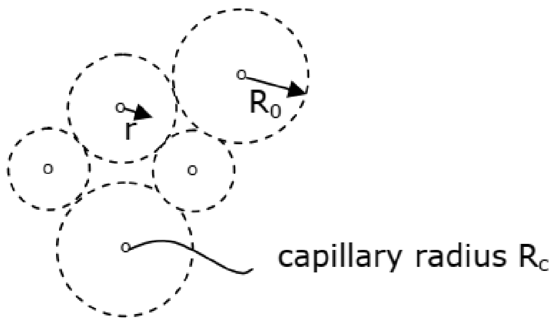


Figure 3. Krogh cylinder model.

One-dimensional steady-state diffusion:

$$\underbrace{\frac{D_{O_2}}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_{O_2}}{\partial r}\right)}_{\text{Fick's Law}} = V_{O_2}$$

← metabolic consumption rate of oxygen, zero-order

(cylindrical coordinates)

Boundary conditions:

symmetry
no-flux

flux=0 @ r=R_0

$$D_{O_2}\frac{\partial C_{O_2}}{\partial r} = 0 \quad @\ r=R_0$$

$$C_{O_2} = C_{O_2,plasma} \quad @\ r=R_c$$

Integrate twice:

$$\frac{C_{O_2}}{C_{O_2,plasma}} = 1+\Phi\left(r^{*2}-R^{*2}-2\ln\frac{r^*}{R^*}\right)$$

where $r^* = r/R_0$, $R^* = R_c/R_0$, $\Phi = \frac{1}{4}\frac{V_{O_2}}{C_{O_2,plasma}}\frac{R^2}{D_{O_2}} = \frac{\text{char. rxn rate}}{\text{char. transport rate}}$

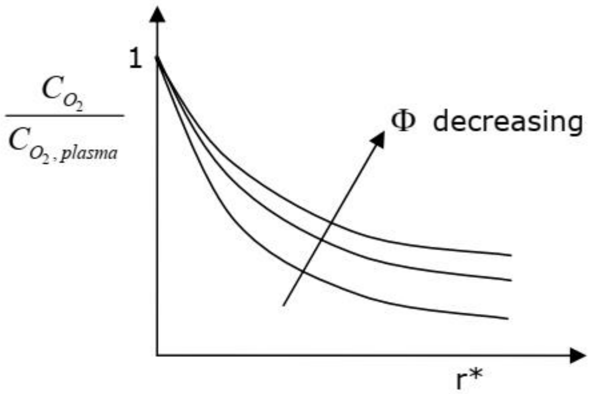


Figure 4. Dissolved oxygen vs. radius for various values of Φ.

O_2 diffuses further before consumption as Φ decreases.

When $R^* \approx 0.05$, $C_{O_2} = 0$ @ $r^* = 1$ when $\Phi \geq 0.2$

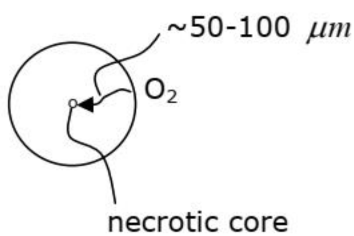
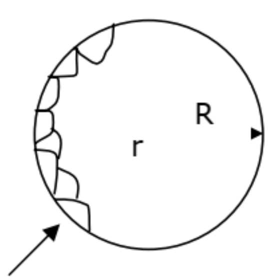


Figure 5. Tumor micrometastases.

Reaction & Diffusion

-Diffusion in a porous solid phase
Ex. Precious metals on ceramic supports or drug/nutrient delivery through tissues
-Derive steady state material balance accounting for diffusion and reaction in a spherical geometry
-Thiele modulus (ϕ)



$[S]_0$= surface concentration of a growth substrate (ex. glucose and O_2)

Figure 1. Sphere of Cells

Assume pseudo-homogeneous medium and Fick's Law describes diffusion

$Flux = -D\dfrac{d[S]}{dr}$, where $Flux\,[=]\dfrac{\#\ molecules}{area \cdot time}$ and $D\,[=]\dfrac{length^2}{time}$

$$-r_s = k_n C_s^n$$
$$-r_s = \frac{V_{\max} C_s}{K_s + C_s}$$

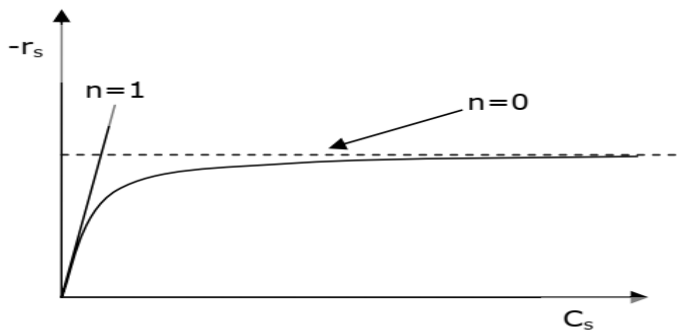


Figure 2. Rate of reaction versus species concentration

$C_s \ll K_s \Rightarrow 1^{st}$ order $\quad r_s \approx \dfrac{V_{\max} C_s}{K_s}$

$C_s \gg K_s \Rightarrow 0^{th}$ order $\quad r_s \approx V_{\max}$

Steady-state Shell Balance

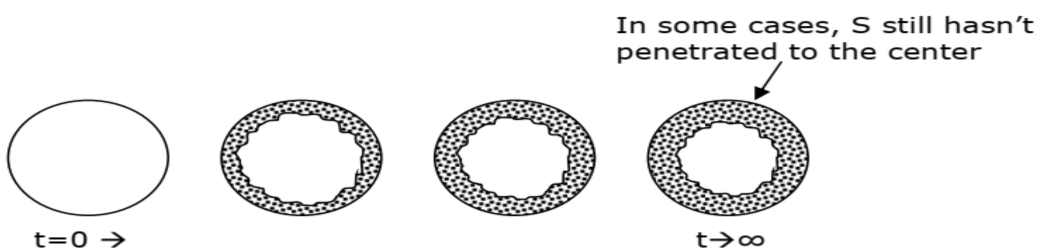


Figure 3. Time progression as species, S, enters the sphere

Thin shell r to (r+Δr)

S_{in} by diffusion $-S_{out}$ by diffusion $-S_{cons}$ by reaction=0

$$Flux \cdot 4\pi r^2\Big|_{r+\Delta r} - Flux \cdot 4\pi r^2\Big|_r - k_n C_s^n 4\pi r^2 \Delta r = 0$$

Divide through by $4\pi\Delta r$ and take the limit as Δr→0

$$\frac{d\left(Flux \cdot r^2\right)}{dr} - k_n C_s^n r^2 = 0$$

$$\frac{d}{dr}\left(-D\frac{dC_s}{dr} \cdot r^2\right) - k_n C_s^n r^2 = 0$$

$$\left.\frac{d^2 C_s}{dr^2} + \frac{2}{r}\frac{dC_s}{dr} - \frac{k_n}{D} C_s^n = 0 \right\} \text{2nd order ODE}$$

2 Boundary conditions:

$$C_s\big|_{r=R} = C_{s,0}$$

C_S is finite everywhere, or

$$\left.\frac{dC_s}{dr}\right|_{r=0} = 0$$

Nondimensionalize

$$\rho = \frac{r}{R} \quad S = \frac{C_s}{C_{s,0}}$$

$$\frac{d^2S}{d\rho^2} + \frac{2}{\rho}\frac{dS}{d\rho} - \phi^2 S^n = 0$$

Boundary conditions: S=1 @ $\rho=1$

S is finite everywhere

$$\phi^2 = \frac{k_n R^2 C_{s,0}^{n-1}}{D} = \frac{\left(R^2/D\right)}{\left(1/k_n C_{s,0}^{n-1}\right)} = \frac{\text{characteristic diffusion time}}{\text{characteristic reaction time}}$$

If diffusion is slow → diffusion dominates
If reaction is slow → reaction dominates

If $\phi^2 << 1$ → reaction limited regime
If $\phi^2 >> 1$ → diffusion limited regime

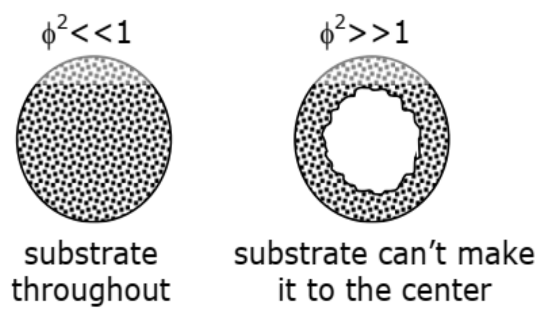


Figure 4. Reaction and diffusion limited regimes

$$S = \frac{1}{\rho}\frac{\sinh(\phi\rho)}{\sinh(\phi)}$$

$$\sinh(z) = \frac{e^z - e^{-z}}{2}$$

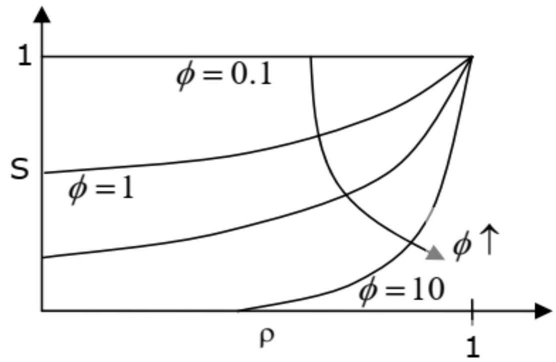


Figure 5. S versus ρ for various values of ϕ

Define "effectiveness factor" η

$$\eta = \frac{\text{overall rate of reaction}}{\text{rate if } C_s = C_{S,0} \text{ everywhere}}$$

overall reaction rate in sphere at steady state = [inward flux @ r=R (ρ=1)]*Area

$$= D \left.\frac{dC_s}{dr}\right|_{r=R} 4\pi R^2$$

$$= 4\pi R D C_{s,0} \left.\frac{dS}{d\rho}\right|_{\rho=1} = 4\pi R D C_{s,0} \left(\phi \coth\phi - 1\right)$$

$$\eta = \frac{3}{\phi^2}\left(\phi \coth\phi - 1\right)$$

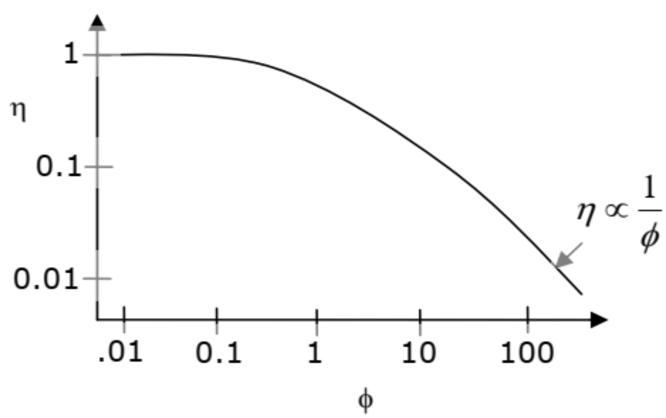


Figure 6. Log-log plot of effectiveness factor versus thiele modulus

Higher values of Thiele modulus → effectiveness goes down

*For a variety of reaction kinetics, geometries and rate laws, plots of η vs ϕ all look the same.

Shrinking Core Model

In cases with noncatalytic and irreversible reaction, diffusion limit is describable by the "shrinking core model".

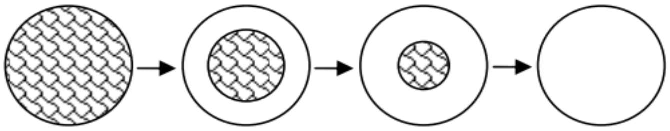


Figure 7. Shrinking core model

Rapid, irreversible reaction limited by rate of diffusion of a reactant from the surface
The following must be written down for the shell balance:

1. Rate of reaction
2. Rate of diffusion
3. Rate of movement of the core