II.1 - Introduction
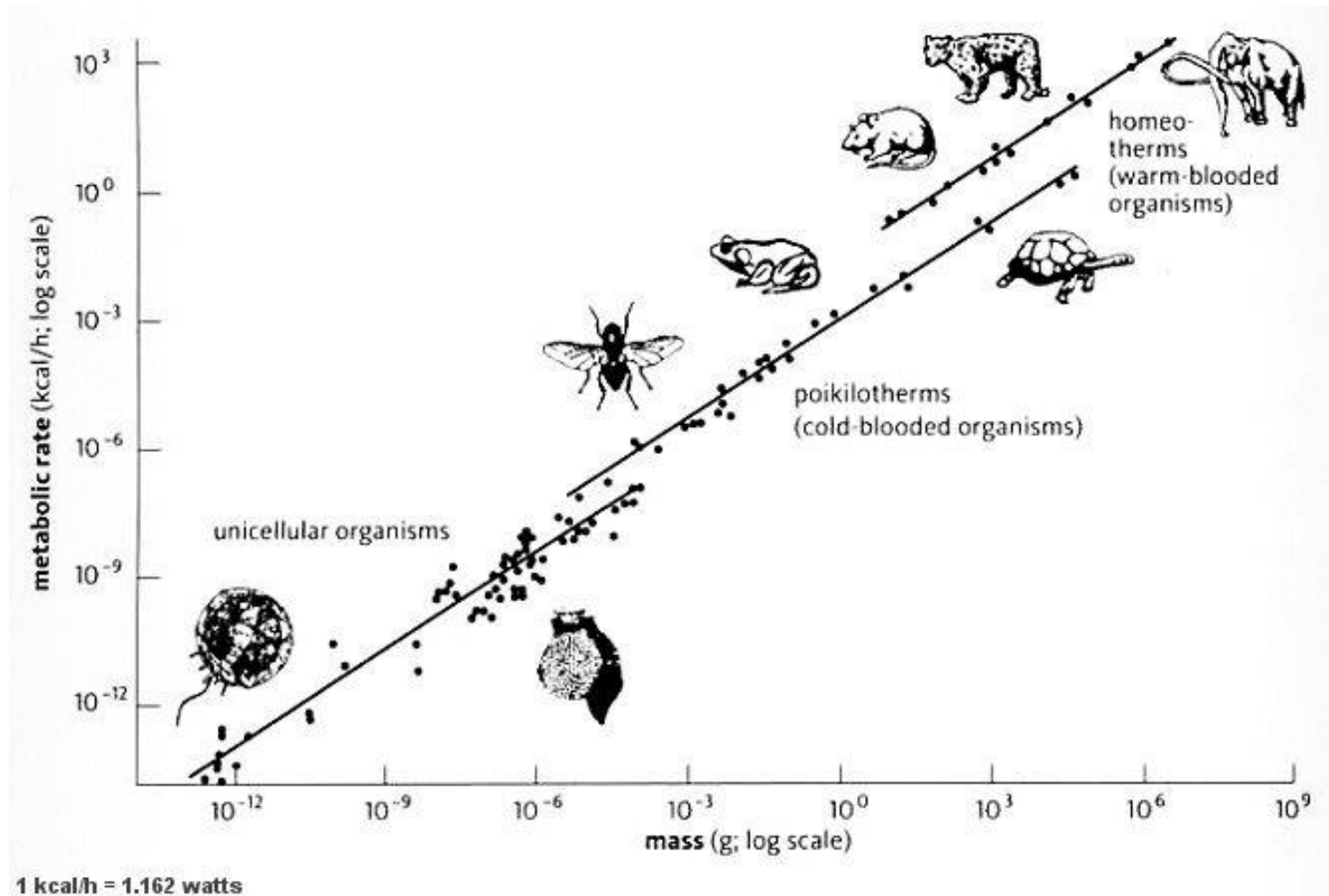

II.2 - Gas-Liquid Mass Transfer Process Modeling

II.3 - Rate of Oxygen Consumption

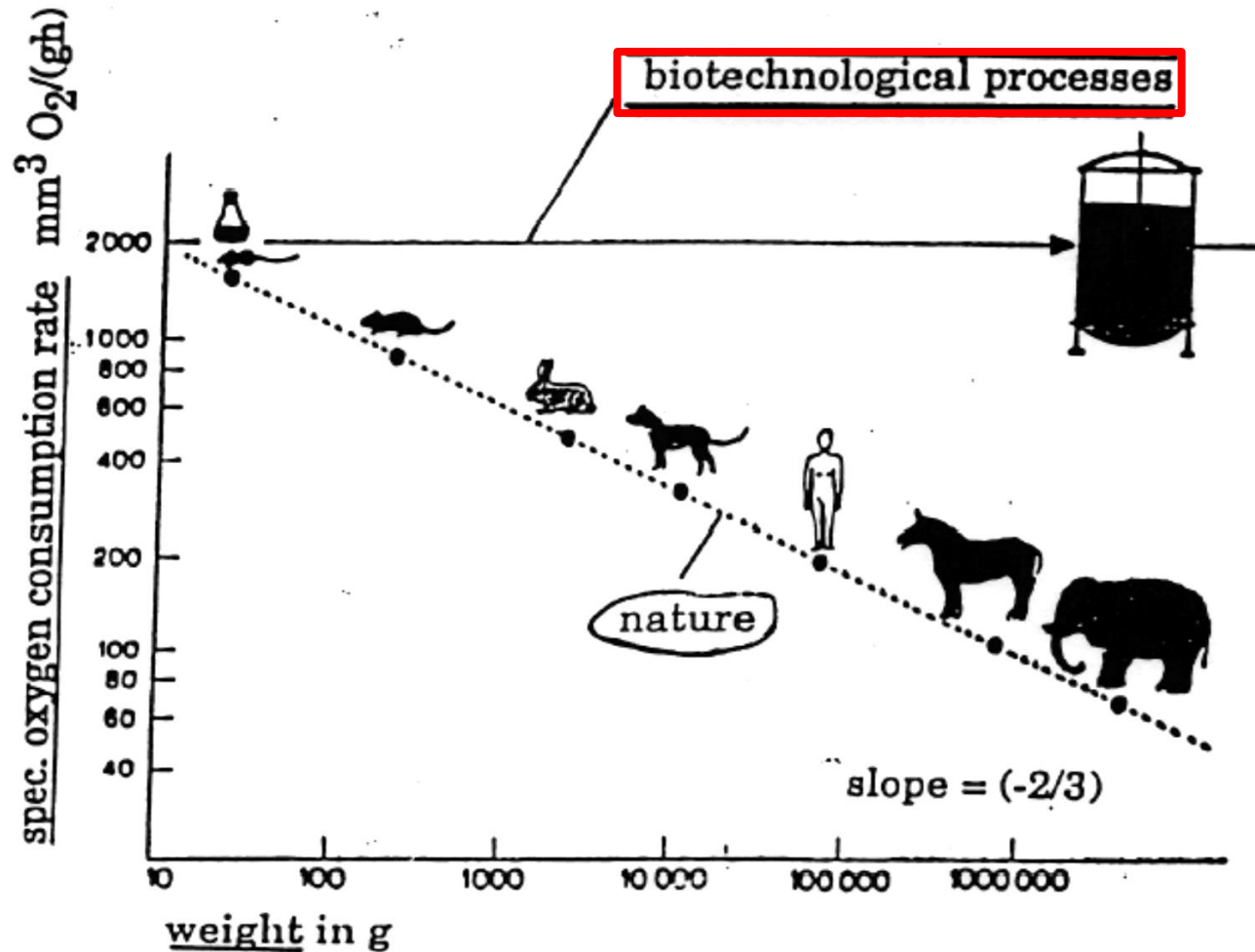**II.4 - Gas-Liquid Mass Transfer in Systems Without Mechanical Agitation**

II.5 - Mass transfer in mechanical agitation systems

In Nature:

1 kcal/h = 1.162 watts

In Nature:

Bioreactors are **artificial systems**

↓

Oxygen needs must be guarantied

↓

Aeration
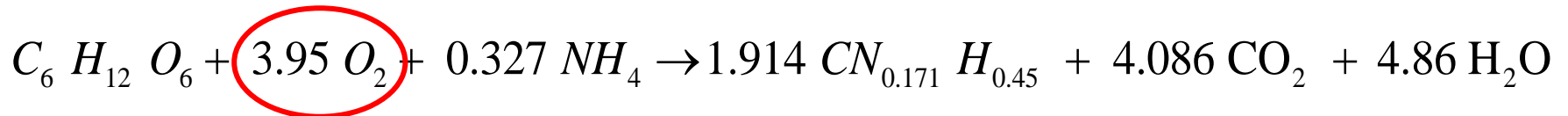Oxygen solubility
Oxygen mass transfer

Importance of the study of mass transfer in biological systems:

- **Nutrients supplied in high concentrations and high solubility**
- **Oxygen has low solubility (7 mg/l)**

➡️ **Limiting step in microbial cultivation**

Example: consumption of O_2 by *S. cerevisiae*

$$C_6\,H_{12}\,O_6 + 3.95\,O_2 + 0.327\,NH_4 \rightarrow 1.914\,CN_{0.171}\,H_{0.45} + 4.086\,CO_2 + 4.86\,H_2O$$

II.1 - Introduction

Oxygen requirements in some processes and by certain microorganisms :

Microorganism/process	Rate of consumption (mg O_2/ g cel h)
Microrganism:	
Aspergillus niger	96
Penicillium chrysogenum	124
S. cerevisae	256
Process:	
Streptomicina	134
Oxitetraciclina	237
Penicilina	64
Levedura	86

1. RATIONALE FOR CONSIDERING OXYGEN TRANSFER

- LOW SOLUBILITY (CAPACITY) IN AQUEOUS BROTH

- OXYGEN REQUIRED IN ALL AEROBIC PROCESSES

- MEASUREABLE (D.O. PROBE)

- TRANSPORT IS PASSIVE (NOT ACTIVE TRANSPORT)

- SHOULD CONSIDER OTHER NUTRIENT TRANSPORT COULD ALSO BE IMPORTANT (OILS, ORGANIC NITROGEN)

2. TIME SCALE FOR OXYGEN DEPLETION

- YEAST ($\mu = 0.2$ h^{-1})

- CELL DENSITY = 15 g/L

- DISSOLVED OXYGEN: FULLY SATURATED = 7 mg O_2/L

- Yx/o = 1 mgX/mgO2

- OXYGEN CONSUMPTION RATE = 0.8 mg O_2/L-sec

- TIME FOR TOTAL DEPLETION $\theta = \dfrac{7.0}{0.80} = 8.7$ seconds

Effect of solutes on solubility

| Concentration (M)	Oxygen solubility (kg m^{-3})		
	HCl	$\frac{1}{2} H_2SO_4$	NaCl
0	4.14×10^{-2}	4.14×10^{-2}	4.14×10^{-2}
0.5	3.87×10^{-2}	3.77×10^{-2}	3.43×10^{-2}
1.0	3.75×10^{-2}	3.60×10^{-2}	2.91×10^{-2}
2.0	3.50×10^{-2}	3.28×10^{-2}	2.07×10^{-2}

Effect of solutes on solubility

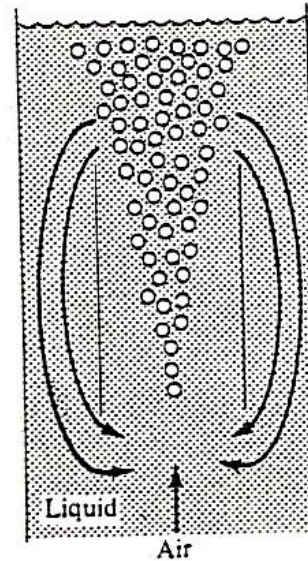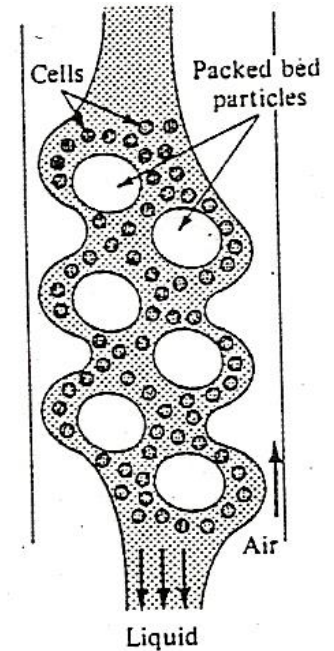| Sugar	Concentration (gmol per kg H_2O)	Temperature (°C)	Oxygen solubility ($kg\,m^{-3}$)
Glucose	0	20	4.50×10^{-2}
	0.7	20	3.81×10^{-2}
	1.5	20	3.18×10^{-2}
	3.0	20	2.54×10^{-2}
Sucrose	0	15	4.95×10^{-2}
	0.4	15	4.25×10^{-2}
	0.9	15	3.47×10^{-2}
	1.2	15	3.08×10^{-2}

Gas-liquid contacting modes
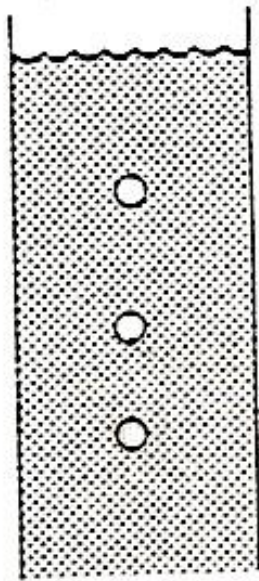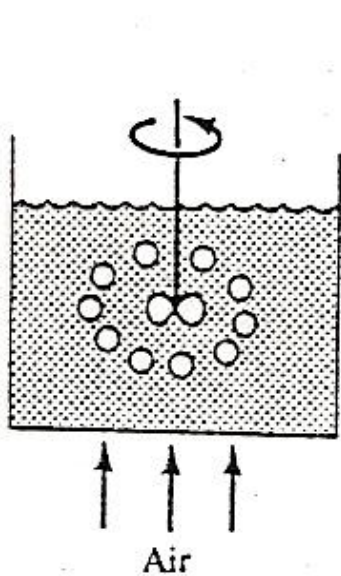

Rising single bubble
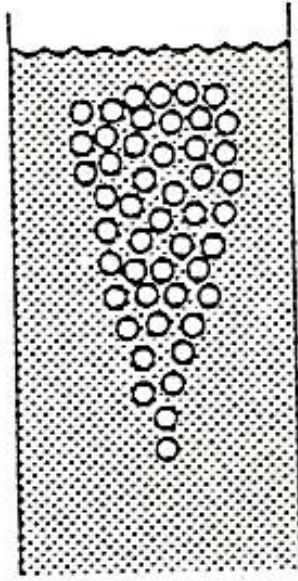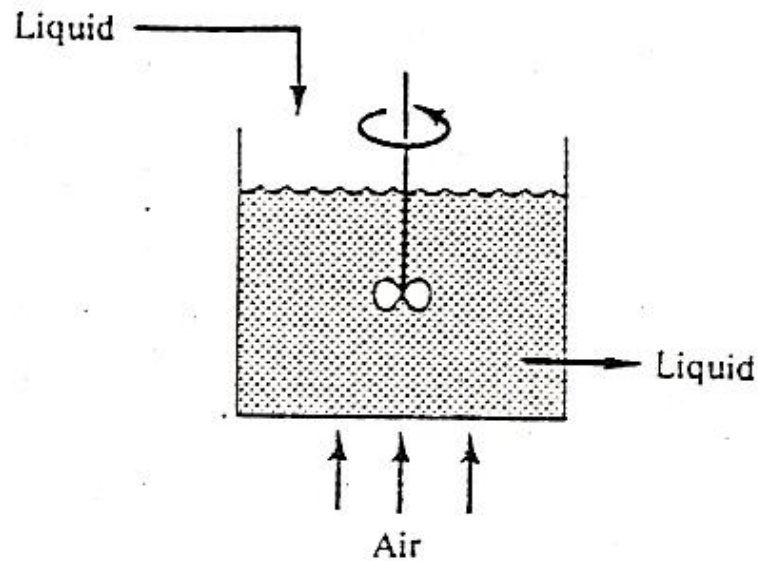
Bubble swarms
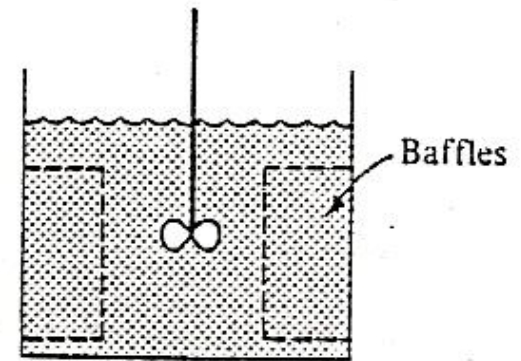
Sparged air lift

Trickling filter counter current
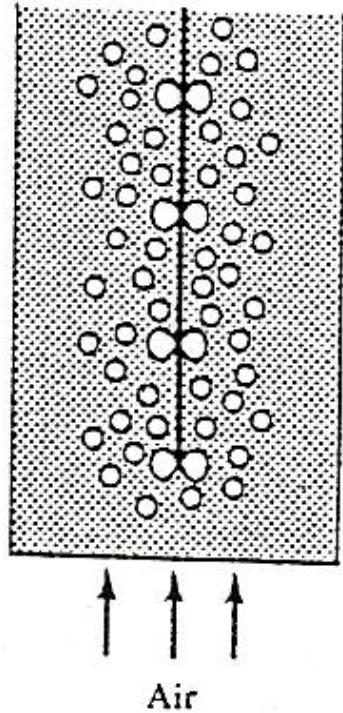
Gas-liquid contacting modes
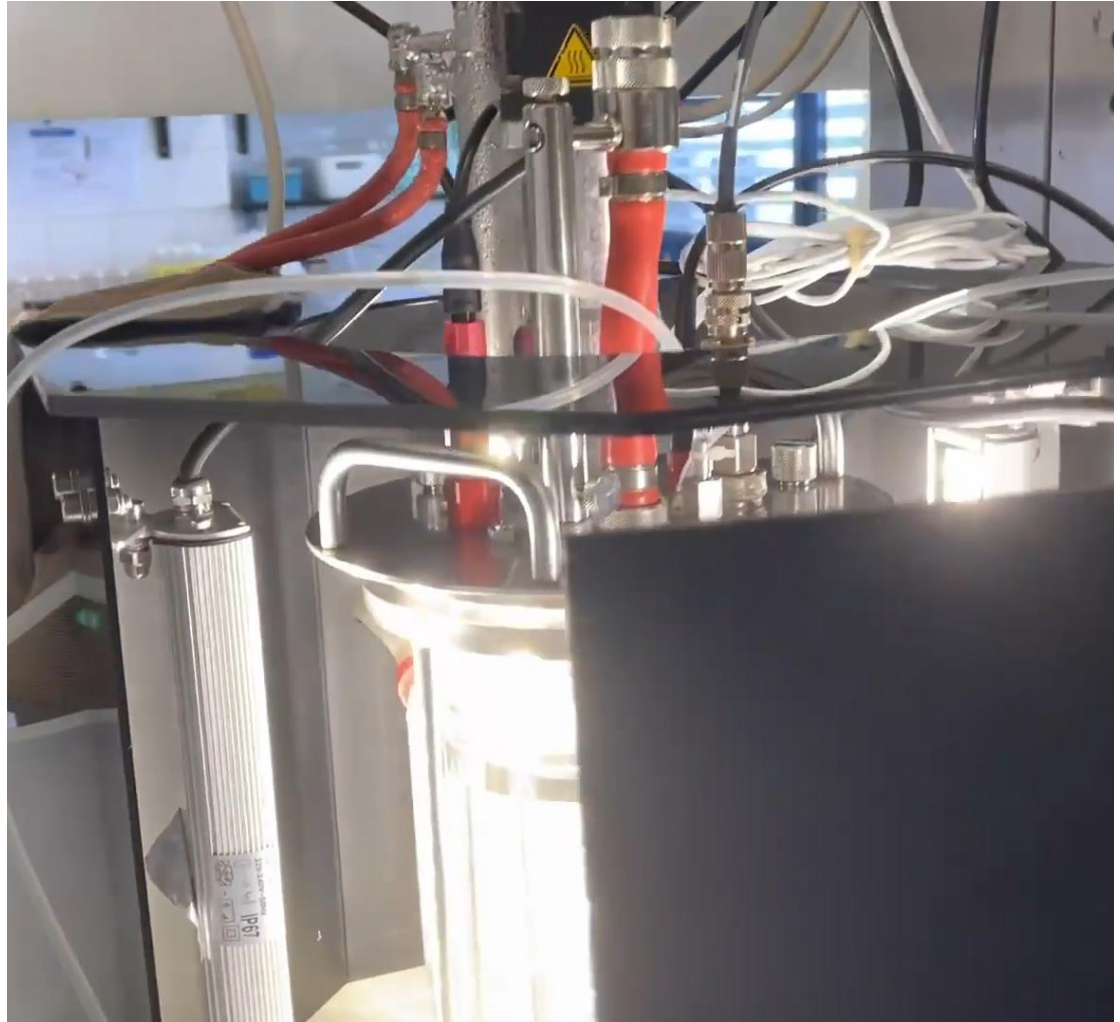

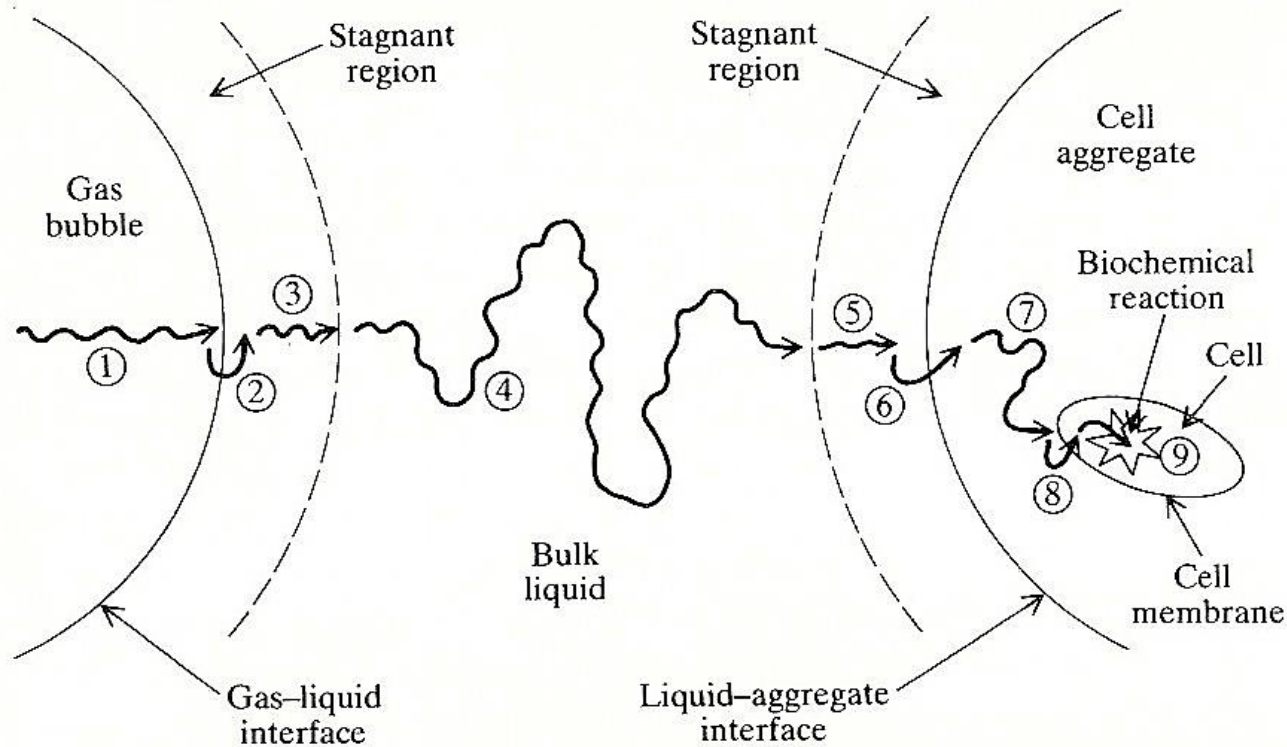| Batch liquid, continuous air | Continuous liquid and air | Stirred tank with baffles |

Gas-liquid contacting modes

Multiple
propeler

Steps involved in O2 transport in biological systems:

Figure 8.1 Schematic diagram of steps involved in transport of oxygen from a gas bubble to inside cell.

When cells are dispersed in the liquid and the medium is well stirred ⟹ the greatest resistance is the one from step 3

Gas-liquid mass transfer is normally modeled by the double-film theory:

Gaseous film | Liquid film

GAS

LIQUID

Cg

Cgi

CLi

CL

Gas-liquid interface

CLi - conc. at the liquid film interface

Cgi - conc. in the gaseous film near the interface
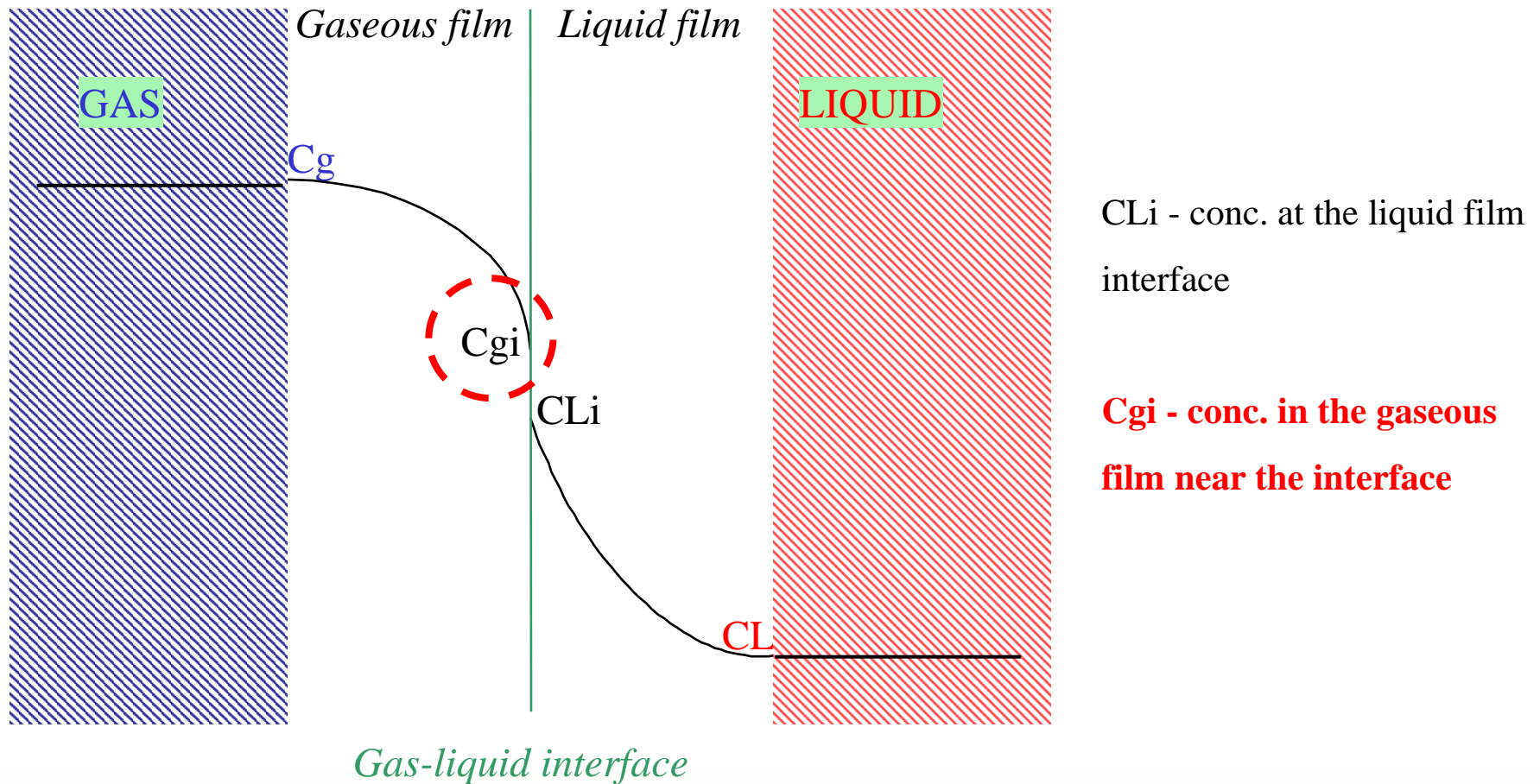
In dilute aqueous solutions (in the case of microbial cultivation), the relationship between concentrations at the gas-liquid interface is given by Henry's Law:

$$C_{Li} \times M = C_{gi}$$

M – equilibrium constant

CLi - conc. at the liquid film interface

Cgi - conc. in the gaseous film near the interface

Oxygen transfer rates in the gaseous film and in the liquid film:

$$N_{ag} = k_g \,(C_g - C_{gi})$$

$$N_{aL} = k_L \,(C_{Li} - C_L)$$

N_{ag} and N_{aL} = oxygen flux (mol cm^{-2} s^{-1})

k_g - mass transfer coefficient in the gaseous film

k_L – mass transfer coefficient in liquid film

C_g - concentration of oxygen in the gas

C_L - oxygen concentration in the liquid

Due to the difficulty in directly measuring interfacial oxygen concentrations, only the global flux is considered:

$$N_a = K_L (C^*_L - C_L) \qquad \text{with:} \quad M \; C^*_L = C_g$$

C^*_L – gas concentration in the liquid phase in equilibrium with the phase gaseous → saturation concentration.

K_L – global mass transfer coeficiente (cm s^{-1})

N_a – global flux of O_2 (mol cm^{-2} s^{-1})

In steady state:

$$N_a = N_{ag} = N_{aL}$$

Global resistance = resistance at liquid film + resistance at gaseous film

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{M\,k_g}$$

For oxygen and carbon dioxide :

– M is greater than 1 $\implies$ $K_L = k_L$

– k_g is typically greater than k_L

The oxygen transfer rate (Q_{O2}) is given by:

$$Q_{O_2} = flux \ \times \ \frac{\text{interface area}}{\text{reactor liquid volume}} = K_L(C_L^* - C_L)\underbrace{\left(\frac{A}{V}\right)}_{a'}$$

Q_{O2} = mol O_2/cm^{3}s

a' = interface área per unit of volume (cm^{-1})

V = Volume of reactor (cm^3)

K_L a' = volumetric mass transfer coefficient

O$_2$ transfer rate $\qquad$ Q$_{O2}$ = K$_L$ a' (C* - C$_L$)

Maximum rate when: $\qquad$ C$_L$ = 0 $\Rightarrow$ Q$_{O2\ max}$ = K$_L$ a' C*

$$r_{O2} = V_{O2}.X = \frac{1}{Y_{x/o2}} \cdot \mu \cdot X$$

$$\mu = \frac{\mu_{max} C_L}{k_{O_2} + C_L}$$

$$r_{O2} = \frac{1}{Y_{x/o2}} \cdot \frac{\mu_{max} C_L}{k_{O2} + C_L} \cdot X$$

Maximum rate: $\qquad \boxed{r_{O2} = \frac{1}{Y_{x/o2}} \cdot \mu_{max} \cdot X}$

In steady state: $\quad r_{O2} = Q_{O2}$

(the oxygen consumption rate, r_{O2}, is equal to the oxygen transfer rate, Q_{O2})

$$K_L\, a'(C_L^* - C_L) = \frac{1}{Y_{x/O_2}}\, \mu x$$

- Kinetic limitation : $\qquad K_L\, a' C_L^* > \dfrac{1}{Y_{x/O_2}}\, \mu_{max}\, x$

- Limitation by mass transfer: $\qquad K_L\, a' C_L^* < \dfrac{1}{Y_{x/O_2}}\, \mu_{max}\, x$

- Calculation of C_L:

If $C_L \ll C_L^*$

$$x_{max} = \frac{K_L a' C_L^*}{\mu} \times Y_{x/O_2}$$

If $C_L \gg$ critical value of O_2 concentration $\Rightarrow$ There is no Limitation (does not depend on O_2)

The critical value varies between 0.003 - 0.05 mmol /l or between 0.1 - 10% of the solubility value

It depends on:
- cell type
- growth phase
- substrate type
- type of process

Type of cells:

TYPICAL CRITICAL DISSOLVED OXYGEN CONCENTRATION (Low Density Cultures)	
ORGANISM	**CRITICAL DISSOLVED OXYGEN (% Air Saturation)**
E. coli	3.4%
S. marcescens	6.3%
S. cerevisiae	1.9%
P. chrysogenum	9.1%
A. niger	8.3%

Table 8.2 Typical values of $c_{O_2, cr}$ in the presence of substrate[†]

Organism	Temp, °C	$c_{O_2, cr}$, mmol/L
Azotobacter vinelandii	30	0.018–0.049
E. coli	37.8	0.0082
	15	0.0031
Serratia marcescens	31	~0.015
Pseudomonas denitrificans	30	~0.009
Yeast	34.8	0.0046
	20	0.0037
Penicillium chrysogenum	24	~0.022
	30	~0.009
Aspergillus oryzae	30	~0.020

[†] Summarized by R. K. Finn, p. 81 in N. Blakebrough (ed.), *Biochemical and Biological Engineering Science*, vol. 1, Academic Press, Inc., New York, 1967.
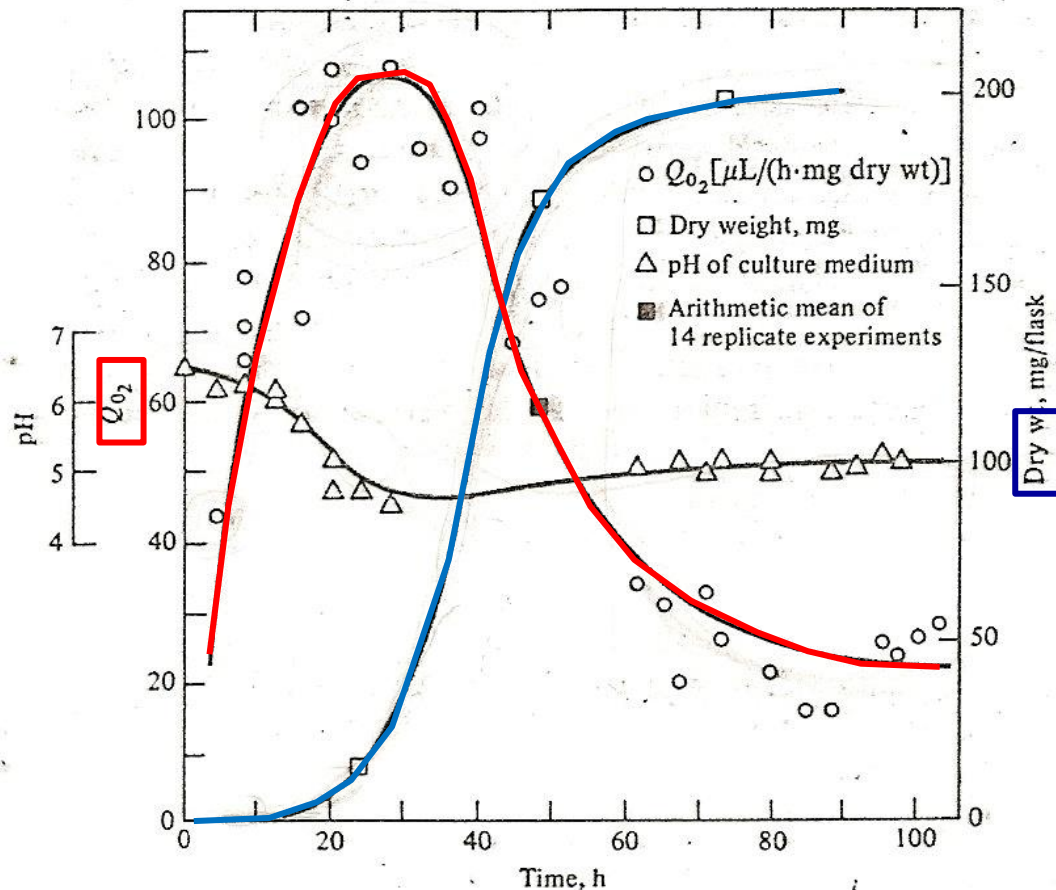
Growth phase:

Figure 8.5 Oxygen utilization rate in batch culture of *Myrothecium verrucaria* [Reprinted from R. T. Darby and D. R. Goddard, Am. J. Bot., vol. 37, p. 379 (1950).]

Type of substrate:

rate of substrate consumption O_2 (mmol/l h)

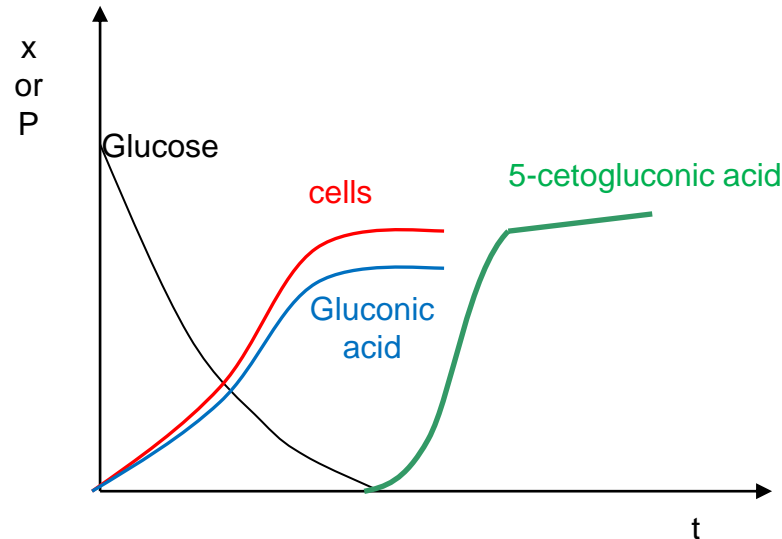(ex: glucose is at higher rate)

• For more reduced compounds ⇨ Higher oxygen consumption

(ex: parafines and methane)

• The consumption of O2 in fermentations with hydrocarbons is 2.5 to
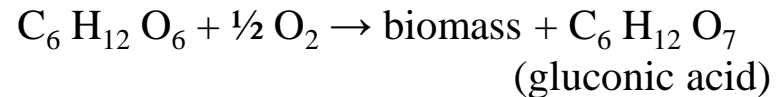
3 times higher than that consumed with carbohydrates.

Type of process:

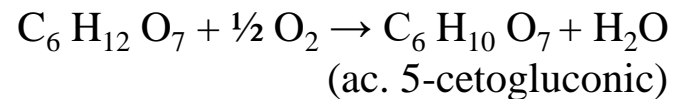a) Biological oxidation: $\qquad$ $C_6 H_{12} O_6 + \frac{1}{2} O_2 \rightarrow$ biomass $+ C_6 H_{12} O_7$

(gluconic acid)

b) Chemical oxidation: $\qquad$ $C_6 H_{12} O_7 + \frac{1}{2} O_2 \rightarrow C_6 H_{10} O_7 + H_2O$

(ac. 5-cetogluconic)

In a) oxygen is used for: biomass and product (gluconic acid)

In b) oxygen is used as reagent (oxidant) $\rightarrow$ biotransformation
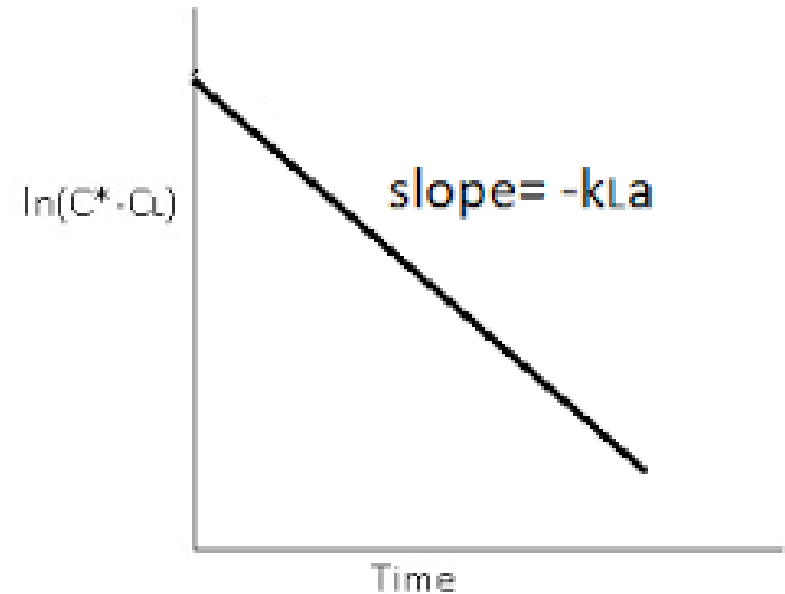
Cálculo do KLa' – Método dinâmico

$$\frac{dO_2}{dt} = K_L a'(C*-CL)$$
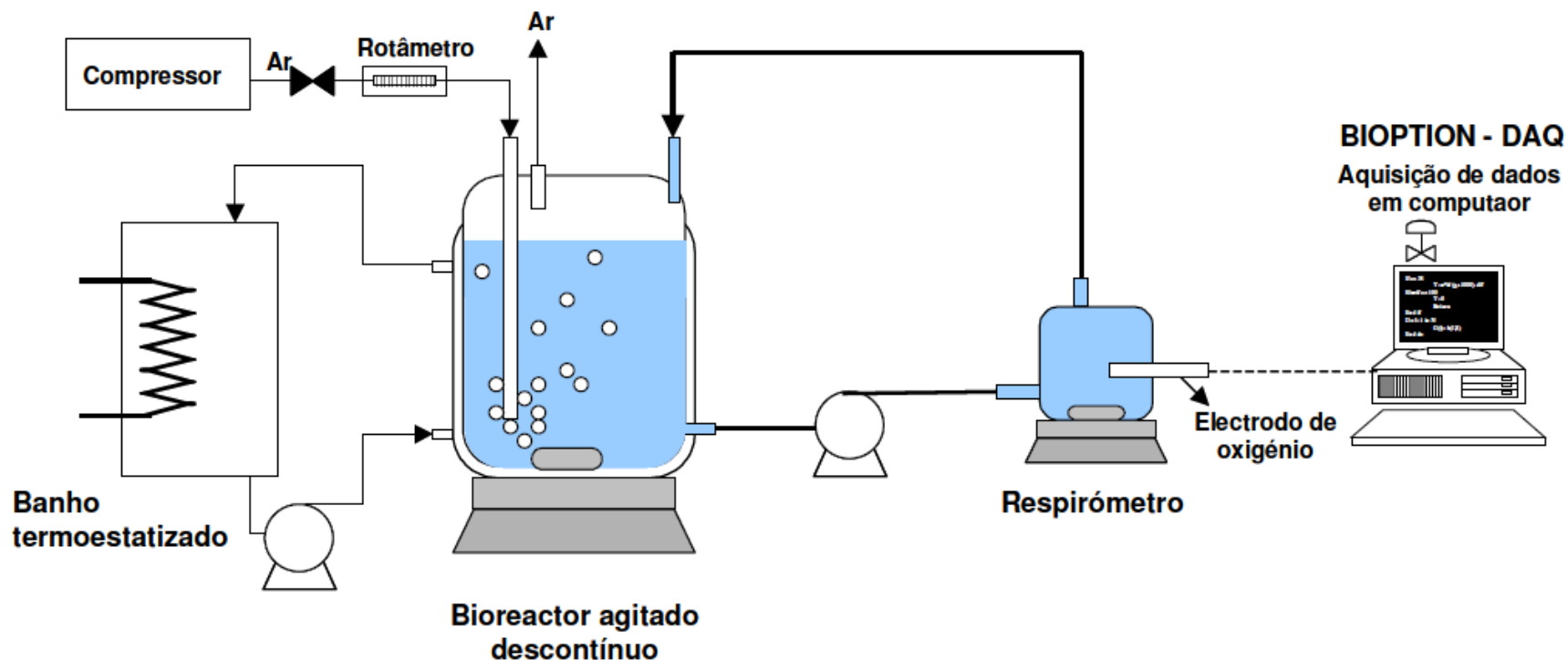
$$\Leftrightarrow dO_2 = K_L a'(C*-CL)\,dt$$

$$\Leftrightarrow \int \frac{1}{(C*-CL)}\,dO_2 = K_L a' \int dt$$

$$\Leftrightarrow \ln(C*-CL) = K_L a't + cte$$

$\ln(C^* \cdot C_L)$ slope= -kLa   Time

Cálculo do KLa' – Método dinâmico

Determination of K_L

the mass transfer coefficient - K_L - varies with: - fluid properties
                                                          - flow conditions
                                                          - physical system geometry

Dimensionless Numbers:

❑ Sherwood number (Sh)   allows to calculate K_L

❑ Grashof number (Gr)   is the ratio of gravitational and viscous forces

❑ Schmidt number (Sc)   gives a measure of the properties of the fluid

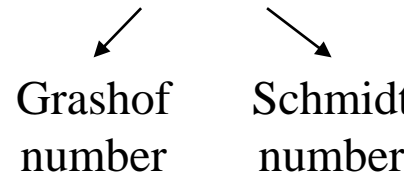❑ Reynolds Number (Re)   gives a measure of the physical properties of the fluid and the fluid velocity

Sherwood number

$$Sh = \frac{K_L . D_p}{D_{O2}}$$

D_p − bubble diameter

D_{O2} − oxygen diffusivity

$$Sh = 0{,}42 . \sqrt[3]{Gr} . \sqrt{Sc}$$

Grashof number   Schmidt number

$$Gr = \frac{D_p^3 . \rho_L . \Delta\rho . g}{\mu_L^2}$$

ρ_L − density of the liquid

$\Delta\rho = \rho_L - \rho_G$

g − gravitational acceleration

$$Sc = \frac{\mu_L}{\rho_L . D_{O2}}$$

μ_L − viscosity of the liquid

Reynolds Number (Re)

Density of fluid

Velocity of fluid

$$Re = \frac{\rho V D}{\mu}$$

Diameter of pipe

Reynolds Number

Dynamic Viscosity of fluid

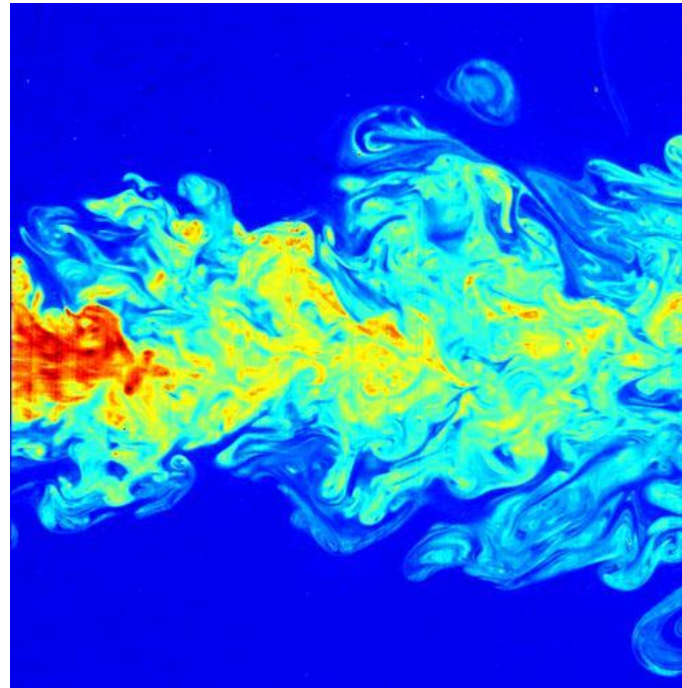•gives a measure of the physical properties of the fluid and the fluid velocity.

Determines the regime	$Re < 2300 \ (\pm \ 10^3)$	laminar regime
of the fluid	$Re > 10^4$	turbulent regime
	Re between 10^3 e 10^4	transition regime

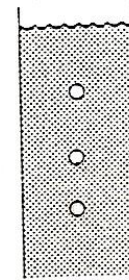**Reynolds Number (Re)**
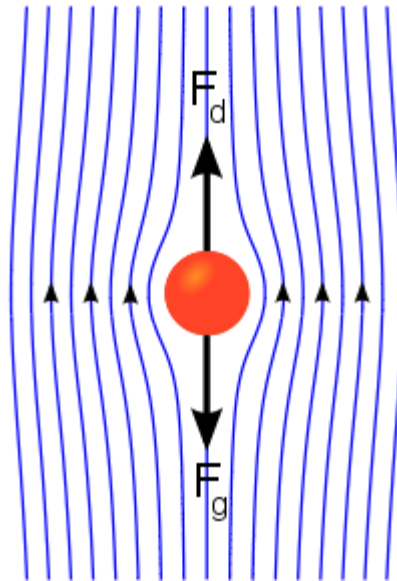
laminar regime

turbulent regime

Reynolds Number (Re)

• Correlations for dispersed bubbles ("single bubbles")

a) for <u>small</u> Reynolds number (Re << 1)

$$Sh = \frac{K_L D_P}{D_{O_2}} = 1.01 \left(\frac{V_t D_P}{D_{O_2}} \right)^{\frac{1}{3}}$$

Pe = Peclet number

$$Sh = 0.39 \, (Gr)^{\frac{1}{3}} (Sc)^{\frac{1}{3}} = 0.39 \, (Ra)^{\frac{1}{3}}$$

Ra = nº Rayleigh

V_t = particle terminal velocity (gas bubble)

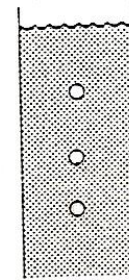$$V_t = \frac{D_P^2 \Delta \rho g}{18 \mu_L}$$

Stokes equation

Reynolds Number (Re)

• Correlations for dispersed bubbles ("single bubbles")
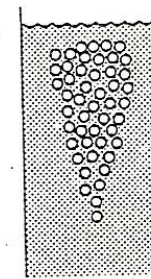
    b) for **high** Reynolds number (Re >> 1)

$$Sh = 2.0 + 0.6 \, Re^{\frac{1}{2}} \, Sc^{\frac{1}{3}}$$

$$Sh = 2.0 + 0.6 \left(\frac{D_P^3 \, \rho \, \Delta\rho \, g}{18 \quad \mu_L^2} \right)^{\frac{1}{2}} (Sc)^{\frac{1}{3}}$$

Gr

Reynolds Number (Re)

• Correlations for bubbles clusters ("bubbles swarms")

Critical bubble diameter - **Dc = 2.5 mm**

i) $D < D_C$ Small bubbles
i) $D > D_C$ Large bubbles

i) Correlations for Small Bubbles : D < 2.5 mm

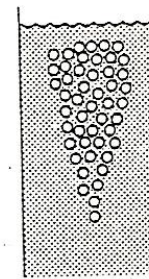$$Sh = 2.0 + 0.31 Ra^{\frac{1}{3}}$$

For $\Delta\rho = 0$ Sh = 2 (minimum value)

$$Sh = 2.0 + 0.31 Gr^{\frac{1}{3}} Sc^{\frac{1}{3}}$$

Reynolds Number (Re)

• Correlations for bubbles clusters ("bubbles swarms")

ii) Correlations for large Bubbles : D > 2.5 mm

$$Sh = 0.42 Gr^{\frac{1}{3}} Sc^{\frac{1}{2}}$$

Comparison between i) and ii):

i) Sh = f (Sc$^{1/3}$)

ii) Sh = f (Sc$^{1/2}$)

It implies a change of hydrodynamic regime

Changing the shape of bubbles

Spherical shape for small bubbles
semi-spherical shape for large bubbles

Determination of the interfacial area and "Hold-Up"

The **interfacial area per volume unit** (a') is defined by :

$$a' = \frac{1}{V_L} \; n \; Fo \; tb \; \frac{6}{D}$$

Aeration
rate

V_L – Liquid volume of the reactor

n – Number of dispersor orifices

Fo – Gas flow per orifice

tb – Residence time of bubbles in the reactor

D – diameter of the bubble

Determination of the interfacial area and "Hold-Up"

The **interfacial area per volume unit** (a') is defined by :

$$a' = \frac{1}{V_L}\, n\, Fo\, tb\, \frac{6}{D}$$

V_L – Liquid volume of the reactor
n – Number of dispersor orifices
Fo – Gas flow per orifice
tb – Residence time of bubbles in the reactor

"**Hold-up**" is defined as:

$$H = \frac{\text{Gas } Volume}{\text{Gas volume } + \; líquid \;\; \text{volume}}$$

can be calculated by:

$$a = H\, \frac{6}{D}$$

a - interfacial area per unit of total volume (gas volume and liquid volume)

relationship between a and a' is given by:

$$a'\,(1\text{-}H) = a$$

Determination of the interfacial area and "Hold-Up"

Residence time of bubbles (tb) is given by:

$$t_b = \int_o^{hr} \frac{dz}{u_b(z)} = \frac{h_r}{v_t}$$

h_r – reactor height
v_t – terminal velocity

The particle **terminal velocity** (v_t) can be calculated by:

Stokes Law
$$v_t = \frac{D^2 \Delta \rho\, g}{18 \mu c}$$
Valid for small bubbles and small Reynolds numbers

$$v_t = 0{,}711(gD)^{\frac{1}{2}} = 22{,}26\,(D)^{\frac{1}{2}}$$
Valid for large bubbles in Newtonian fluids

<u>Factors influencing K_La´</u>

- K_L

  - Diffusivity of the gas in the liquid

  - Surfactants that affect interfacial properties

  - Liquid rheology

  - Bubble size

  - Liquid flow regime

- $a´$

  - Bubble size: - mechanical stress

                              - use of surfactants

   - Terminal velocity of bubbles

  - "Hold-up"

Factors influencing K$_L$a´

Adition of surfactants – antifoams:

$\Rightarrow$ Decreases surface free energy $\Rightarrow$ σ is lower

$\Rightarrow$ D is smaller

$\Rightarrow$ greater liquid gas interfacial area

$\Rightarrow$ Interface gas-liquid $\Rightarrow$ increases the resistance

more rigid   to transport

II.4 - Systems Without Mechanical Agitation

$K_L a´$ values in industrial fermenters

The mass transfer rate is affected by physical and chemical factors that influence K_L, a' and $(C^*_L - C_L)$

In industrial fermenters the K_L values vary :

$$3 - 4 \times 10^{-4} \text{ m/s} \qquad \text{for bubbles} > 2\text{-}3 \text{ mm}$$

$$1 \times 10^{-4} \text{ m/s} \qquad \text{for bubbles} < 2 \text{ mm}$$

To improve mass transfer rate, a' is the key parameter.

In industrial fermenters the value of K_L a' is : $0,02 - 0,25$ s^{-1}.

i)   agitation causes a decrease in the size of the bubble

⇒ a' increases ⇒ mass transfer increases (if there is no coalescence of bubbles)

ii) stirring leads to a homogeneous dispersion of different phases (solid-liquid)

iii) agitation leads to a decrease in the size of the mycelium/fungus and cell aggregates ⇒ lower diffusion resistance inside

(Agitation can cause loss of enzymatic activity (enzyme damage), morphological change)

iv) Agitation is particularly useful in viscous systems (improves the degree of mixing in the fermentation medium).

v) Agitation increases heat transfer rates - dissipation of heat generated by biological reaction and mechanical work.

Type of Impellers

Helical Agitator

Propeller Agitator

Turbine Agitator

Anchor Agitator

Paddle Agitator

https://chemicalengineeringworld.com
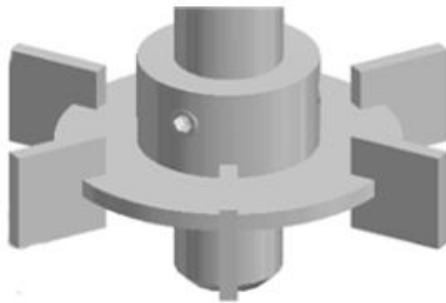
Type of Impellers

Rushton

radial flow
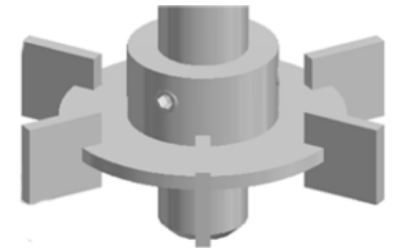for microbial applications

Pitch-blade / marine

axial flow
shear sensitive applications

Type of Impellers

a) **Axial Flow Impellers** - Blades have a slope with the impeller

b) **Radial Flow Impellers** - Blades are parallel to agitator axis

- High agitation rates
- n° blades > 4
} Turbines

- Low agitation rates
- 2 or 4 blades
} Impellers with blades

Type of Impellers

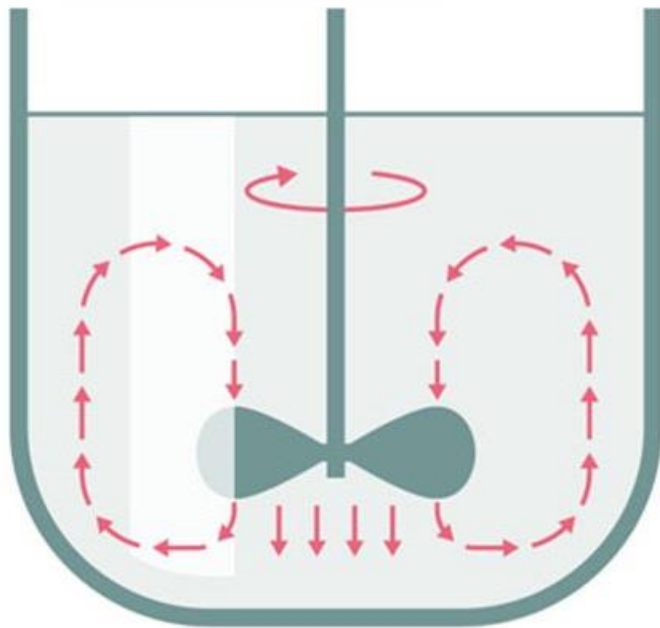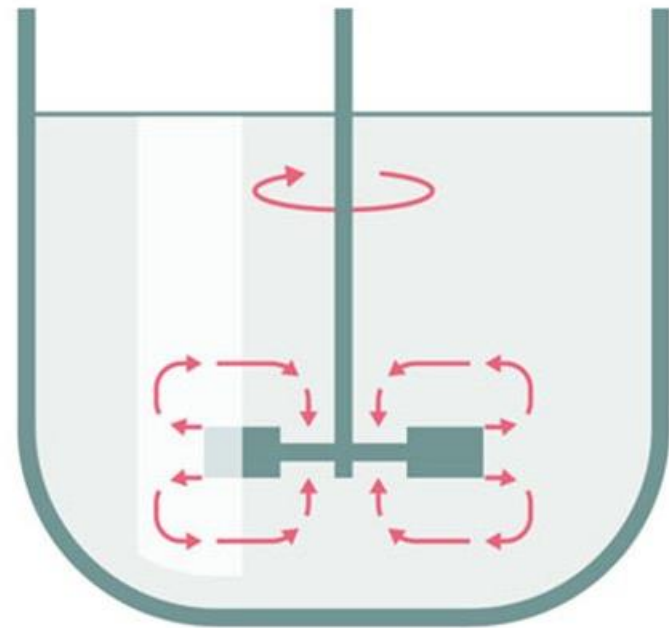|					
(C) RADIAL	Rushton Turbine (RT)	Straight Blade (SB)	Curved Blade (CB)	R130 impeller	Curved Blade with Disc (CBWD)
(D) AXIAL	Rushton Turbine 45 (RT 45)	Pitched Blade Turbine (PBT)	A320 impeller	HE3 impeller	

Type of Impellers

> **Reynolds number in relation to the fluid:**

$$Re = \frac{\rho_L \, D \, v}{\mu_L}$$

ρ_L – density of the liquid

D – diameter

v – fluid velocity

μ_L – viscosity of the liquid

> **Reynolds number in relation to the impeller:**

$$Re = \frac{\rho_L \, D_i^2 \, N_i}{\mu_L}$$

ρ_L – density of the liquid

D_i – impeler diameter

N_i – stirring rate

μ_L – viscosity of the liquid

II.5 - Mass transfer in mechanical agitation systems

➢ **Agitation Power:** Only Newtonian Fluids will be considered

Power number – P_{no}

$$P_{no} = \frac{P}{N_i^3 \, D_i^5 \, \rho}$$

P = agitation power (W = Kg m^2/s^3)
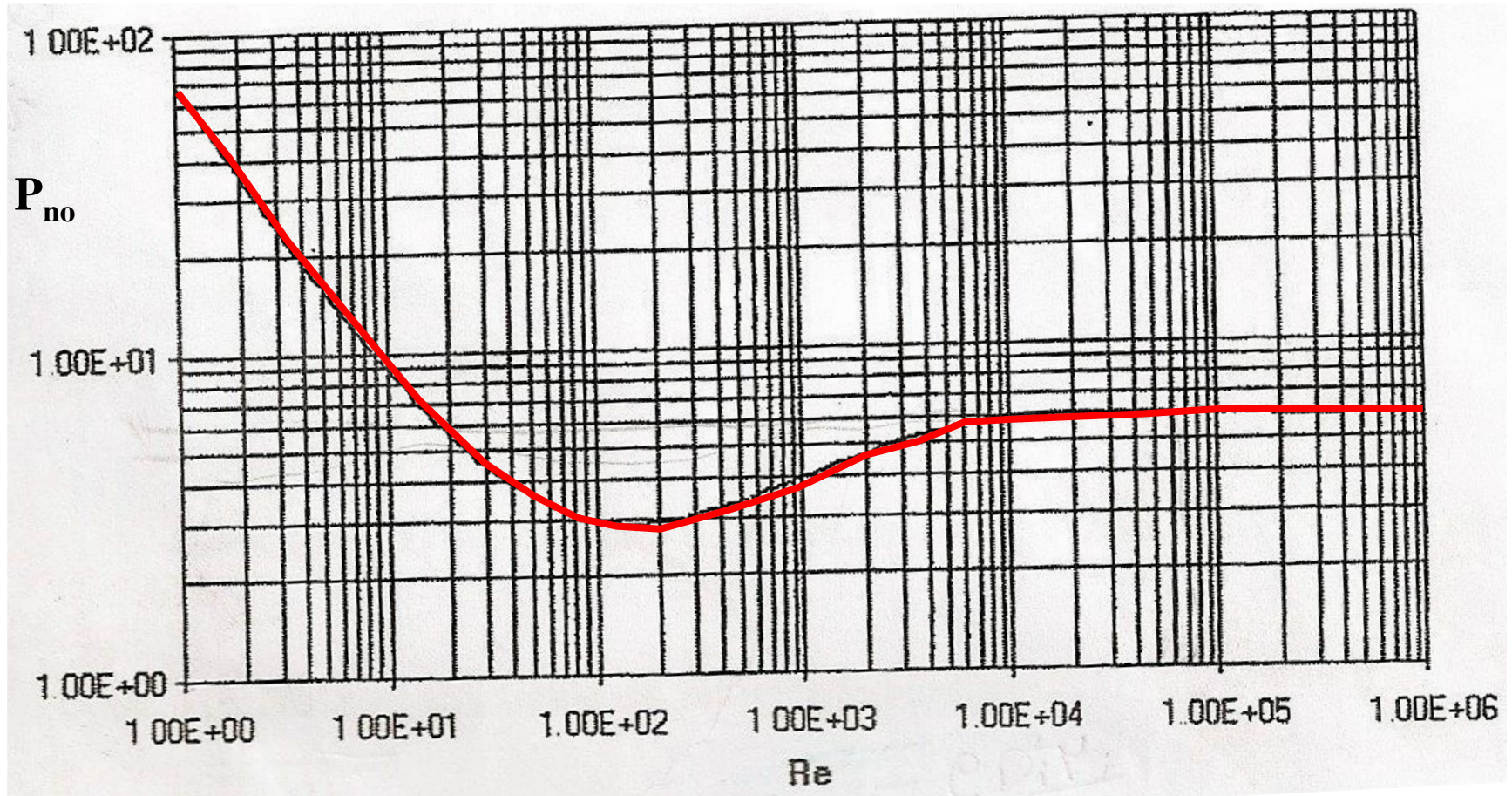g = 9.81 m/s^2
Ni = stirring rate (s^{-1})
Di = impeller diameter (m)
ρ = density (Kg/m^3)

turbulent regime : $\quad P_{no} = \dfrac{P}{N_i^3 \, D_i^5 \, \rho} \Rightarrow P = P_{no} \, N_i^3 \, D_i^5 \rho$ independent of fluid viscosity and proportional to fluid density

laminar regime : $\quad P_{no} \propto \dfrac{1}{R_{ei}} \Rightarrow P \propto N_i^2 \, D_i^3 \, \mu$ independent of fluid density and is directly proportional to fluid viscosity

➢ **Agitation Power:**

➢ **Power in aerated systems with stirring:**

In these systems the power requirements are lower than in non-aerated systems.

The decrease in power requirement depends on the aeration rate and the type of impeller.

The aeration velocity is characterized by the aeration number Na:

$$N_a = \frac{F_g / D_i^2}{N_i\, D_i} = \frac{F_g}{N_i\, D_i^3}$$

Fg – Volumetric gas flow rate

Fg / Di^2 – surface flow rate

> **Power with aeration:** for Newtonian Fluids

$$\frac{P_a}{P} = 0.10 \left(\frac{F_g}{N_i\, V} \right)^{-0.25} \left(\frac{N_i^{\,2} D_i^{\,4}}{g\, w_i\, V^{2/3}} \right)^{-0.20}$$

P_a – Power with aeration
P – Power without aeration
F_g – Gas flow rate
N_i – Agitator agitation speed
V – Liquid Volume
D_i – Impeller diameter
g – Aceleration of gravity
w_i – Agitator Blade Width

Power consumption per unit volume for Industrial fermenters is around 10 kW/m³ for small volumes (0.1 m³) and 1 – 2 kW/m³ for large volumes (100 m³).