The Abdus Salam International Centre for Theoretical Physics

2218-12

Mediterranean School on Nano-Physics
held in Marrakech - MOROCCO

2 - 11 December 2010

Pressure driven membrane process and their applications

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PRESSURE-DRIVEN MEMBRANE PROCESSES AND THEIR APPLICATIONS

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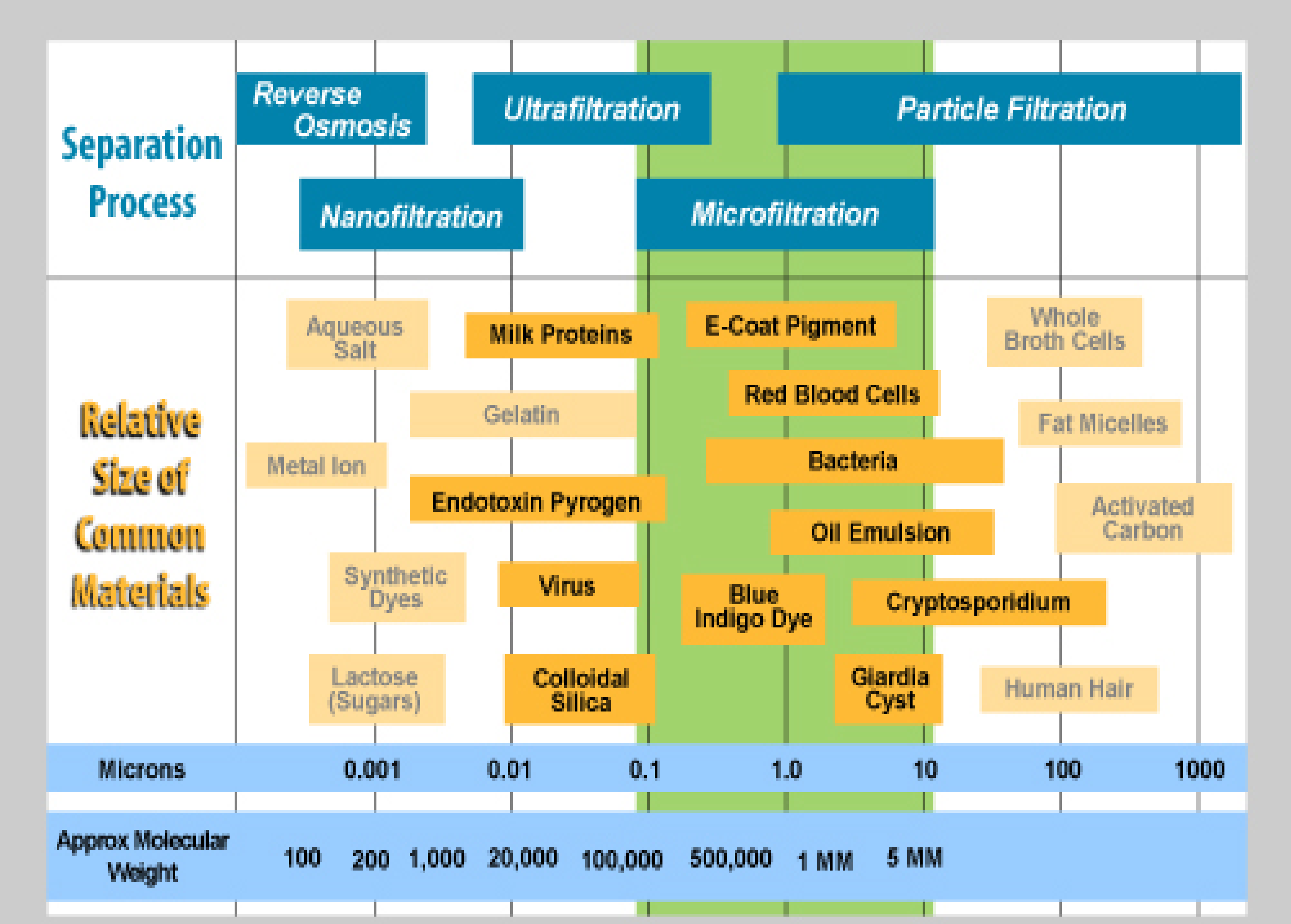
MEMBRANE SEPARATION PROCESSES

DRIVING FORCE

Hydrostatic pressure gradient	Conentration gradient	Electrochemical potential	Partial pressure gradient
MF, UF, NF, RO, gas separation	Dialysis	Electro-dialysis, EDR	Pervaporation MD, OD

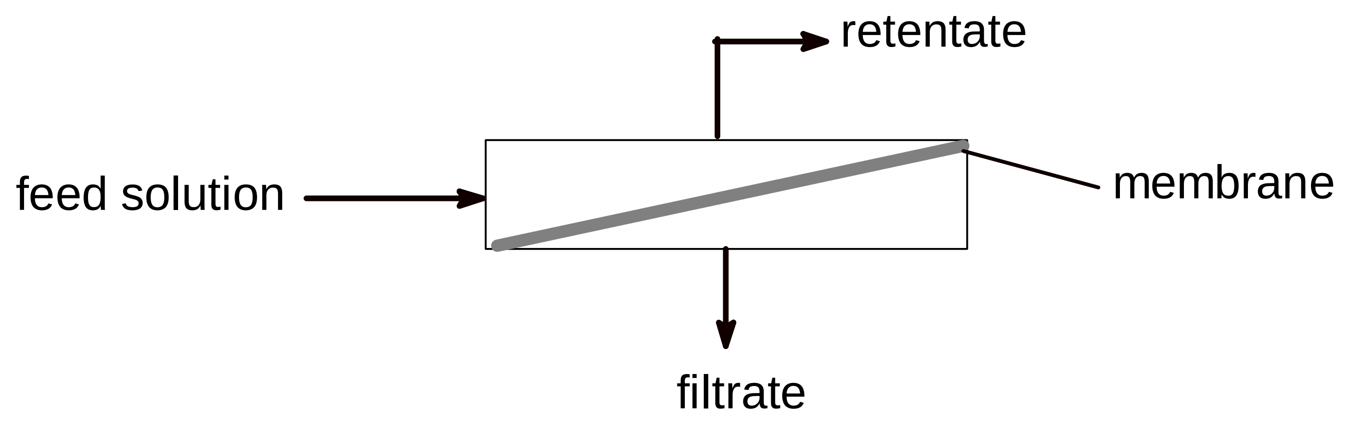
Technically relevant pressure-driven membrane separation processes

Separation process	Membrane type used	Applied driving force	Mode of separation	Applications
Microfiltration (MF)	symmetric macroporous, pore radius 0.1-10 µm	hydrostatic pressure 0.05-0.2 MPa	size exclusion, convection	water purification, sterilization
Ultrafiltration (UF)	asymmetric macroporous, pore radius 2-10 nm	hydrostatic pressure 0.1-0.5 MPa	size exclusion, convection	separation of molecular mixtures
Diafiltration (DF)	asymmetric macroporous, pore radius 2-10 nm	hydrostatic pressure 0.1-0.5 MPa	size exclusion and dialysation, diffusion	purification of molecular mixtures artificial kidney
Nanofiltration (NF)	asymmetric mesoporous, pore radius 0.5-2 nm	Hydrostatic pressure 0.3 – 3 MPa	Size exclusion, diffusion, Donnan-exclusion	separation of molecular mixtures and ions
Reverse osmosis (RO)	asymmetric skin-type, dense or microporous	hydrostatic pressure 1-10 MPa	solution-diffusion mechanism	sea & brackish water desalination



Note: 1 micron (micrometer) = 4 x 10-5 inches = 1 x 104 Angstrom units

GENERAL SCHEME OF A SEPARATION PROCESS



The performance of pressure-driven membrane separation process is mainly determined by:

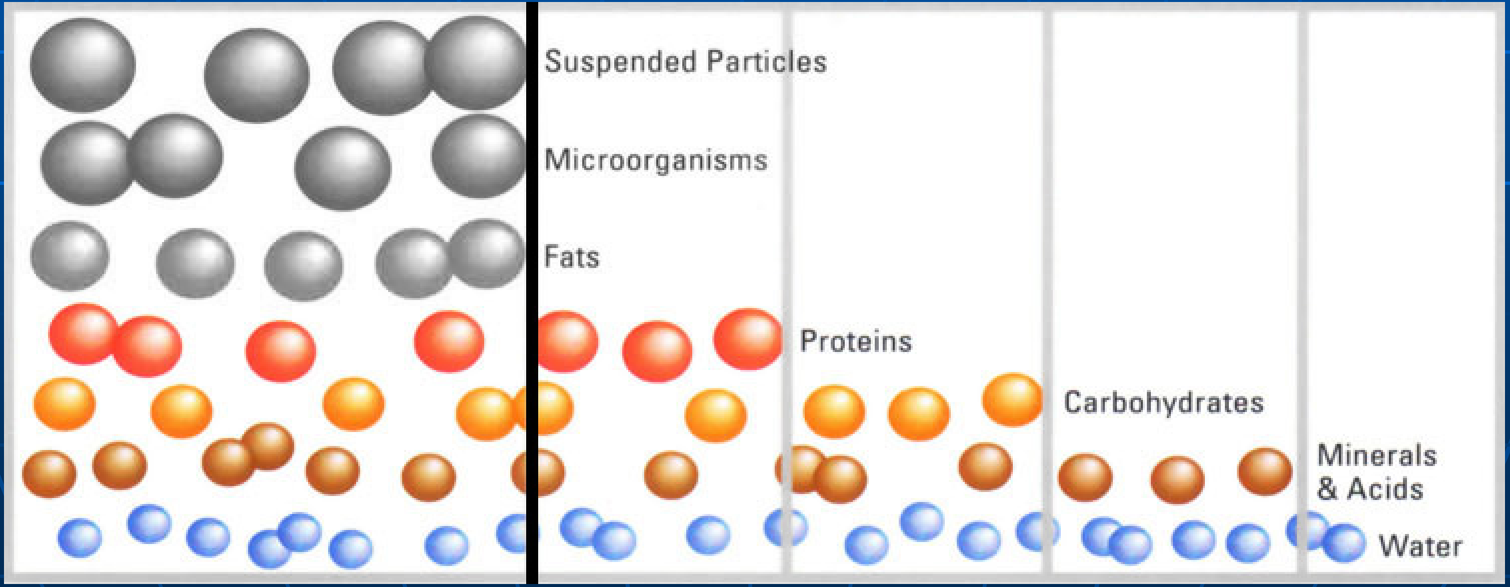
- filtration rate (membrane flux)

- membrane rejection

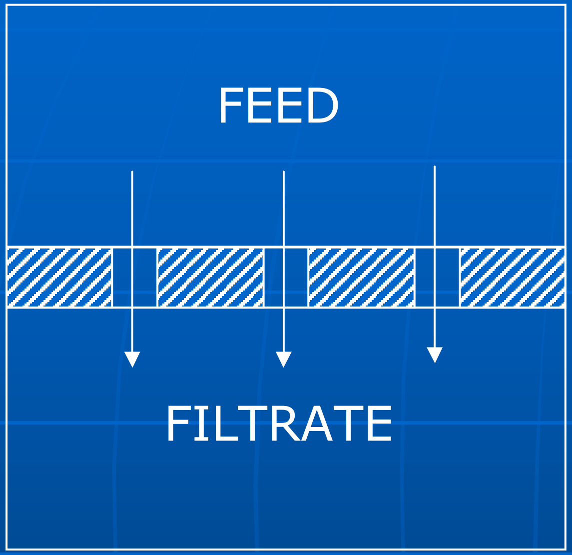
REJECTION COEFFICIENT

$$R_i = \left(1 - \frac{C_i^p}{C_i^f}\right) \leq 1$$

C: concentration; superscripts *f* and *p:* feed and permeate or filtrate solutions, respectively.



Referring to the system:



FEED

FILTRATE

$V^f C_i^f$

$V^p C_i^p$

Recovery ratio: ratio of the filtrate to the feed volume.

$$\Delta = \frac{V^p}{V^f}$$

MASS BALANCE:

$$V^f C_i^f = V^r C_i^r + V^p C_i^p$$

feed

retentate

permeate
or filtrate

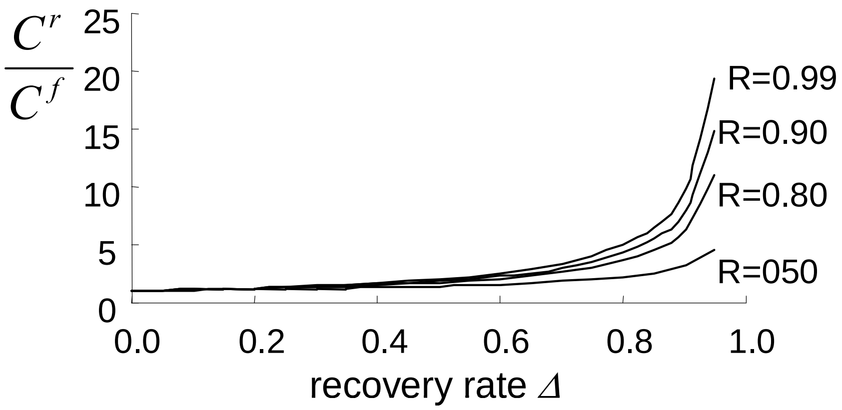
Rearranging previous equations:

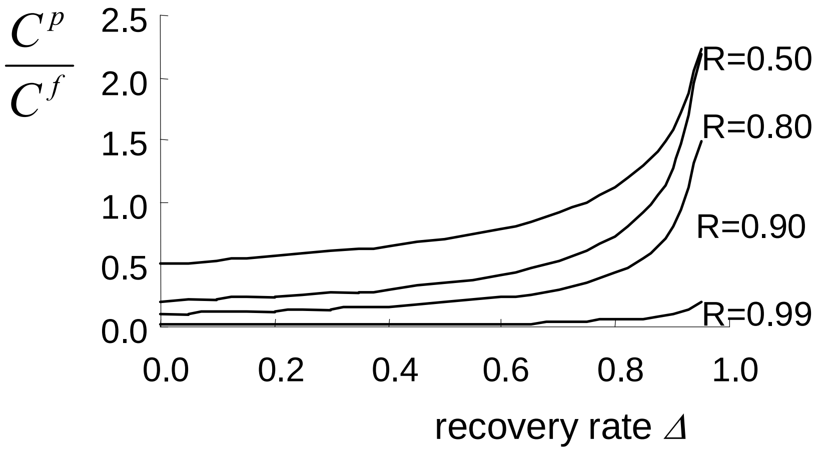
RETENTATE

$$C_i^r = C_i^f \left(1 - \Delta\right)^{-R}$$

PERMEATE

$$C_i^p = C_i^f \left(1 - R\right)\left(1 - \Delta\right)^{-R}$$





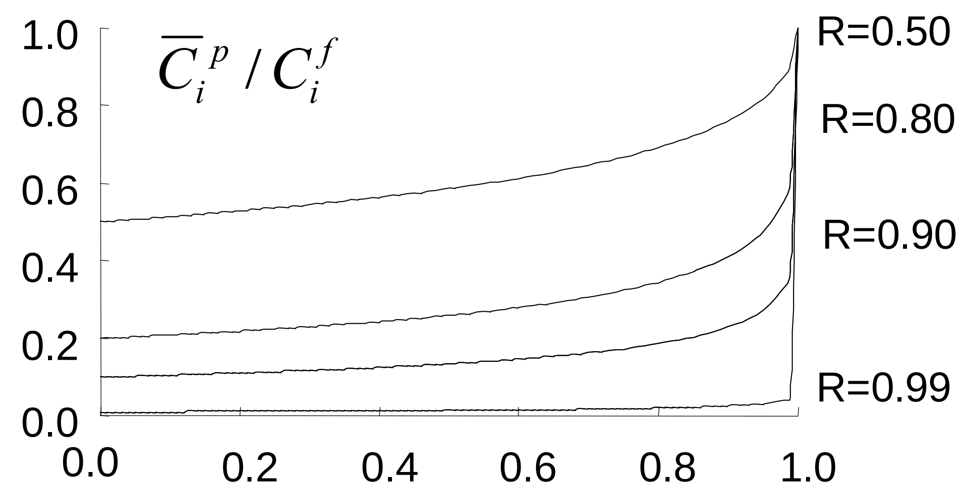
Definition: MIXING CUP CONCENTRATION

The value of concentration obtained when the entire filtrate up to a given recovery rate is collected and mixed

$$\overline{C}_i^p = \frac{C_i^f}{\Delta}\left[1-(1-\Delta)^{1-R}\right]$$

In membrane evaluation or characterization tests, the rejection *R* of a membrane can be calculated from two easily measurable values, i.e. the mixing cup filtrate concentration and feed concentration:

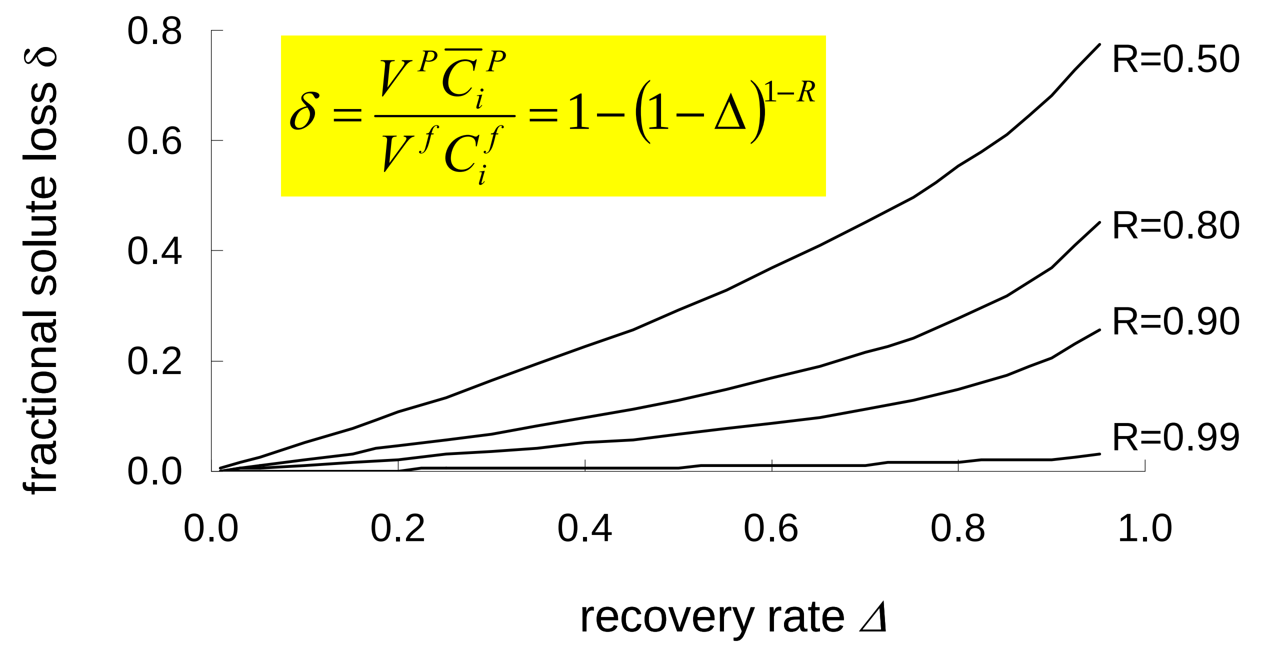
$$R = 1 - \frac{\ln\left(1-\frac{\overline{C}_i^p\Delta}{C_i^f}\right)}{\ln(1-\Delta)}$$



SOLUTE LOSSES IN MEMBRANE FILTRATION PROCESSES

For membranes that are not strictly semipermeable some solute will permeate the membrane with the filtrate. This may affect the quality of the filtrate, or lead to product losses.

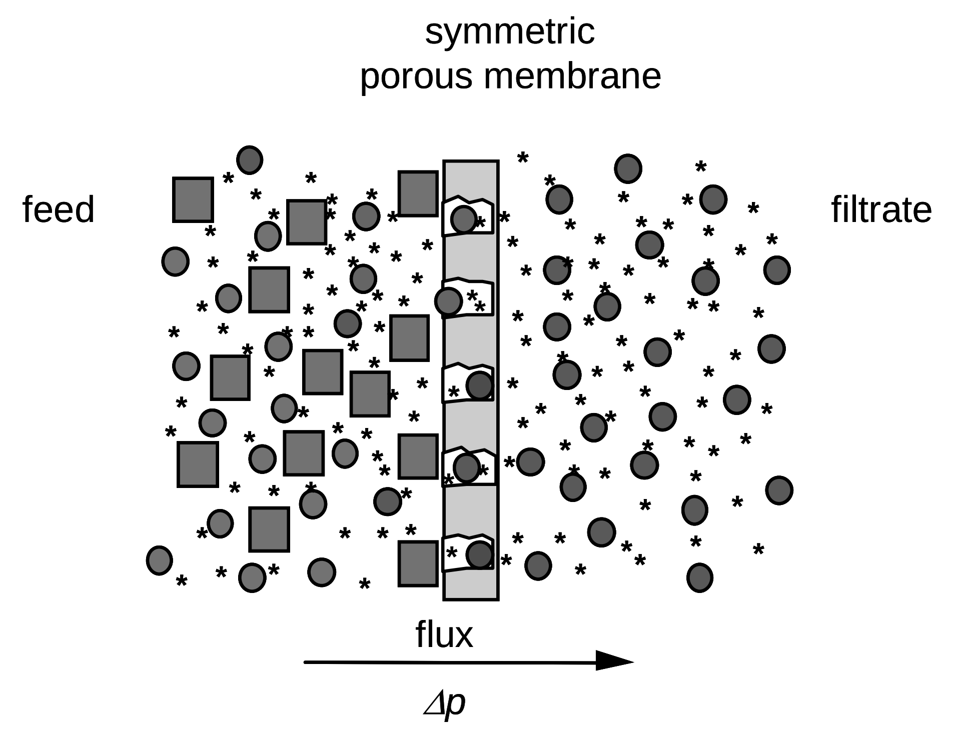
The *fractional solute loss* δ of a component *i* is usually expressed by the amount of solute lost with the filtrate divided by the total amount of solute in the feed solution:



$$\delta = \frac{V^P \overline{C}_i^P}{V^f C_i^f} = 1 - (1 - \Delta)^{1-R}$$

MICROFILTRATION

Only large particles with diameters of micron are separated by the membrane, the diffusion of particles and the osmotic pressure difference between the feed and filtrate solution are negligibly low.



$$J_v = \sum_i J_i \overline{V_i} \cong L_v \frac{\Delta p}{\Delta z}$$

J_v: volumetric flux across the membrane

V: partial molar volume

Δp: pressure

L_v: hydrodynamic permeability of the membrane

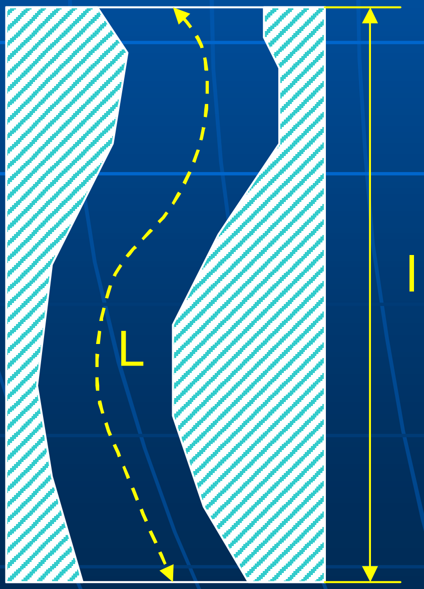
Δz is the thickness of the membrane.

The mass transport in microfiltration membranes takes place by viscous flow through the pores.

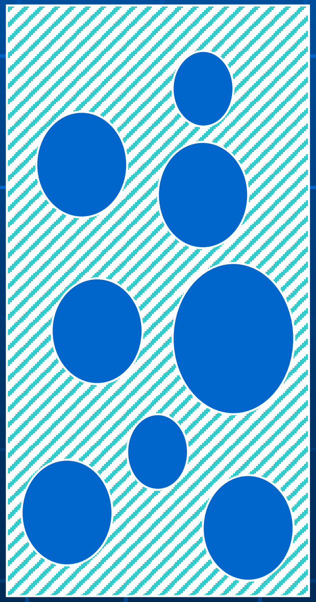
In MF, hydrodynamic permeability is expressed in terms of the membrane pore size and the porosity and the solution viscosity according to Hagen-Poiseuille's law:

$$L_p = \frac{\varepsilon r^2}{8\eta\tau}$$

ε: membrane porosity; r: pore radius;
η: viscosity; τ : tortuosity.



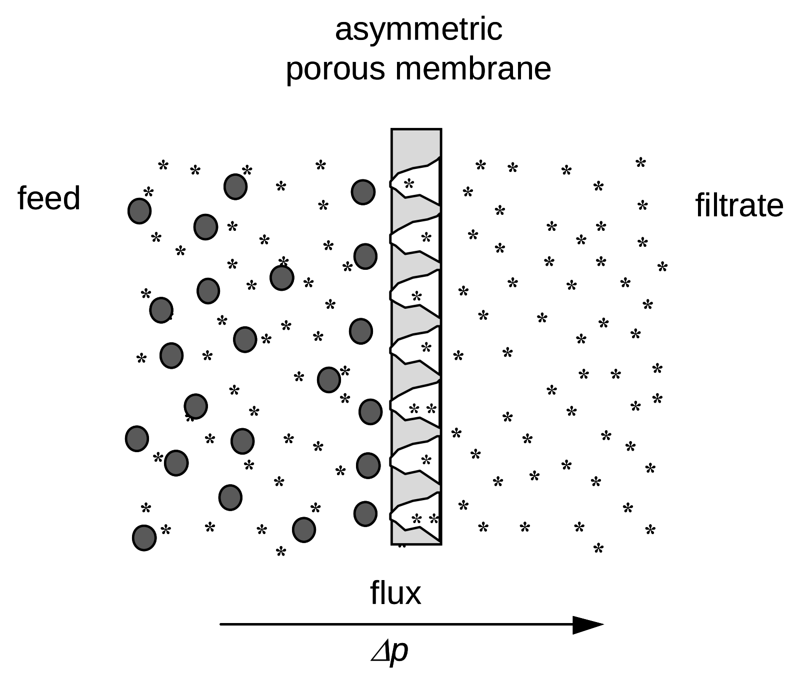
$$\tau = \frac{L}{l} \geq 1$$



$$\varepsilon = \frac{Total\ area\ of\ pores}{Total\ area} \leq 1$$

ULTRAFILTRATION

In UF, the structure of an ultrafiltration membrane is asymmetric having the smallest pores on the surface facing the feed solution, and its pores are significantly smaller than those of a microfiltration membrane.



Since ultrafiltration membranes retain also some relatively low molecular weight solutes, **osmotic pressure differences between the feed and the filtrate can be significant and diffusive fluxes of the solutes across the membrane are no longer negligibly low.**

Flux of individual components in ultrafiltration:

$$J_v = \sum_i J_i \overline{V}_i = \sum_i \overline{V}_i L_i \frac{d\mu_i}{dz} + L_v \frac{dp}{dz} = \sum_i \overline{V}_i L_i \frac{d}{dz}\left(\overline{V}_i p + RT \ln a_i\right) + L_v \frac{dp}{dz}$$

CHEMICAL POTENTIAL GRADIENT

HYDROSTATIC PRESSURE GRADIENT

L: phenomenological coefficients referring to interactions of the permeating components with the membrane matrix;

V: partial molar volume;

μ: chemical potential;

p: hydrostatic pressure;

a: activity

Simplifications: 1) for diluted solutions, the total volume flux can be expressed to a first approximation by the flux of the solvent (water)

$$J_v \cong J_w$$

Simplifications: 2) the activity of the solvent in the solution *a* can be expressed in terms of **osmotic pressure gradient ($\Delta\pi$)**.

After arrangements:

$$J_v \cong J_w = \bar{V}_w^{\,2} L_w \frac{\Delta p - \Delta\pi}{\Delta z} + L_v \frac{\Delta p}{\Delta z}$$

L_v is the hydrodynamic permeability

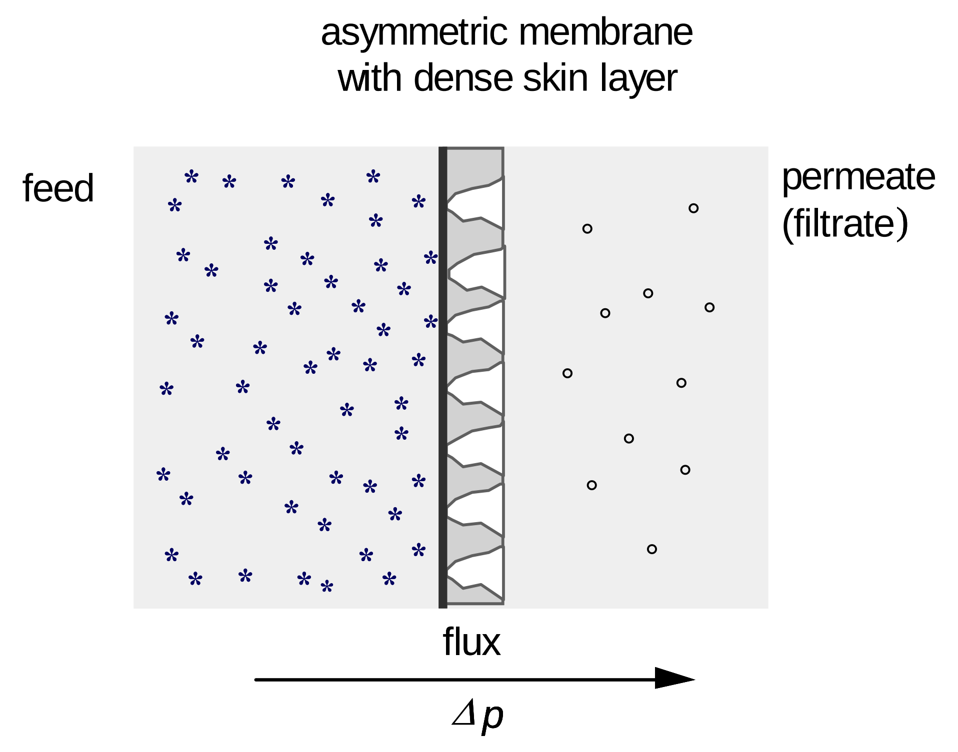
L_w is the diffusive permeability of the solvent

However, in most practical applications of UF, $L_w << L_v$:

$$J_v = L_v \frac{\Delta p}{\Delta z}$$

NANOFILTRATION

The separation properties of nanofiltration membrane are determined in general by two distinct properties: 1) the pore size of the membranes, which corresponds to a molecular weight cut-off value of about 400 (±100) Dalton, and 2) the surface charge which can be positive or negative and affects the permeability of charged components such as salt ions.



The transport of individual component i-th (J_i) can be described by:

$$J_i = L_i \frac{d\mu_i}{dz} = L_i \frac{d}{dz}\left(\overline{V}_i p + RT \ln a_i\right) + L_v{}^m C_i \frac{dp}{dz}$$

L_i: phenomenological coefficients referring to diffusion of the permeating components within the membrane matrix;

L_v: hydraulic permeability of the membrane;

V: partial molar volume;

μ: chemical potential;

p: hydrostatic pressure;

a: activity

CHEMICAL POTENTIAL GRADIENT

HYDROSTATIC PRESSURE GRADIENT

The total volumetric flux (J_v) through the membrane is, therefore:

$$J_v = \sum_i J_i \overline{V}_i = \sum_i \overline{V}_i L_i \frac{d}{dz}\left(\overline{V}_i p + RT \ln{}^m a_i\right) + L_v \frac{dp}{dz}$$

Simplification 1: for diluted solutions, the total volume flux can be expressed to a first approximation by the flux of the solvent (water)

$$J_v \cong J_w$$

Simplification 2: the activity of the solvent in the solution *a* can be expressed in terms of **osmotic pressure gradient ($\Delta\pi$)**.

After arrangements:

$$J_v \cong J_w = \overline{V}_w^{\,2} L_w \frac{\Delta p - \Delta\pi}{\Delta z} + L_v \frac{\Delta p}{\Delta z}$$

L_v is the hydrodynamic permeability

L_w is the diffusive permeability of the solvent

Expressing the phenomenological coefficient L_w by:

$$L_w = \frac{D_w \ C_w}{RT}$$

follows that:

$$J_v \cong \frac{\overline{V}_w^{\,2} L_w}{\Delta z}\left(\Delta p + \Delta\pi\right) + L_v \frac{\Delta p}{\Delta z} = \left(\frac{D_w \overline{V}_w}{RT} + L_v\right)\frac{\Delta p}{\Delta z} + \frac{D_w \overline{V}_w}{RT}\frac{\Delta\pi}{\Delta z}$$

For nanofiltration membranes with pore sizes in the range of ca. 1 nm the term $\frac{D_w \overline{V}_w}{RT}$ is of the same order of magnitude or large than the L_v. Thus, unlike in ultrafiltration the effect of the osmotic pressure on the solvent flux can not be neglected in nanofiltration.

Simplification 3: it is assumed that the solutions treated in NF are relatively dilute and that to a first approximation the activities of the individual components can be replaced by their concentrations.

$$J_i = {}^mD_i \frac{d}{dz}\left(\frac{\overline{V}_i\,{}^mC_i}{RT}\,dp + d\,{}^mC_i\right) + L_v\,{}^mC_i\,\frac{dp}{dz} \qquad [\bullet]$$

where:

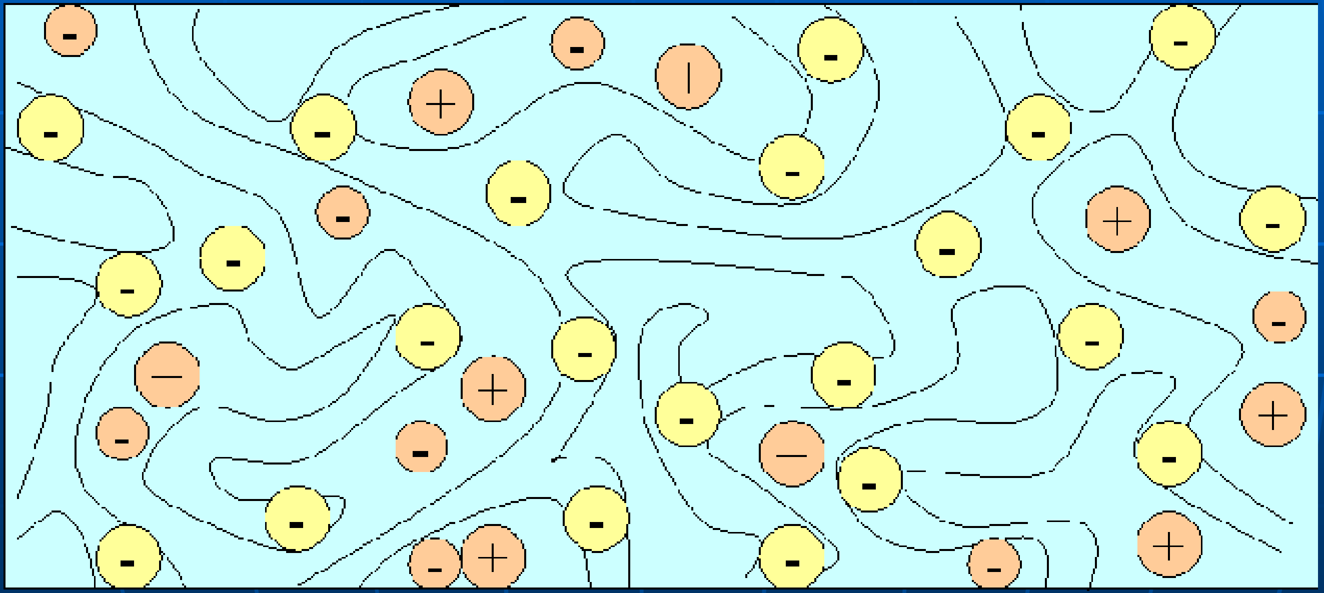
$${}^mD_i = L_i\,\frac{RT}{{}^mC_i}$$

A partition coefficient correlates the concentration at the membrane interface ${}^mC_i$ to the concentration in the solution ${}^sC_i$:

$${}^mC_i = k_i\,{}^sC_i$$

DONNAN POTENTIAL AND DONNAN EXCLUSION

If the membrane carries positive or negative electric charges at the surface, the partition coefficient for ionic components such as salt ions is not only determined by size exclusion but also by the so-called Donnan exclusion which postulates that **ions carrying the same charge as the membrane, i.e. the so-called co-ions, will be excluded from the membrane**.



⊖ Fixed charge on the membrane

⊕ Counter-ion

⊖ Co-ion

The Donnan potential between an ion-exchange membrane and a dilute electrolyte solution is given to a first approximation by:

$$\varphi_{Don} = \sum_i \frac{1}{z_i F}\left[\mathrm{RT}\ln\frac{{}^{\mathrm{s}}\mathrm{C}_{\mathrm{i}}}{{}^{\mathrm{m}}\mathrm{C}_{\mathrm{i}}}\right]$$

φ_{Don} :Donnan potential; ${}^{s}C_i$ and ${}^{m}C_i$: concentration of an ion in the solution and the membrane, respectively.

The exclusion of the co-ions in a dilute solution of a single mono-valent electrolyte is given to a first approximation by:

$$ {}^{m}C_{co} = \frac{{}^{s}C_s^{\,2}}{C_{fix}}$$

${}^{m}C_{co}$, ${}^{s}C_s$ and C_{fix} are the co-ion concentration in the membrane, the electrolyte concentration in the solution and the fixed-ion concentration of the membrane.

As a result of the Donnan exclusion the partition coefficient for a component between a nanofiltration membrane carrying positive or negative fixed charges and an electrolyte solution depends on two parameters, one is the size exclusion (k_{size}) and the other is the Donnan exclusion (k_{Don}). It is:

$$\boxed{k_i = k_{size} k_{Don}} \qquad 0 \le k \le 1$$

Therefore, the flux of individual components through a nanofiltration membrane containing fixed positive or negative charges is given by:

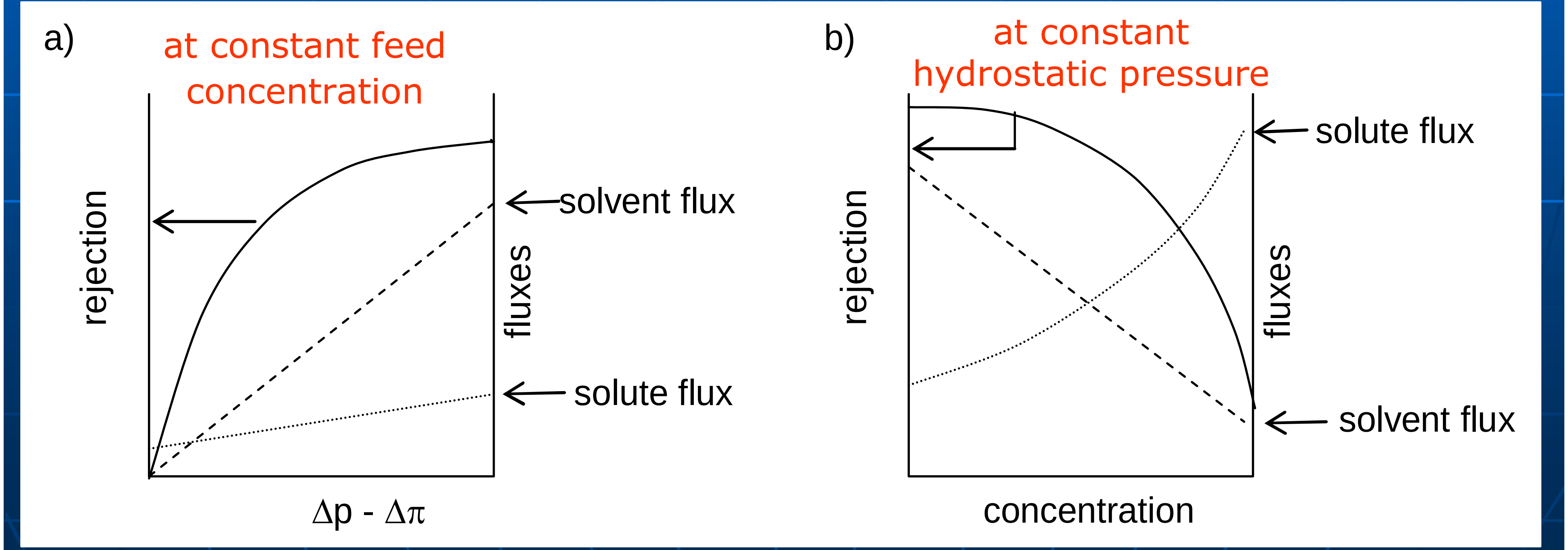
$$J_i = {}^{m}D_i \left[\left[\left(\frac{\bar{V}_i k_{size} k_{Don} \, {}^{s}C_i}{RT} \frac{dp}{dz} + k_{size} k_{Don} \frac{d\,{}^{s}C_i}{dz} \right) + \boxed{\frac{z_i F \; k_{size} k_{Don} \, {}^{s}C_i}{RT} \frac{d\varphi_{Don}}{dz}} \right] \right] + L_v k_{size} k_{Don} \, {}^{s}C_i \frac{dp}{dz}$$

(from eq. [•])

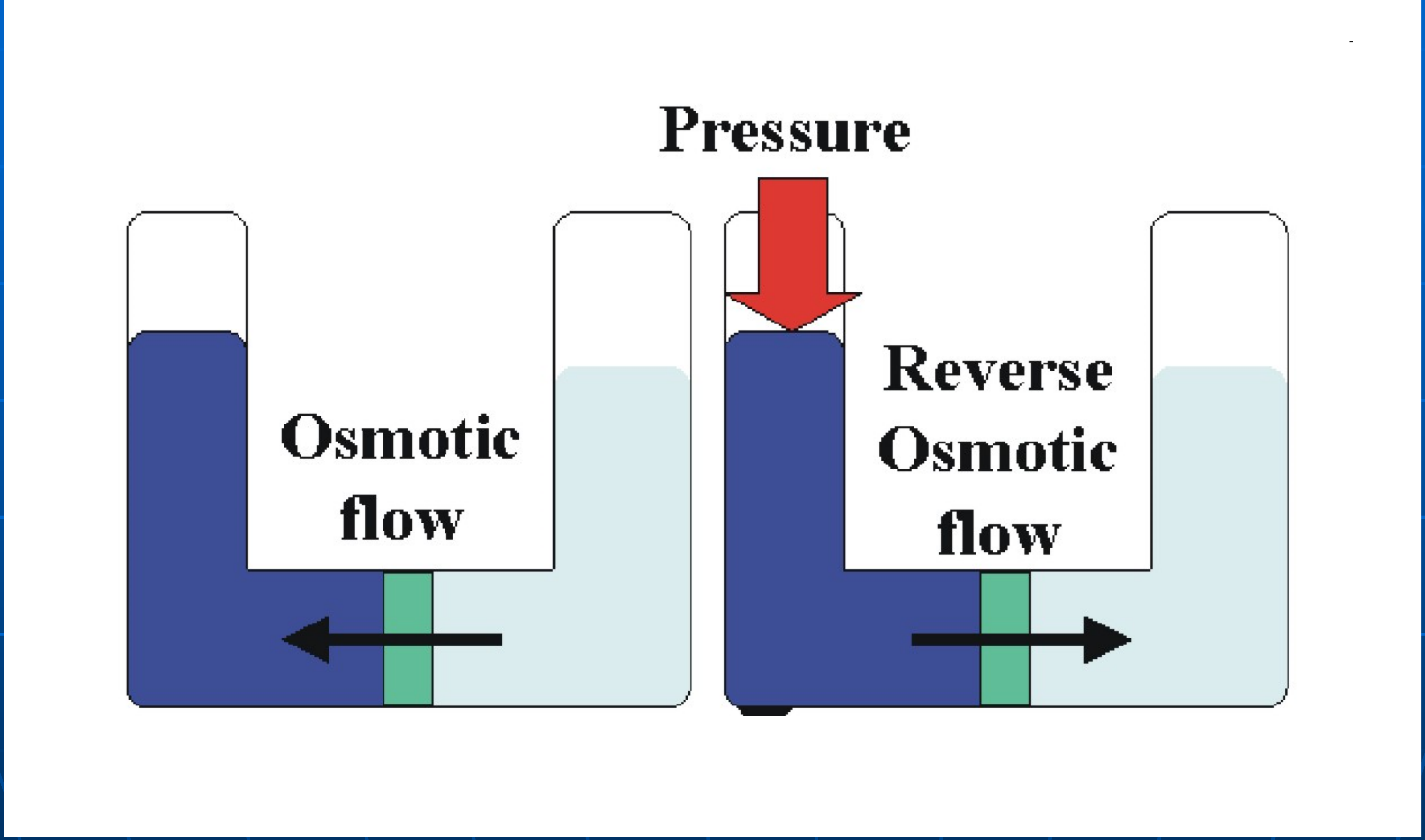
Since concentrations are different at feed and permeate side of NF membrane, an electrical potential difference across the membrane is established which affects the transport of charged components through the membrane.

The consequence of the additional driving force of the Donnan potential difference between two solutions separated by a nanofiltration membrane is that components with the same electrical charge such as mono- and divalent cations or anions can be separated when their diffusivity in the membrane is different.

Rejection of a salt by a nanofiltration membrane carrying positive or negative fixed charges at the surface:



REVERSE OSMOSIS



A hydrostatic pressure difference applied across the membrane resulting in a flux of solvent from the solution into the pure solvent.

SOLUTION-DIFFUSION MODEL

In the solution-diffusion model, the flux of different components through a membrane is assumed to be by diffusion only and can be described by the product of its concentration and mobility in the membrane matrix and the chemical potential gradient of the component in the membrane.

Assumptions: 1) no kinetic coupling between fluxes; 2) the total volume flux is approximately equal to the flux of the solvent; 3) the solute flux due to the pressure gradient is negligibly small compared to the solute flux due to the activity gradient.

Flux of the i-th component

$$J_i = L_i d\mu_i = L_i\left(\overline{V}_i dp + RTd\ln a_i\right) = \frac{D_i{}^m C_i}{RT}\left(\overline{V}_i dp + RTd\ln a_i\right)$$

For the solvent ($i=w$):

$$J_v \cong J_w$$

$$C_w \overline{V}_w = 1$$

For the solute ($i=s$):

$$d\mu_s \cong RTd \, ln \, a_s$$

$$\pi \cong \frac{RT \, ln \, a_w}{\overline{V}_w}$$

Integrating over the cross-section of the membrane and expressing the activity of the solvent by the osmotic pressure and that of the solute by its concentration gives the volume flux to:

$$J_v = \frac{D_w \overline{V}_w^{\,2}}{RT}(\Delta p - \Delta \pi)$$

Total volumetric flux

$$J_s = D_s \, {}^{m}C_s d\ln {}^{m}C_s = D_s d \, {}^{m}C_s$$

Solute flux

By introducing the partition coefficient k_i:

$${}^{m}C_i = k_i C_i$$

…follows…

Total volumetric flux

$$J_v = \frac{k_w D_w C_w \overline{V}_w^{\,2}}{RT}\left(\Delta p - \Delta\pi\right) = \frac{k_w D_w \overline{V}_w}{RT}\left(\Delta p - \Delta\pi\right)$$

Solute flux

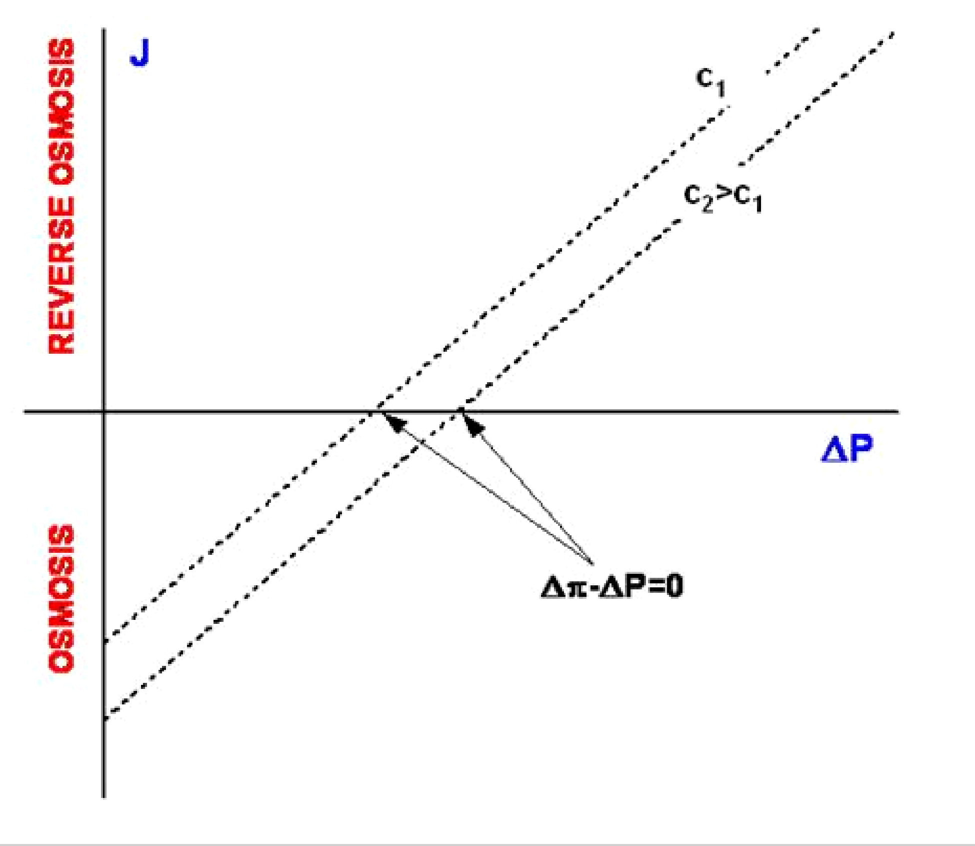
$$J_s = k_s D_s \left(C_s^f - C_s^p\right)$$

J_v : volume flux
J_s : solute flux
D: diffusion coefficient
k: partition coefficient of the components between the membrane surface and the bulk

C: concentration
p : hydrostatic pressure
π: osmotic pressure

Subscripts *s* and *w* refer to solute and water, respectively

superscripts *m*, *f and p* refer to the membrane, the feed and the permeate.



CONCENTRATION POLARIZATION

Mass balance

$$J \cdot c - D\frac{dc}{dx} = J \cdot c_P$$

Boundary conditions

$$x = 0, c = c_m$$

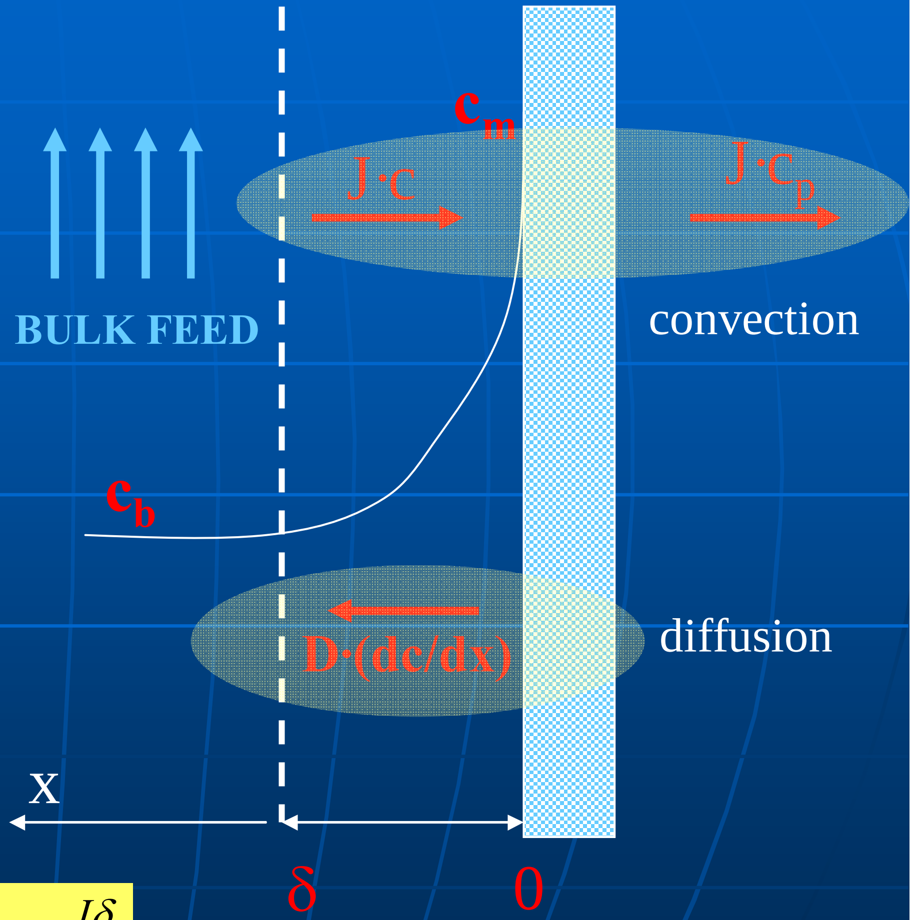
$$x = \delta, c = c_b$$

By integration:

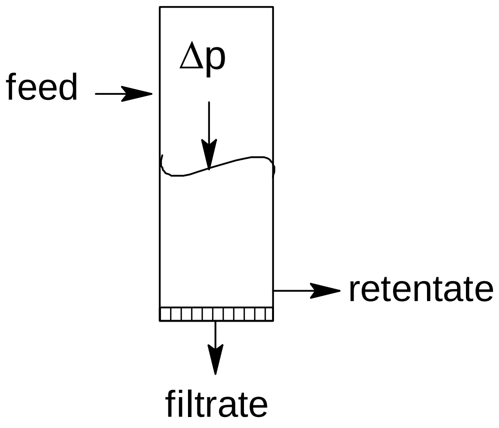
$$\ln\frac{c_m - c_p}{c_b - c_p} = \frac{J\delta}{D}$$

or:

$$\frac{c_m - c_p}{c_b - c_p} = e^{\frac{J\delta}{D}}$$

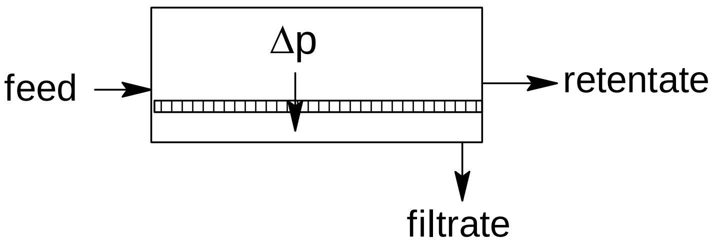


OPERATION MODES IN FILTRATION PROCESSES



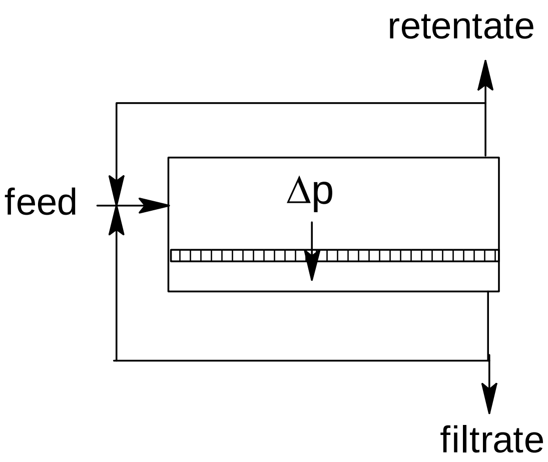
BATCH PROCESS

Under a hydrostatic pressure certain components, i.e. mainly a solvent, permeate the membrane and are collected as filtrate. When a certain concentration in the retentate is achieved the process is terminated.



CONTINUOS PROCESS

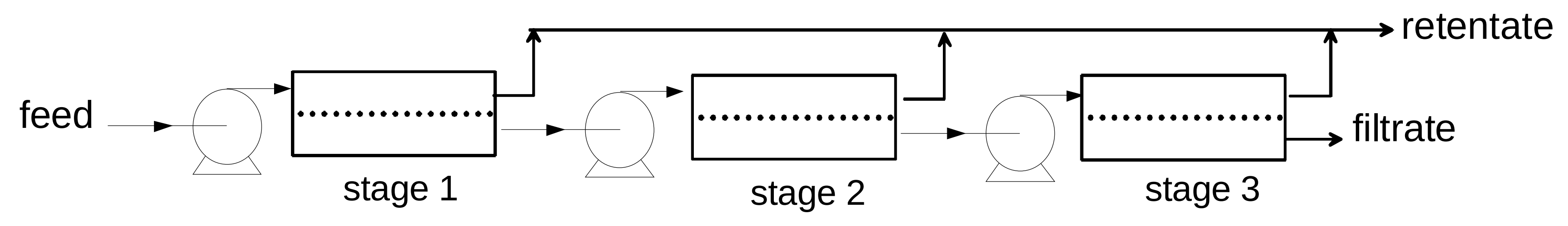
Solution is continuously fed into the filtration device. The retained components are concentrated during the path-way through the device leaving at the end of the process path as the retentate.



FEED & BLEED PROCESS

Part of the retentate is recycled to the device inlet and mixed with the feed solution.

Three stage filtration cascade



Three stage retentate cascade