Lecture 18

Thermodynamics
and
Biophysics part 2

Phase equilibrium. Simple equilibrium

If n_i moles diffuse the free energy change in combined A+B system is:

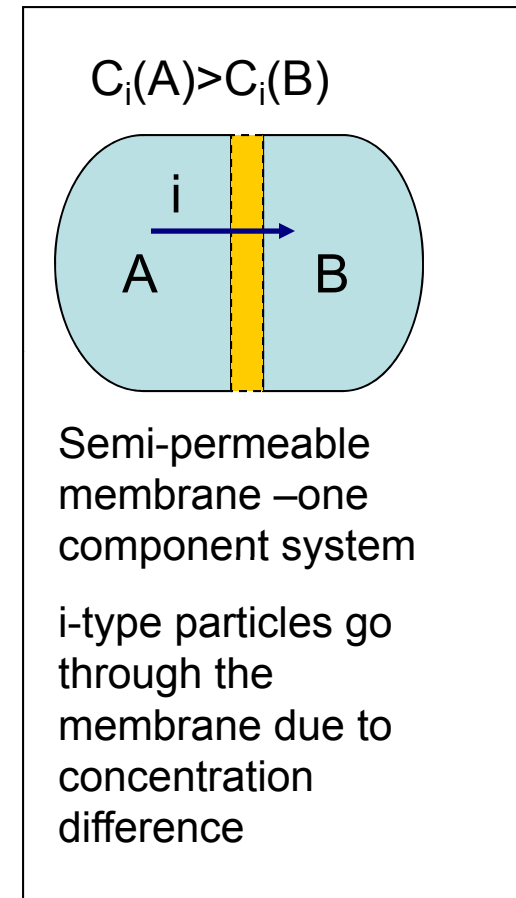$$\Delta G = \mu_{iA}(-n_i) + \mu_{iB}(n_i)$$

Assume that flow occurs in quasi-equilibrium steps at constant T and P

Two phases are in equilibrium if a steady non-equilibrium state is maintained for the combined system, so that ΔG=0, therefore chemical potential of each active component in both phases must be the same:

$$\mu_{iA} = \mu_{iB}$$

For multi-component system:

$$\Sigma\mu_{iA} = \Sigma\mu_{iB}$$

$C_i(A)>C_i(B)$

i

A   B

Semi-permeable membrane –one component system

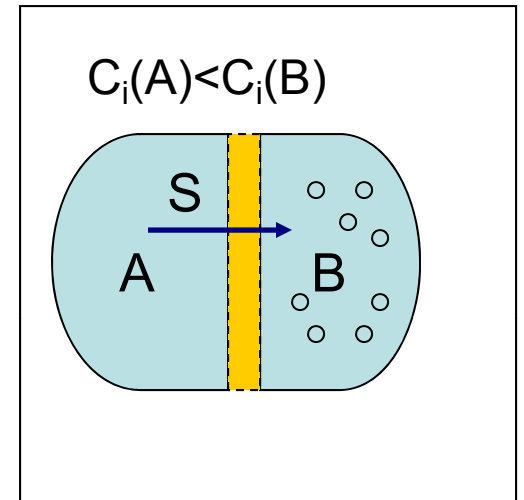i-type particles go through the membrane due to concentration difference

Osmotic flux:

In Equilibrium:

$$\mu_S^A = \mu_S^B$$

Semi-permeable membrane –two
components system : solvent S and i type
solute
Solvent molecules S go through the
membrane driving force - concentration
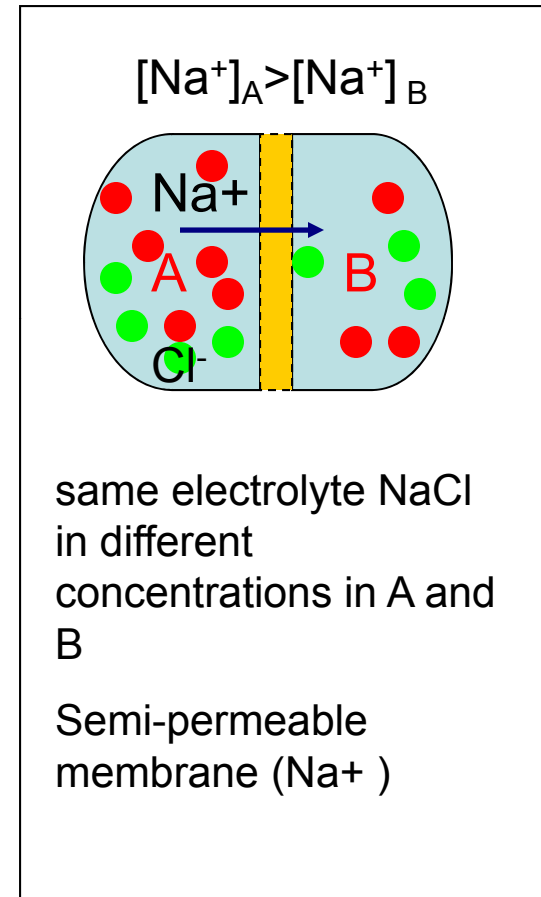gradient of solute i

$C_i(A)<C_i(B)$

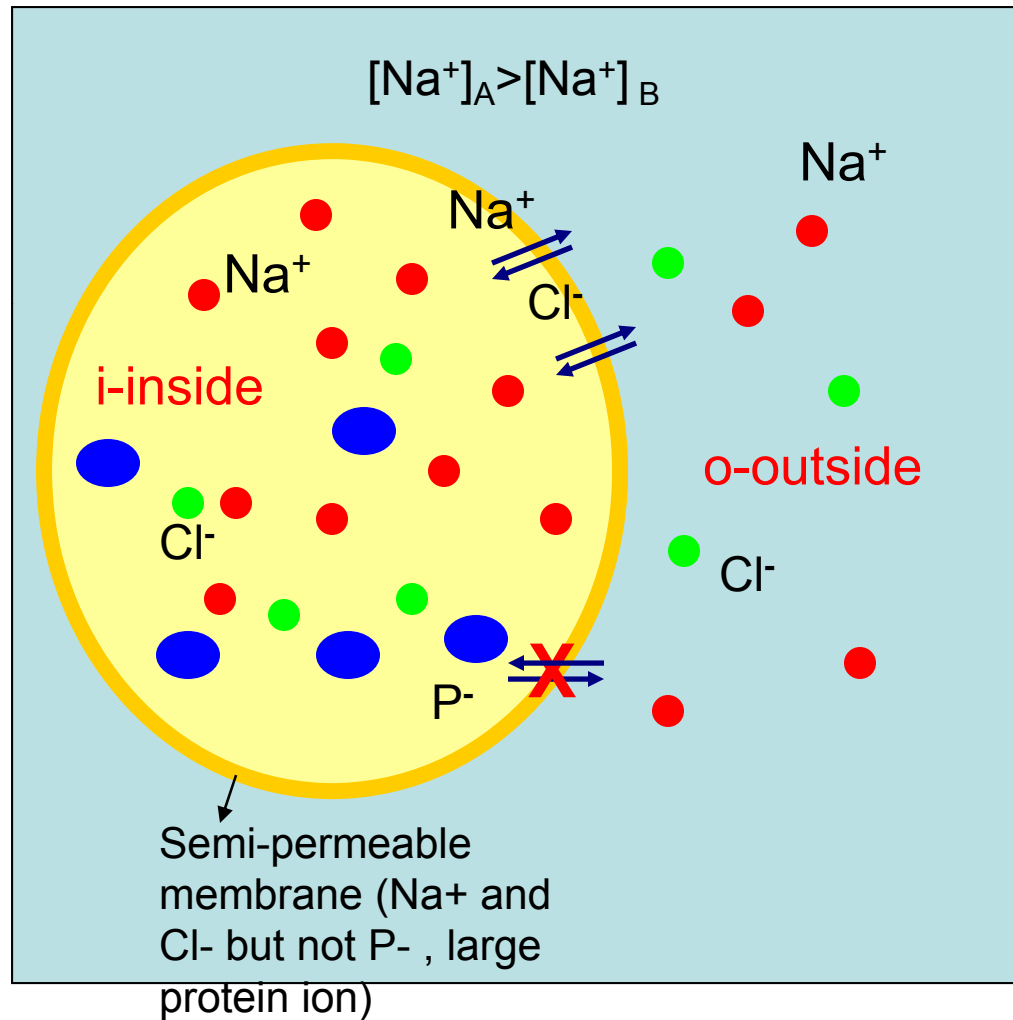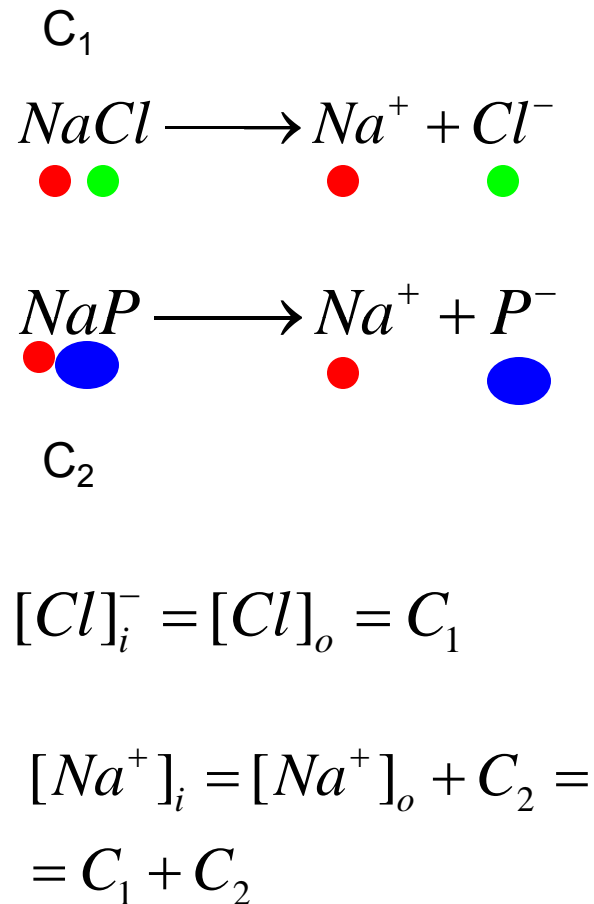# Electrochemical equilibrium.

● Na+ moves through,

but not ● Cl-,

this will create the difference in concentrations of Na+ and Cl- in the A and B phases – electric double layer,

excess of cations on one side and excess of anions on the other side,

cations do not go to far because of electrostatic attraction to negative charge at the membrane where anions were stopped

$[Na^+]_A > [Na^+]_B$

Na+

A   B

Cl⁻

same electrolyte NaCl in different concentrations in A and B

Semi-permeable membrane (Na+)

Donnan Equilibrium

C_1

$$NaCl \longrightarrow Na^+ + Cl^-$$

$$NaP \longrightarrow Na^+ + P^-$$

C_2

$$[Cl]_i^- = [Cl]_o = C_1$$

$$[Na^+]_i = [Na^+]_o + C_2 =$$
$$= C_1 + C_2$$

$[Na^+]_A > [Na^+]_B$

Na$^+$

Na$^+$

Na$^+$

i-inside

o-outside

Cl$^-$

Cl$^-$

Cl$^-$

P$^-$

Semi-permeable
membrane (Na+ and
Cl- but not P- , large
protein ion)

Donnan Equilibrium

In equilibrium concentrations of + and - ions are balanced to achieve electric neutrality,

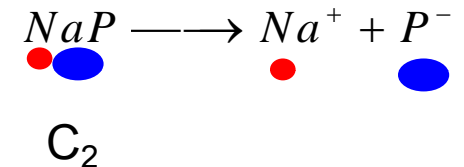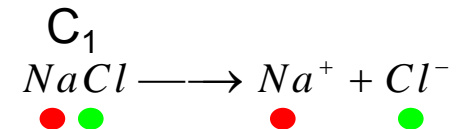[Na]+ inside larger than outside, Na+ will move outside:

$$C_1$$
$$NaCl \longrightarrow Na^+ + Cl^-$$

$$[Na^+]_o = [Cl^-]_o = C_1 + \Delta C$$

$$NaP \longrightarrow Na^+ + P^-$$

$$[Na^+]_i = C_1 + C_2 - \Delta C \qquad [Cl^-]_i = C_1 - \Delta C \qquad C_2$$
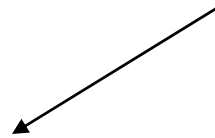
$$[Na^+]_i = [Cl^-]_i + C_2$$

change of concentration outside to achieve equilibrium, Cl- will also move out

- **Characteristics of Donnan equilibrium:**
- Both phases are separately electrically neutral N (+) = N (-)
- Concentrations of different mobile ions are different in different phases

In equilibrium between (in) and (out) the net chemical potentials due to different permeable ions are equal:

$$\Delta G = \mu_i + \mu_o = 0 \qquad \left(\Sigma \mu_i\right)_{inside} = \left(\Sigma \mu_i\right)_{outside}$$

$$\mu_i = \mu_i^o + RT \ln[C]_i$$

$$RT \ln[Na^+]_i + RT \ln[Cl^-]_i = RT \ln[Na^+]_o + RT \ln[Cl^-]_o$$

$$\ln[Na^+]_i[Cl^-]_i = \ln[Na^+]_o[Cl^-]_o$$

$$[Na^+]_i[Cl^-]_i = [Na^+]_o[Cl^-]_o$$

$$\frac{[Na^+]_i}{[Na^+]_o} = \frac{[Cl^-]_o}{[Cl^-]_i}$$

Donnan equilibrium: because of the impermeable ionic residues like P-, a differential ionic distribution is developed across the membrane, however, electric neutrality is maintained on both sides

$$\left[Cl^- \right]_i = C_1 - \Delta C \quad \left[Cl^- \right]_o = C_1 + \Delta C$$

inside		outside
	$\left[P^- \right] = C_2$	
Before	$\left[Na^+ \right] = C_2 + C_1$	$\left[Na^+ \right] = C_1$
	$\left[Cl^- \right] = C_1$	$\left[Cl^- \right] = C_1$

	$\left[P^- \right] = C_2$	
After	$\left[Na^+ \right] = C_2 + C_1 - \Delta C$	$\left[Na^+ \right] = C_1 + \Delta C$
	$\left[Cl^- \right] = C_1 - \Delta C$	$\left[Cl^- \right] = C_1 + \Delta C$

Summary: Donnan equilibrium:

- Both phases are separately electrically neutral (N+=N-)

- Concentration of different mobile ions are different in different phases

- Immobile heavy charged molecules, such as protein P^- stay inside the cell and indirectly affect the distribution of mobile ions, this leads to Donnan phenomenon

More on irreversible thermodynamics

- biological system is:

- open system

- non-equilibrium system

- interacts with its environment – exchanges matter and energy

- It can be near equilibrium in a steady state

- The steady state is maintained by external forces and flows of matter, and energy to or from surroundings, causes changes of entropy

- To describe such a system we use equilibrium thermodynamics and include external forces and flows.

Flux and force in irreversible processes

Near- equilibrium $\xrightarrow[\text{processes}]{\text{Irreversible}}$ equilibrium

ΔS/Δt depends on the rate of these processes

Process = thermodynamic parameter (T, C, V) changes with time

In general change of thermodynamic parameter with time is called thermodynamic flux J, the process is caused by force X

$$J \propto X \qquad \boxed{J = LX}$$

Constant of proportionality

Examples:

1. Fick's Law – diffusion at near equilibrium under the concentration gradient:

2. Ohm's Law – current or charge flow under electrical potential

Poiseuille's Law – liquid flow under pressure gradient at near equilibrium

3. The rate of chemical reaction is proportional to Δμ , which is a driving force for chemical reactions

4. In general, at near equilibrium, the flux J_k of the k-th irreversible process is linearly proportional to the conjugate force X_k

$$J_k = L_{kk} X_k$$

Onsager flux-force relations

If diffusing particles are polar – two driving forces:

concentration gradient and/or electric potential gradient.

$$J_n = L_{nn}X_n + L_{ne}X_e$$

J_n - diffusion flux, X_n –conjugate force, X_e – non-conjugate force

Onsager coefficients, independent on forces

$$J_e = L_{en}X_n + L_{ee}X_e$$

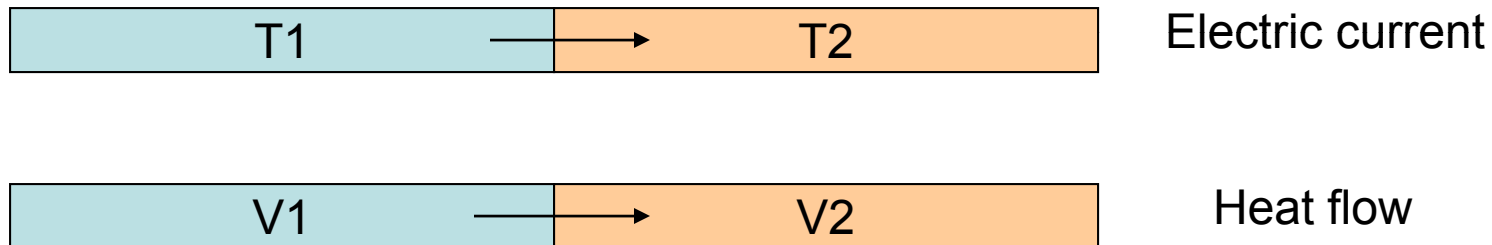J_e – charge flux, X_e –conjugate force, X_n – non-conjugate force

$$L_{en} = L_{ne}$$ near equilibrium, fluxes and forces are coupled in linear way, coupling coefficients between two non-conjugate forces are equal

$$L_{ij} = L_{ji} \quad (i \neq j) \qquad J_i = \sum_j L_{ij}X_j \qquad i, j = 1,...,m$$

Other examples:

- 1. Thermoelectric behavior of conductors – irreversible coupling between heat and current

| T1 | → | T2 | Electric current |

| V1 | → | V2 | Heat flow |

- 2. Coupling between diffusion and heat flow:

- Difference in temperature $\longrightarrow$ convection flow - diffusion
- Difference in concentration $\longrightarrow$ T difference and heat flow

- 3. Coupling of chemical reactions to other forces

- Chemical reaction is also a process which brings a system to equilibrium,

- chemical reaction is characterized by the force (affinity) and flux (rate of reaction). The rate of chemical reaction is a scalar.

- In isotropic medium all thermodynamic properties are the same in all directions – no directional flux or force. Chemical reaction can occur in isotropic medium, but there is no coupling with force or flux.

- In anisotropic medium chemical reaction can couple with flux (transport across lipid membrane mediated by carrier molecules)

Entropy Production and Dissipation Function

All irreversible processes lead to increase of entropy S and loss of free energy T ΔS. The time rate of energy dissipation is defined by dissipation function σ:

$$\sigma = T \frac{\Delta_i S}{\Delta t}$$

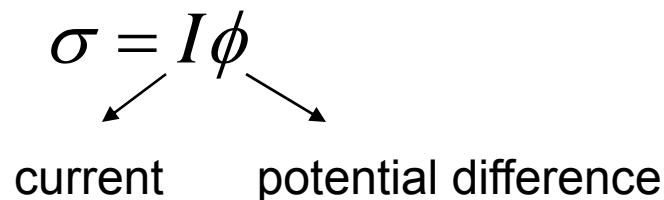For simple diffusion:

$$T \frac{\Delta_i S}{\Delta t} = J_n X_n$$

$$J = \frac{\Delta n}{\Delta t}$$

flux

$$X_n = \Delta \mu$$

force

$$\sigma = J_n X_n = Flux \times Force \longrightarrow$$

holds for many irreversible processes, in general:

Ohm's Law:

$$\sigma = I\phi$$

current   potential difference

$$\sigma = T \frac{\Delta_i S}{\Delta t} = \sum_{k=1}^{m} J_k X_k$$

The steady state

Isolated thermodynamic system $\longrightarrow$ equilibrium ($\Delta S/ \Delta t=0$)

Living system (open system) $\longrightarrow$ steady state ($\Delta S/ \Delta t=\text{min}$)

For two forces and two fluxes in steady state:

$$J_1 = L_{11}X_1 + L_{12}X_2 \qquad J_2 = L_{21}X_1 + L_{22}X_2$$

Dissipation function:

$$\sigma = J_1 X_1 + J_2 X_2 = L_{11}X_1^2 + L_{22}X_2^2 + 2L_{12}X_1 X_2$$

$$L_{12} = L_{21}$$

If X_1 and X_2 are fixed, J_1 and J_2 and σ are fixed values, determined by coefficients L_{12} and L_{21} - steady state of second order

If X_1 is fixed but X_2 can vary, then system will go to steady state where σ is min with respect to X_2 (steady state of first order):

$$\frac{d\sigma}{dX_2} = 2L_{22}X_2 + 2L_{12}X_1 = 0 \qquad\qquad X_2 = -\frac{L_{12}}{L_{22}}X_1$$

$$J_2 = 0 \qquad J_1 = \left(L_{11} - \frac{L_{12}^2}{L_{22}} \right) X_1 \qquad \sigma_{min} = J_1 X_1 = \left(L_{11} - \frac{L_{12}^2}{L_{22}} \right) X_1^2$$

Since $\sigma \geq 0$ $\longrightarrow$ $L_{11}L_{22} \geq L_{12}^2$ Coefficients are constrained

$\sigma = 0$ $\longrightarrow$ $L_{11}L_{22} = L_{12}^2$ $\qquad J_2 = 0$ Steady state of 0-th order = equilibrium state
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad J_1 = 0$

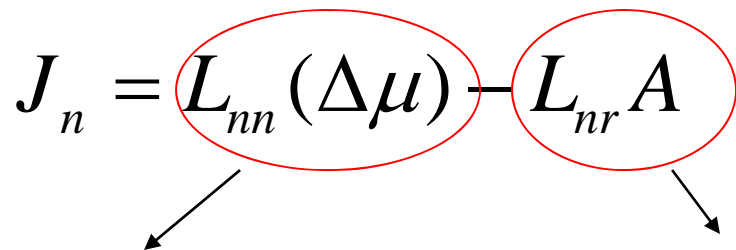# The transport of Na+ across the cell membrane

Driving forces:

Diffusion gradient

Electric potential gradient (inside 80 mV less than outside)

Besides passive transport there is active transport which is coupled with chemical reaction (carrier-substance)

Total Particle flux:

$$J_n = L_{nn}(\Delta\mu) - L_{nr}A$$

In the absence of active transport

Due to active transport

the rate of chemical reaction which causes active transport is called metabolic current (J_r),

it is coupled to electrochemical gradient:

$$J_r = L_{rn}(\Delta\mu) - L_{rr}A$$

Metabolic current – the rate of chemical reaction which causes active transport is coupled to electro-chemical gradient, this means that the rate of chemical reactions transporting Na+ ions is coupled to electrochemical gradient:

$$J_r = L_{rn}(\Delta\mu) - L_{rr}A \qquad\qquad L_{rn} = L_{nr}$$

If $\quad L_{rn} = 0 \quad$ Na+ current only due to diffusion,

and chemical reaction (metabolism) depends only on affinity A

L_{rn} or L_{nr} — Is a measure of coupling between chemical reaction and diffusion

We can use these equations to determine affinity A of chemical reaction of active transport of Na+,

If A is a constant then:

$$\frac{dJ_r}{d\Delta\mu} = L_{rn} = L_{nr}$$

if $\quad \Delta\mu = 0 \quad \longrightarrow \quad A = \dfrac{J_n}{L_{nr}} = \dfrac{J_n}{\left(\dfrac{dJ_r}{d\Delta\mu}\right)}$

A=const