

Development of Complex Curricula for Molecular Bionics and Infobionics Programs within a consortial* framework**

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**Molekuláris bionika és Infobionika Szakok tananyagának komplex fejlesztése konzorciumi keretben

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INTRODUCTION TO BIOPHYSICS

(Bevezetés a biofizikába)

THERMODYNAMICS OF ELECTROLYTES

(Elektrolitok termodinamikája)

GYÖRFFY DÁNIEL

Introduction

- While laws described in the previous chapter apply to uncharged particles, in the present chapter, we attempt to give a description of systems containing charged particles
- Solutions containing charged particles, for example ions, are called electrolytes
- Electrolytes are electrically conductive

Thermodynamics of electrolytes

- Let us suppose we have a NaCl solution with total free energy G
- By the additivity rule

$$G = \mu_{H_2O} n_{H_2O} + \mu_{NaCl} n_{NaCl}$$

- We could imagine building up the solution by adding one Na^+ ion at a time followed by one Cl^- ion each time

$$G = \mu_{\text{H}_2\text{O}} n_{\text{H}_2\text{O}} + \mu_{\text{Na}^+} n_{\text{Na}^+} + \mu_{\text{Cl}^-} n_{\text{Cl}^-}$$

- In our case

$$n_{\text{NaCl}} = n_{\text{Na}^+} = n_{\text{Cl}^-}$$

and

$$\mu_{\text{NaCl}} = \mu_{\text{Na}^+} + \mu_{\text{Cl}^-}$$

- Now, we wonder how μ_{Na^+} relates to $[Na^+]$?
- First of all, let us generalize the problem by considering not Na^+ and Cl^- ions but a general ion with unit positive charge (+ sign in subscript) and another one with unit negative charge (- sign in subscript)

$$\mu_+ = \mu_+^0 + RT \ln \gamma_+ c_+$$

and

$$\mu_- = \mu_-^0 + RT \ln \gamma_- c_-$$

where μ_+ and μ_- are the chemical potential, μ_+^0 and μ_-^0 are the standard chemical potential, γ_+ and γ_- are the activity coefficient, and c_+ and c_- are the molar concentrations of the positively and negatively charged particles, respectively

- Summing the chemical potentials of the positively and negatively charged ions we get

$$\mu_{salt} = \mu_+ + \mu_- = \mu_+^0 + \mu_-^0 + RT \ln \gamma_+ \gamma_- c_+ c_-$$

- It turns out that we cannot really measure μ_+ and μ_- experimentally
- But we can measure $\mu_+ + \mu_-$, that is μ_{salt}
- Let us define

$$\mu_{\pm}^0 \equiv \frac{\mu_+^0 + \mu_-^0}{2}$$

which is called the *mean ion standard chemical potential*

- Furthermore, we cannot measure γ_+ and γ_- but we can measure $\gamma_+ \gamma_-$.
- Let us define

$$\gamma_{\pm}^2 \equiv \gamma_+ \gamma_-$$

which is called the *mean ion activity coefficient*

- Thus

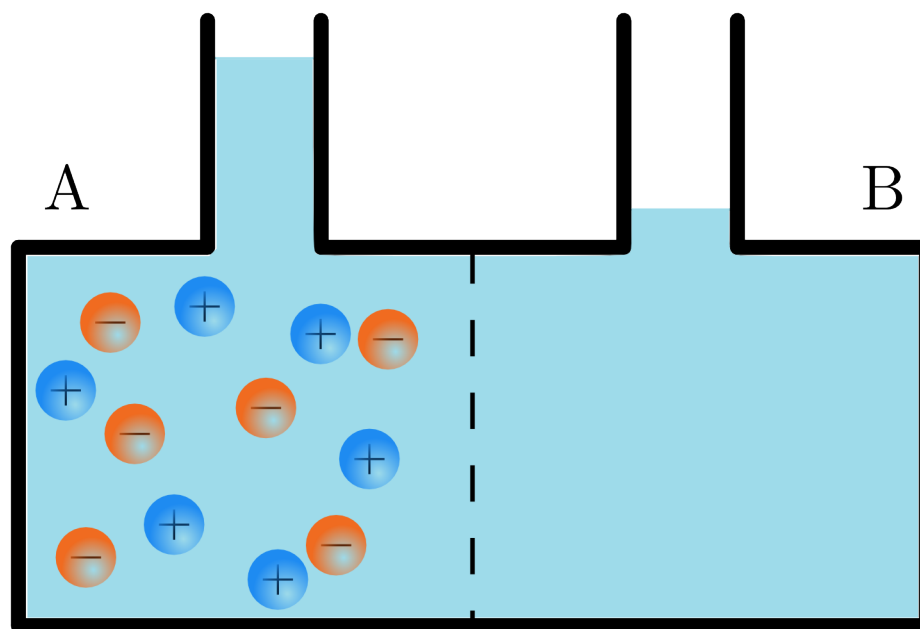
$$\mu_{salt} = 2 \mu_{\pm}^0 + RT \ln \gamma_{\pm}^2 c_+ c_-$$

- Now, let us suppose we put a protein with one ionizable group into chamber A of an osmometer
- For simplicity, we will set

$$V_A = V_B$$

again, where V_A and V_B are the volumes of chamber A and B, respectively

Osmometer with ions



- - and + signs in the solution in the figure denote the protein molecules with a single negative charge and the ions with a single positive charge, for example a Na^+ ion, respectively
- Since the molar concentration of the two types of ions are the same

$$[P^-] = a$$

and

$$[Na^+] = a$$

- Let us notice that if we do not take the positively charged ions into account then

$$\pi = RT \sum_i c_i$$

thus

$$\pi = RT [P^-] + RT [Na^+]$$

and

$$\pi = RT a + RT a = RT 2a$$

- Thus, the measured M_2 will be off by a factor of 2
- For a protein with n ionizable groups

$$\pi = RT \, n \, a$$

- To avoid this problem, let us add a lot of additional electrolyte, for example NaCl, to side B at a concentration b

- Let us suppose that the amount of Na^+ which has diffused over to A, at equilibrium is x
- An equivalent amount x of Cl^- will also diffuse over to maintain equivalent μ and electro-neutrality
- Let us compare the initial concentrations of the different ion types in side A and B with these concentrations at equilibrium

Initial and equilibrium concentrations of the ions

Ion	Initially		At equilibrium	
	A	B	A	B
$[P^-]$	a	0	a	0
$[Na^+]$	a	b	$a+x$	$b-x$
$[Cl^-]$	0	b	x	$b-x$

Initial concentrations of ions

$$[Na^+]_A = a$$

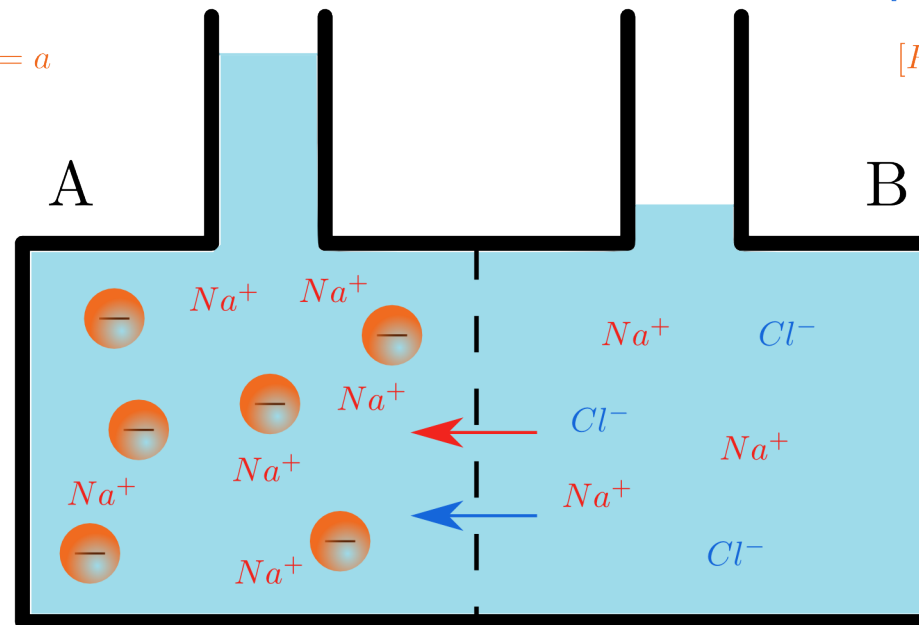
$$[Cl^-]_A = 0$$

$$[P^-]_A = a$$

$$[Na^+]_B = b$$

$$[Cl^-]_B = b$$

$$[P^-]_B = 0$$



Concentrations of ions at equilibrium

$$[Na^+]_A = a + x$$

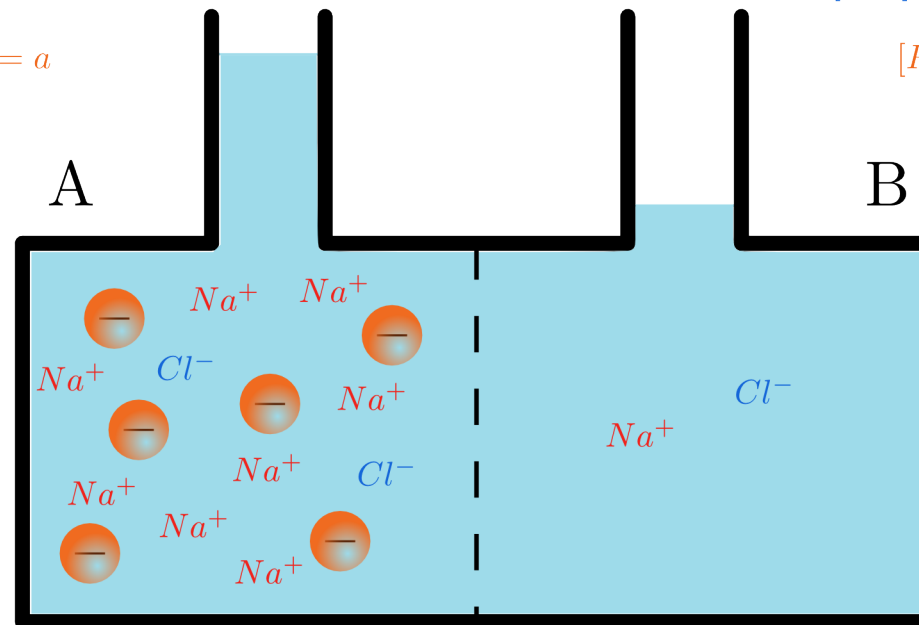
$$[Cl^-]_A = x$$

$$[P^-]_A = a$$

$$[Na^+]_B = b - x$$

$$[Cl^-]_B = b - x$$

$$[P^-]_B = 0$$



- To calculate the osmotic pressure, π , let us take the difference between the total concentrations in sides A and B and multiply by RT
- We can solve this problem for x in two ways

First method

- Intuitively, we can imagine that Na^+ and Cl^- can occasionally come together to form NaCl in solution



- The dissociation constant is

$$K_d = \frac{1}{K_a} = \frac{[\text{Na}^+]_A [\text{Cl}^-]_A}{[\text{NaCl}]_A} = \frac{[\text{Na}^+]_B [\text{Cl}^-]_B}{[\text{NaCl}]_B}$$

- Now, NaCl is uncharged and can freely diffuse through the membrane giving the same concentration on both sides

$$[Na^+]_A [Cl^-]_A = [Na^+]_B [Cl^-]_B$$

with symbolic letters

$$(a + x) x = (b - x)^2$$

and after rearrangement

$$x = \frac{b^2}{a + 2b}$$

Second method

- More rigorously, in a heterogeneous system

$$\mu_{NaCl, A} = \mu_{NaCl, B}$$

substituting the expressions describing the chemical potentials we obtain

$$\begin{aligned} & \left(2\mu_{\pm}^0(p + \pi) + RT \ln \gamma_{\pm}^2 c_+ c_- \right)_A \\ &= \left(2\mu_{\pm}^0(p) + RT \ln \gamma_{\pm}^2 c_+ c_- \right)_B \end{aligned}$$

- After rearrangement

$$2 \mu_{\pm, A}^0(p + \pi) - 2 \mu_{\pm, B}^0(p) = \bar{V}_{NaCl}^0 \pi = RT \ln \frac{\left(\gamma_{\pm}^2 c_+ c_- \right)_A}{\left(\gamma_{\pm}^2 c_+ c_- \right)_B}$$

- Exponentiating both sides we get

$$e^{-\pi \bar{V}_{NaCl}^0 / RT} = \frac{\left(\gamma_{\pm}^2 c_+ c_- \right)_A}{\left(\gamma_{\pm}^2 c_+ c_- \right)_B}$$

- Let us look at an example

$$\pi = 0.01 \text{ atm}$$

$$\bar{V}_{NaCl}^0 = 0.015$$

$$T = 298 \text{ K}$$

$$R = 0.082 \frac{\text{dm}^3 \cdot \text{atm}}{\text{mol} \cdot \text{K}}$$

- Substituting these values into the expression above we get

$$e^{-\pi \bar{V}_{NaCl}^0 / RT} = e^{0.01 \cdot 0.015 / 0.082 \cdot 298} = e^{6.14 \cdot 10^{-6}} \simeq 1$$

- This says that the concentrations of salt on both sides are about the same

$$\gamma_{\pm, A}^2 \approx \gamma_{\pm, B}^2$$

SO

$$(c_+ c_-)_A \approx (c_+ c_-)_B$$

and with symbolic letters

$$(a - x) x = (b - x)^2$$

- After rearrangement

$$x = \frac{b^2}{a + 2b}$$

as with the first method

- Let us return to the osmotic pressure (additivity rule)

$$\pi = RT \left([P^-]_A + [Na^+]_A + [Cl^-]_A - [Na^+]_B - [Cl^-]_B \right)$$

with symbolic letters

$$\pi = RT \left(a + (a + x) + x - (b - x) - (b - x) \right)$$

$$\pi = RT \left(2a + 4x + 2b \right)$$

- Since

$$x = \frac{b^2}{a + 2b}$$

the expression above will be

$$\pi = RT \left(\frac{2a^2 + 2ab}{a + 2b} \right)$$

- What if we do not add NaCl to side B?

$$b = 0 \quad \text{and} \quad \pi = RT \, 2 \, a$$

- What if we add lots of NaCl to side B?

$$b \gg a \quad \text{and} \quad \pi = RT \, a$$

we can measure the molecular weight of the protein

- What if the protein releases n Na^+ 's?

$$[Na^+]_A = na + x$$

and thus

$$x = \frac{b^2}{na + 2b}$$

thus the osmotic pressure is

$$\pi = RT \left(a + (na + x) + x - (b - x) - (b - x) \right)$$

Donnan potential

- The *Donnan potential* involves a closer examination of the forces keeping Na^+ ions on side A even if no NaCl was added to side B
- To be able to investigate the Donnan potential, we should evaluate the concept of *electrical potential*

Electrical potential

- The *electrical potential*, Φ , is the amount of electrical work that must be performed to move one unit positive charge from a location where $\Phi=0$ to where the electrical potential is Φ

- If

$$\Phi > 0$$

we must do work

- If

$$\Phi < 0$$

the system can perform work, so we obtain work

- The units of electrical potential are work/unit charge
- In physics, we use units of

$$\text{Joule / Coulomb} = \text{Volt}$$

- An important constant is the Faraday constant, F , which is a convenient conversion factor from a single charge to a mole of charges

$$F = N_A \cdot e = 96485 \text{ C mol}^{-1}$$

where $N_A = 6.022 \cdot 10^{23}$ is the Avogadro constant and $e = 1.602 \cdot 10^{-19}$ is the elementary charge that is the charge of a proton

Michael Faraday



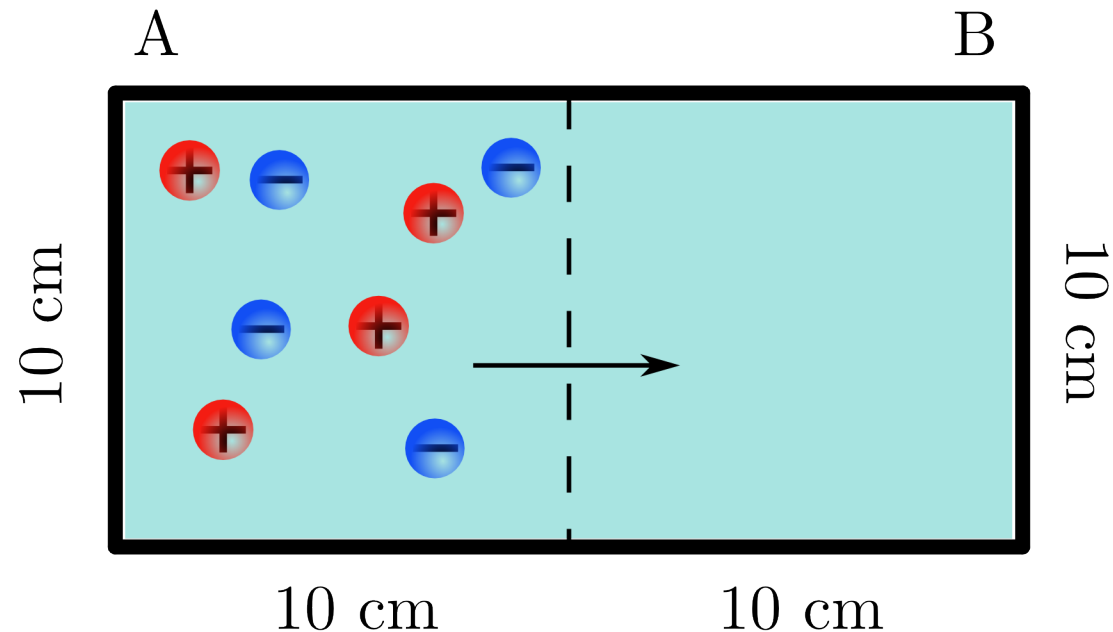
- The work to move one mole of charges is

$$w = z N_A e \Phi = z F \Phi$$

where z is the signed valence

- Now we will discuss the mechanism that generates the *Donnan potential*
- Connect two boxes (10 cm on a side) by a semipermeable membrane
- The volume of each side will be one dm³
- Let us put a protein with one ionizable group and Na⁺ ions into the side A

Generation of the Donnan potential



Initial concentration of ions

Ion	A	B
$[P^-]$	10^{-5} M	0
$[Na^+]$	10^{-5} M	0

- Does any Na^+ go across the membrane?
 - A little bit does diffuse across
- At equilibrium

$$[\text{Na}^+]_B \approx 10^{-11} \text{ M}$$

- This does not change $[\text{Na}^+]_A$ significantly and the movement of Na^+ ions creating a small charge separation is not significant for calculations

- The Na^+ which leaks across the membrane is found along the walls of chamber B
- These positive charges repel each other and push each other to the edge of the container (to get as far apart as possible)
- There will be a small excess negative charge in chamber A
- There will be an excess negative charge is also found along the walls of chamber A

- Let us imagine that we take a unit positive charge from a long distance (where $\Phi=0$) and move it into B
- We would perform Φ_B work

$$w = \Phi_B$$

- Likewise, if we take a unit positive charge from a long distance and move it into A, we would perform Φ_A work

$$w = \Phi_A$$

- Therefore to take a unit positive charge from side A to side B requires

$$\Phi = \Phi_B - \Phi_A$$

work

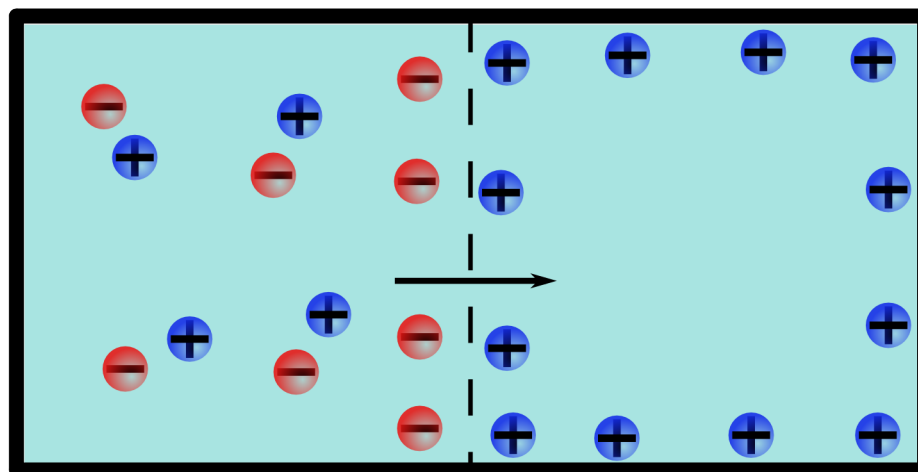
- This work is called the *Donnan potential*
- The *Donnan potential* in our case is

$$\Delta \Phi = \Phi_B - \Phi_A \approx 360 \text{ mV}$$

Frederick Donnan



Donnan potential



- The (powerful) electrical field created at the membrane is what prevents Na^+ from going across
- Φ_A and Φ_B have opposite signs

$$\Delta \Phi = \Phi_B - \Phi_A$$

is the Donnan potential for a Na^+ going from A to B

- To calculate the Donnan potential, we use a modified version of the *fundamental law*
- **In a heterogeneous, closed system at equilibrium, the *electrochemical potential* of any substance (charged or uncharged) is the same in all phases between which it can freely pass**

- Let $\bar{\mu}$ denote the electrochemical potential

$$\bar{\mu}_+ = \left(\frac{\partial G}{\partial n_+} \right)_{T, p, n_-}$$

is the change in free energy of a solution upon addition of an infinitesimal amount of Na^+

- Let us imagine that we can separate Na^+ from its charge
- Then we can put Na into the solution first and then add the positive charge
- We can then distinguish how much electrical work is needed to add a positive charge

$$\bar{\mu}_+ = \mu_+^0 + RT \ln \gamma_+ c_+ + zF \Phi$$

is the *electrochemical potential*

- Now,

$$(\bar{\mu}_+) _A = (\bar{\mu}_+) _B$$

- Let us subtract the expression for side A from that for side B

$$\begin{aligned} & \mu_B^0 + RT \ln (\gamma_+ c_+) _B + zF \Phi_B \\ & - \mu_A^0 + RT \ln (\gamma_+ c_+) _A + zF \Phi_A = 0 \end{aligned}$$

- Since the standard chemical potentials depend only on the properties of the substance and not on the concentration of it,

$$\mu_B^0 = \mu_A^0$$

- Thus these terms disappear from the expression above

$$RT \ln \frac{(\gamma_+ c_+)_B}{(\gamma_+ c_+)_A} + zF (\Phi_B - \Phi_A) = 0$$

- After rearrangement we obtain

$$\Delta \Phi = \Phi_B - \Phi_A = -RT \ln \frac{(\gamma_+ c_+)_B}{(\gamma_+ c_+)_A}$$

- At 10^{-5} M concentration,

$$\gamma_+ \rightarrow 1$$

so

$$\Delta \Phi = -\frac{RT}{zF} \ln \left(\frac{(c_+)_B}{(c_+)_A} \right)$$

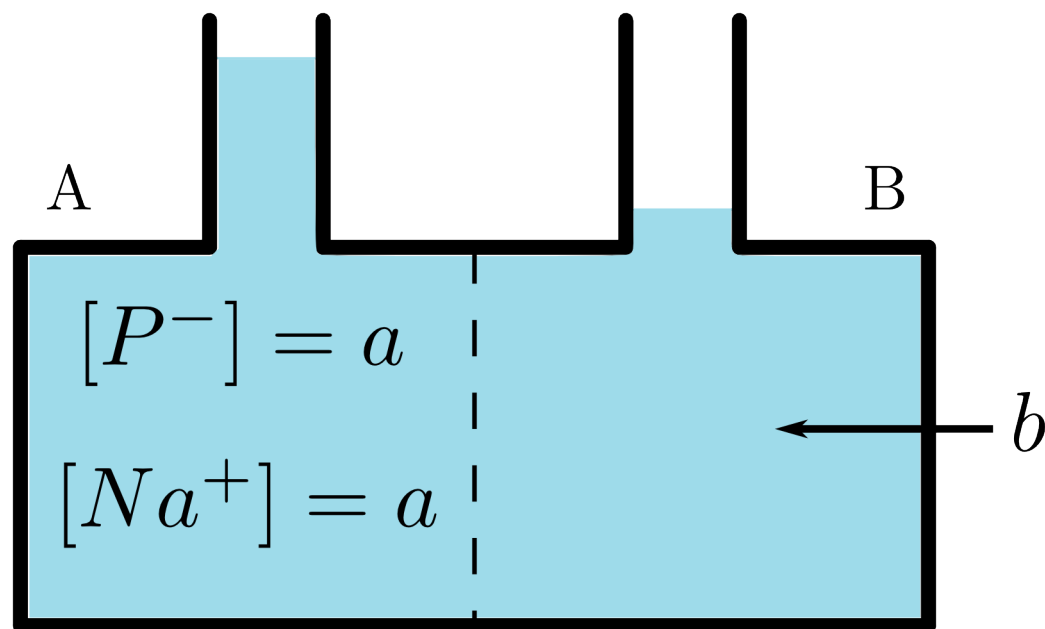
- Plugging in $c_{+,A}=10^{-5}$ M and $c_{+,B}=10^{-11}$ M, the *Donnan potential* is

$$\Delta \Phi \simeq 360 \text{ mV}$$

- This small potential keeps most of Na^+ ions in the side A with the protein

- Let us return to the osmometer problem and examine how dumping in salt suppresses the *Donnan potential*

Donnan potential in an osmometer



- After adding NaCl at an initial concentration b , x amount of NaCl diffuses to side A until equilibrium is reached

Ions	Side A	Side B
$[P^-]$	a	0
$[Na^+]$	$a+x$	$b-x$
$[Cl^-]$	x	$b-x$

- Now, we use either $[\text{Na}^+]$ or $[\text{Cl}^-]$ to calculate the *Donnan potential*, $\Delta\Phi$,

$$\Delta\Phi = -\frac{RT}{zF} \ln \frac{b-x}{a+x}$$

- Substituting

$$x = \frac{b^2}{a+2b}$$

we get

$$\Delta\Phi = -\frac{RT}{zF} \ln \frac{b}{a+b}$$

- What if we throw in lots of NaCl, that is

$$b \gg a$$

Then we can ignore a in the denominator and get

$$\Delta \Phi = -\frac{RT}{zF} \ln \frac{b}{b} = 0$$

- We have suppressed the *Donnan potential* by throwing in a lot of salt

- What if we throw in no salt, that is

$$b = 0$$

Then

$$\ln \frac{0}{a} = -\infty$$

but $\Delta\Phi$ does not go to infinity due to a little Na^+ going across

- We showed earlier that for this case

$$\Delta\Phi \simeq 360 \text{ mV}$$

Debye-Hückel theory

- The Debye-Hückel theory allows us to calculate the mean activity coefficient, $\gamma_{\pm}$, for electrolytes, taking nonideality into account

- Let us recall that

$$\mu_{+} = 2 \mu_{\pm}^0 + RT \ln \gamma_{\pm}^2 c_{+} c_{-}$$

or

$$\mu_{+} = 2 \mu_{\pm}^0 + RT \ln \gamma_{\pm}^2 + RT \ln c_{+} c_{-}$$

- The second term on the right hand side is an energy term related to the interactions between ions in the solution:
 - $\text{Na}^{+}/\text{Na}^{+}$
 - $\text{Cl}^{-}/\text{Cl}^{-}$
 - and $\text{Na}^{+}/\text{Cl}^{-}$

- $\gamma_{\pm}$ is a measure of nonideality of electrolyte solutions
- Let us recall that the ideal case assumes no interactions between particles in solution
- There are strong ionic interactions between ions in solution leading to large deviations from ideality
- The *Debye-Hückel theory* allows us to calculate $\gamma_{\pm}$ for electrolytes and take nonideality into account

- The result is

$$\log_{10} \gamma_{\pm} = -0.51 |z_+ z_-| I^{1/2}$$

where -0.51 is a constant for H₂O as a solvent at 298 K, z_+ and z_- are the ionic charges and I is the total ionic strength

Ionic strength

- The *ionic strength* is

$$I \equiv \sum_i c_i z_i^2$$

where c_i is the molar concentration of the i 'th ion and z_i is the charge of it

Examples for ionic strengths

	c (M)	I
NaCl	0.01	0.01
CuSO ₄	0.01	0.04
CaCl ₂	0.01	0.03

- How much is $\gamma_{\pm}$ for a non-electrolyte (sucrose)?

c (M)	γ
0.006	1.000
0.029	1.008
0.132	1.015
0.877	1.129

- For an uncharged solute, γ becomes significant, that is different from 1 by more than 1% at a concentration at about 0.1 M

- How much is γ for electrolytes?

	c (M)	γ
NaCl	10^{-4}	0.988
CuSO_4	10^{-6}	0.991

- For electrolytes, γ is already significant in the μM range

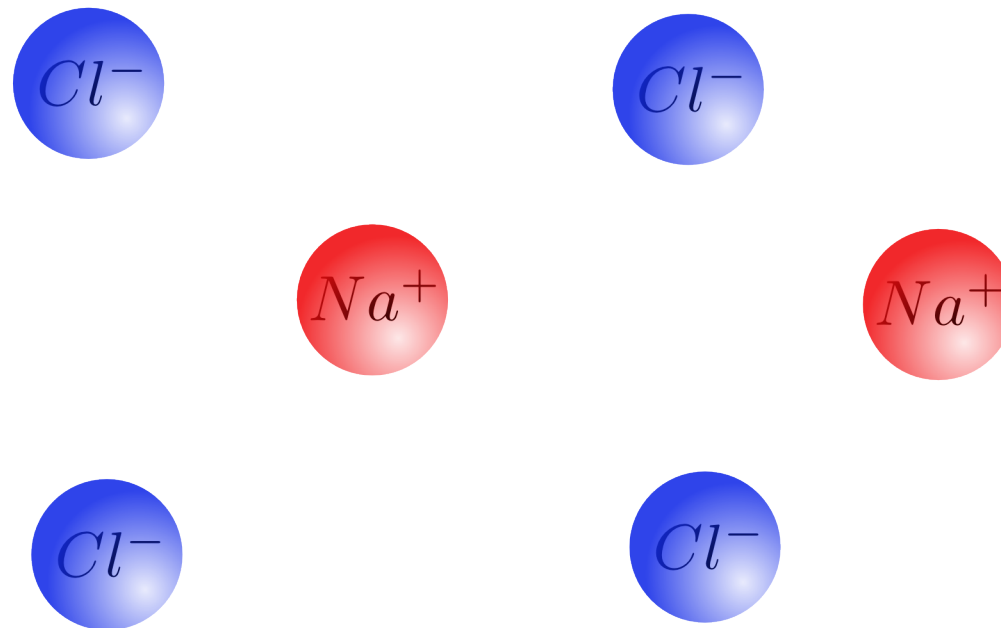
- How good is our equation for predicting $\gamma_{\pm}$?

	c (M)	$\gamma_{\pm}$ observed	$\gamma_{\pm}$ calculated
HCl	10^{-2}	0.904	0.889
KCl		0.901	
NaCl		0.914	
HCl	10^{-3}	0.966	0.964
KCl		0.965	
NaCl		0.966	
CuSO ₄	10^{-2}	0.41	0.391
MgSO ₄		0.400	

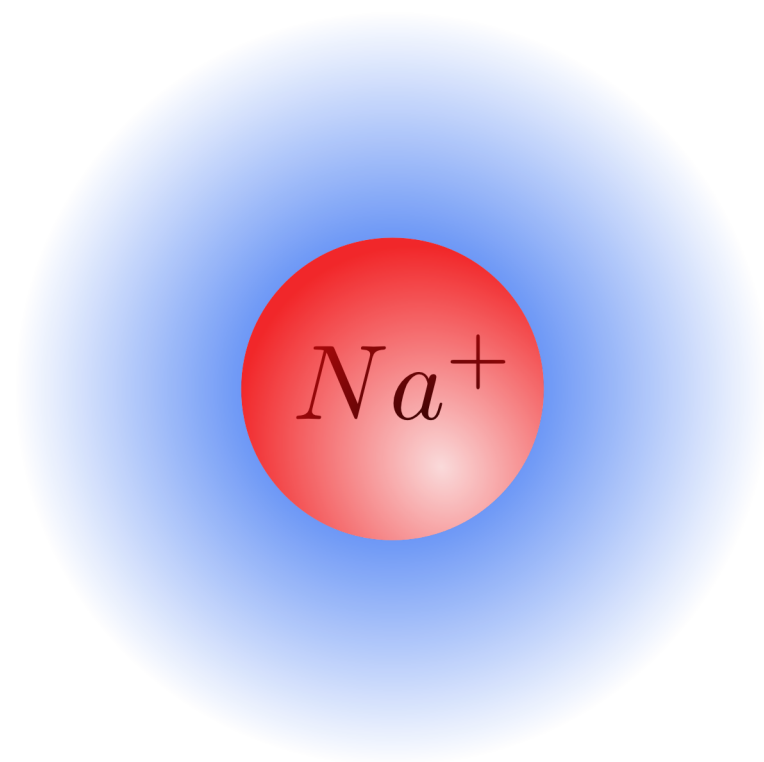
- This was a simple model
- A more sophisticated model that takes into account ionic radii works up to a concentration near that where deviation from ideality occurs for non-electrolytes

- The *Debye-Hückel* theory assumes that at low concentrations, deviations from ideality for electrolyte solutions are entirely due to *coulombic forces*
- Let us imagine that we could take a snapshot of the Na^+ and Cl^- ions in a NaCl solution
- On average, the density of Cl^- ions in the vicinity of Na^+ ions would be a little greater than the average density of Cl^- ions
- The same would be true of the density of Na^+ ions around a Cl^- ion

Ionic density in the vicinity of other ions



Ion atmosphere around a Na^+ ion



- Actually, the ions are undergoing violent Brownian motion, so a more realistic picture involves the time averaged density
- In the figure above, shading represents the time-averaged excess negative charge density around a Na^+ ion
- The darker the shading the greater the density
- The distribution of negative charge around the Na^+ ion is spherically symmetrical
- It is called the *ion atmosphere*

- We can plot the ion atmosphere as a function of distance, r , from the centre of the Na^+ ion
- It can be seen that at

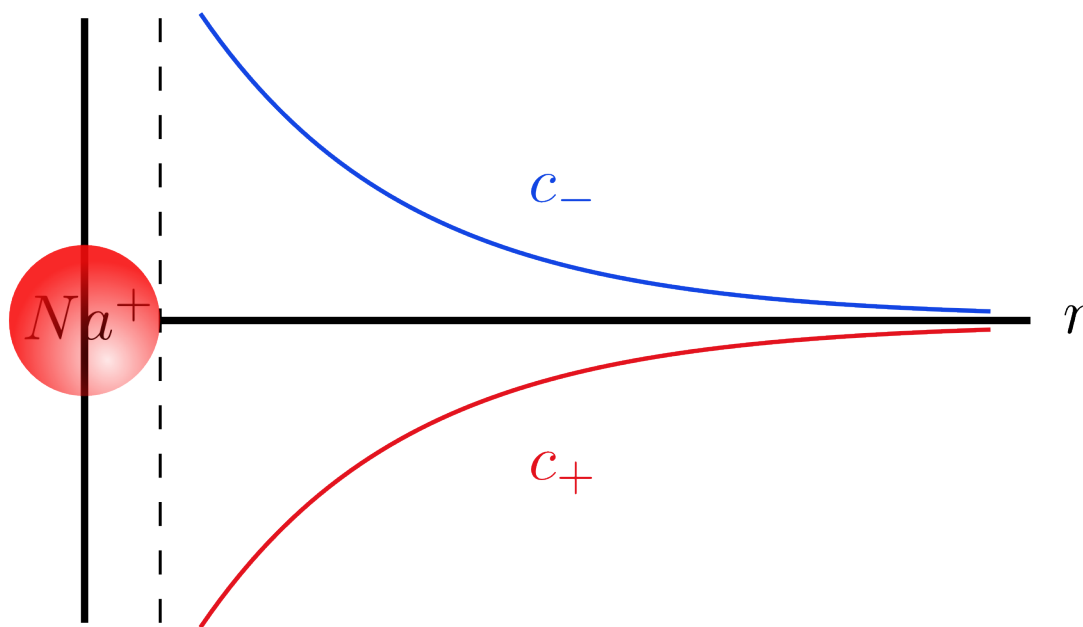
$$r = \infty$$

$$c_+ = c_- = c_\infty$$

where c_- is the concentration of Cl^- ion

- The curves are symmetrical to the r axis

The ion atmosphere as a function of r



Peter Debye



Erich Hückel



Coulomb's law

- The force between two charges, F , can be calculated from Coulomb's law

$$F = \frac{z_1 z_2}{D r^2}$$

where D is the dielectric constant, z_1 and z_2 are ion charges and r is the distance between the ions

- It is worth noting that

$$D = 1$$

in vacuum and

$$D = 80$$

in water

- It means that the force between two charges is 80 times greater in vacuum than it is in water

Charles Augustine de Coulomb



Electrical field strength

- The electrical field strength is the force per unit charge and is denoted by E
- The electrical field around a charge, z , is determined by placing a positive test charge, z_2 , at some distance, r , from z , and measuring the force on z_2

$$E = \frac{F}{z_2} = \frac{z_1}{D r^2}$$

- E is a vector quantity
- It points away from z , if z_1 is positive
- The direction of E is now irrelevant for us; we only use its magnitude

Electrical potential

- The electrical potential is a quantity whose negative derivative with respect to distance is the electric field, which represents the force acting on a unit charge
- The electrical potential is denoted by Φ

$$-\frac{\partial \Phi}{\partial r} = E$$

- And since

$$E = \frac{F}{z_2}$$

the derivative of electric potential with respect to distance is

$$-\frac{\partial \Phi}{\partial r} = \frac{F}{z_2}$$

- To obtain the electrical potential, we should integrate the expression above from ∞ to r

$$\int_{\infty}^r \partial \Phi = - \int_{\infty}^r \frac{F}{z_2} \partial r$$

- We get

$$\Phi(r) - \Phi(\infty) = - \int_{\infty}^r \frac{F}{z_2} \partial r$$

- Since

$$\Phi(\infty) = 0$$

$$\Phi(r) = - \int_{\infty}^r \frac{F}{z_2} \partial r$$

- As we know, force times distance is work
- Therefore, $\Phi(r)$ is the work required to bring a unit positive test charge (z_2) from a location where the potential is zero to where the potential is $\Phi(r)$

- According to Coulomb's law

$$\frac{F}{z_2} = \frac{z_1}{D r^2}$$

so

$$\Phi(r) = -\frac{z_1}{D} \int_{\infty}^r \frac{\partial r}{r^2} = \frac{z_1}{D r}$$

- We can plot Φ as a function of r , for a single Na^+ ion in the absence of an ion atmosphere

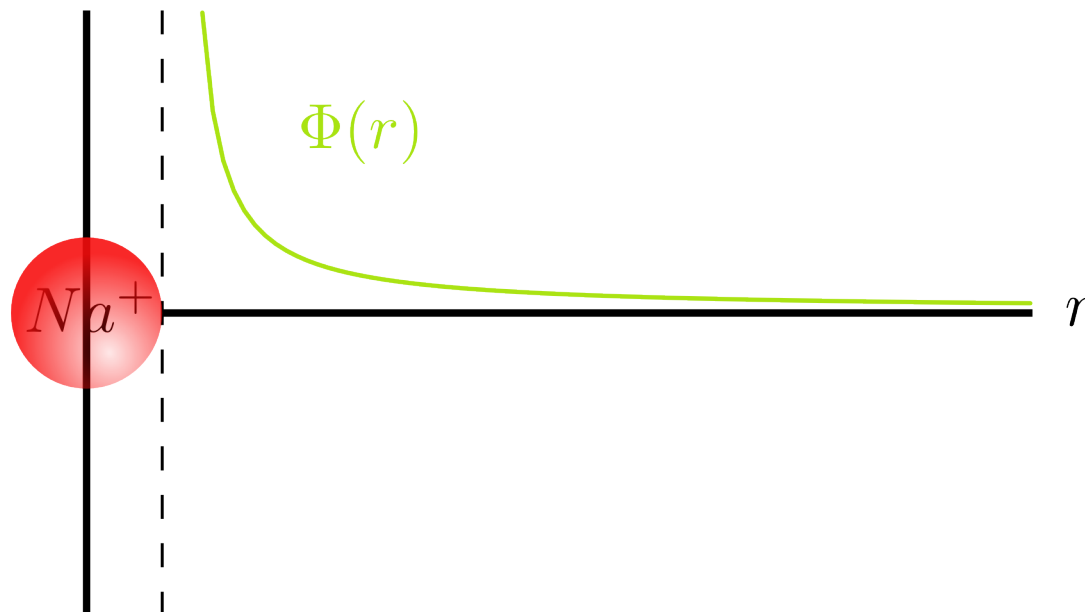
$$z_1 = e z_+$$

where e is the elementary charge and z_+ is the valence of the positive ion

- So

$$\Phi(r) = \frac{z_+ e}{D r}$$

Electrical potential vs. r



- Now, we wonder whether there is a relationship between the electrical potential, Φ , of an ion and the ion atmosphere
- We can calculate this relationship using the *Maxwell-Boltzmann distribution* and *Gauss's law*

Gauss's law

- A special consequence of Gauss' law is that for a spherically symmetrical charge distribution, the electric field at radius r will be equal to that caused by the sum of the charges inside a sphere of radius r , acting as if they were at the centre of the sphere

Carl Friedrich Gauss



- We can relate the electric potential, Φ , to the ionic strength, I

$$\Phi = \frac{z}{D r} e^{-\kappa r}$$

where

$$\kappa^2 = \frac{8\pi N_A e^2 I}{1000 D k_B T}$$

where N_A is the Avogadro constant and k_B is the Boltzmann constant

- If we plot Φ as a function of r both in the presence and absence of the ion atmosphere we see that

$$\Phi_{i.a.} < \Phi_{no\ i.a.}$$

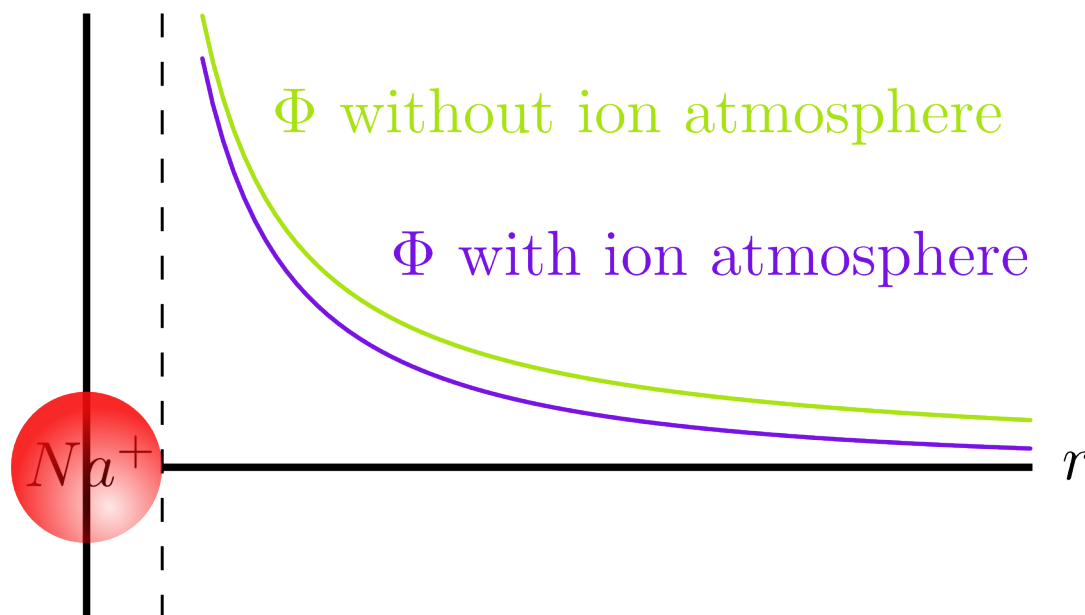
where $\Phi_{i.a.}$ and $\Phi_{no\ i.a.}$ are the electric potential with and without ion atmosphere, since

$$\Phi_{i.a.} = \frac{Z}{D r} e^{-\kappa r}$$

and if $I=0$

$$\Phi_{no\ i.a.} = \frac{Z}{D r}$$

Electric potential with and without an ion atmosphere



- How much energy is required to put one positive charge on a neutral Na atom?
- Let us recall that

$$RT \ln \gamma_+$$

is the energy to create the ion atmosphere for 1 mole of Na^+ ions, so

$$k_B T \ln \gamma_+$$

is the energy to create the ion atmosphere around one Na^+ ion

- Now, let us calculate the work to charge one neutral Na atom

$$w = \int_0^{z_+ e} \Phi dz$$

- In absence of *ion atmosphere*

$$w_1 = \int_0^{z_+ e} \Phi dz = \int_0^{z_+ e} \frac{z}{D r_{Na}} dz = \frac{(z e)^2}{2 D r_{Na}}$$

- In presence of *ion atmosphere*

$$w_2 = \int_0^{z_+ e} \Phi dz = \int_0^{z_+ e} \frac{z}{D r_{Na}} e^{-\kappa r_{Na}} dz = \frac{(z e)^2}{2 D r_{Na}} e^{-\kappa r_{Na}}$$

where r_{Na} is the radius of Na

- The difference between w_1 and w_2 is the work required to create the *ion atmosphere*

$$k_B T \ln \gamma_+ = \frac{(ze)^2}{2D r_{Na}} \left(e^{-\kappa r_{Na}} - 1 \right)$$

- Since

$$\kappa r_{Na}$$

is very small,

$$e^{-\kappa r_{Na}} \approx 1 - \kappa r_{Na}$$

- So

$$k_B T \ln \gamma_+ = \frac{(ze)^2}{2D r_{Na}} (1 - \kappa r_{Na} - 1) = -\frac{(ze)^2}{2D} \kappa$$

- Similarly, for negative charge

$$k_B T \ln \gamma_- = -\frac{(ze)^2}{2D} \kappa$$

- Since by definition

$$\gamma_{\pm}^2 = \gamma_{+} \gamma_{-}$$

the expression above can be written as

$$\begin{aligned} 2 k_B T \ln \gamma_{\pm} &= k_B T \ln \gamma_{+} + k_B T \ln \gamma_{-} \\ &= -\frac{z_{+}^2 e^2 \kappa}{2 D} - \frac{z_{-}^2 e^2 \kappa}{2 D} = -\frac{e^2 \kappa'}{2 D} (z_{+}^2 + z_{-}^2) I^{1/2} \end{aligned}$$

where

$$\kappa' = \frac{\kappa}{I^{1/2}}$$

- It can be shown for Na^+ and Cl^- ions that

$$\frac{(z_+^2 + z_-^2)}{2} = |z_+ z_-|$$

- Now, for H_2O at 298 K

$$\ln \gamma_{\pm} = -1.17 |z_+ z_-| I^{1/2}$$

or

$$\log_{10} \gamma_{\pm} = -\frac{1.17}{2.303} |z_+ z_-| I^{1/2} = -0.51 |z_+ z_-| I^{1/2}$$

- This is an important equation because it allows us to calculate a thermodynamic property, the *mean ionic activity coefficient*, $\gamma_{\pm}$, from molecular properties
- Let us notice that

$$\ln \gamma_{\pm} \leq 0$$

so

$$\gamma_{\pm} \leq 1$$

- Let us notice that the Debye-Hückel theory always predicts

$$\gamma_{\pm} \leq 1$$

- This occurs because the interaction between an ion and its ionic atmosphere is always favourable