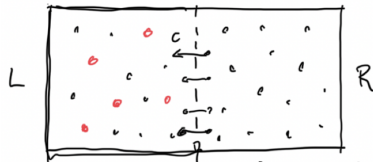


# FYS4715 2021 Lectures 6,7

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## 1 Osmosis



A fixed volume,  $V$  where the left and right subvolume  $V_L = V_R = V/2$  are separated by a semipermeable membrane that only the black particles can cross. The red particles are stuck on the left side. The number of red solute particles  $N_2$  is much smaller than the number of black solvent particles  $N_1$ :  $N_2 \ll N_1$ . In a biological system black particles are water, red particles are proteins, ions...

- What will happen?
- How will the water particles  $N_{1,L}$ ,  $N_{1,R}$  distribute?
- From intuition and ideal gas: Entropy  $S$  is maximized when concentration is even,  $N_{1,L} = N_{1,R}$ .
- $P_L$ ,  $P_R$ ?
- For ideal solutions  $N_{1,L} = N_{1,R} \Rightarrow P_{1,L} = P_{1,R}$ .
- What is the effect of the excess of particles on left side?
- Basic assumption: Dilute solution  $\Rightarrow$  non-interacting particles  $\Rightarrow$  Ideal gas model

The ideal gas is a collection of non-interacting particles *in thermal motion* which our solute particles are. Ideal gas EOS on the left side:

$$P_2 V_L = N_2 k T \quad (1)$$

$$\Delta P = P_L - P_R = P_2 = C_2 k T = c_2 R T, \quad C_2 = \frac{N_2}{V_L} \quad (2)$$

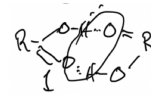
Can this shockingly simple argument be true?

## 1.1 Van't Hoff equation

$$\Delta P = \sum_i \phi_i c_i RT, \quad (3)$$

where  $c_i$  are the molar solute concentrations and  $\phi_i$  the number of particles in solution from one solute particles.

- $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^- \Rightarrow \phi = 2$
- Glucose  $\rightarrow$  glucose  $\Rightarrow \phi = 1$
- Carboxylic acid  $\rightarrow$  dimer of carboxylic acid  $\Rightarrow \phi = 1/2$

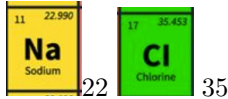


It's the number of "ideal gas" particles that counts.

## 1.2 Numbers



- Physiological saline solution: 9g NaCl/1000 g H<sub>2</sub>O
- How do we calculate molar concentration?



- Units? g/mol,  $R=8.3 \text{ J}/(\text{K mol})$
- $c_2 = \frac{9\text{g}}{(23+35)\text{g/mol} \cdot 1\text{l}} = 0.15\text{mol/l} = 150 \text{ mol/m}^3$

$$\Delta P = 2cRT = 2 * 150 * 8.3 * 300 = 7.2 \cdot 10^5 \text{ Pa} = 7.2\text{bar}$$

More than in the tyres of a racing bike!

## 2 Sidestep: Chemical potential

The equilibrium conditions at constant  $T$  and  $P$  and  $V$  are given by the Gibbs  $G$  and Helmholtz  $F$  free energies. Equilibrium with respect to number of particles is defined by the equality of chemical potential

$$\mu = \left( \frac{\partial G}{\partial N} \right)_{P,T} = \left( \frac{\partial F}{\partial N} \right)_{V,T} = T \left( \frac{\partial S}{\partial N} \right)_{E,V} \quad (4)$$

This is the fundamental equilibrium condition, not equality of concentration.

## 2.1 The Gibbs-Duhem relation

When there are I components in a system only I-1 components have independent values for the chemical potential. The Gibbs-Duhem relation is a relation between changes in chemical potential for the different components:

$$\sum_i n_i d\mu_i = -SdT + VdP \quad (5)$$

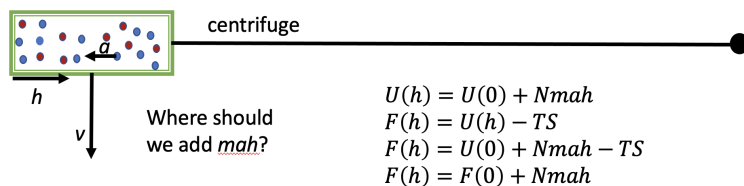
## 2.2 Chemical potential of ideal solutions

An ideal solution has no volume change upon mixing and the enthalpy of mixing is zero. Thus in a binary solution  $c = \frac{N}{V}$  is constant independent of  $x_1 = \frac{N_1}{N} = \frac{N_1}{N_1+N_2}$ . The chemical potential of an ideal solution is

$$\mu(P, T, c_1) = \mu^0(P, T) + RT \ln c_1 \quad (6)$$

## 2.3 Chemical potential of external fields

The chemical potential measures the energy required to insert a particle into the system. The “internal” chemical potential concerns concentrations in different systems without any differences external potentials. The “external” chemical potential includes the differences in pressure or external potentials. For example



$$\mu = \left( \frac{\partial F}{\partial N} \right)_{V,T} = \mu(c) + mah \quad (7)$$

$$\mu_{tot} = \mu_{int} + \mu_{ext} \quad (8)$$

This can be used in order to derive the barometric pressure formula. In equilibrium the chemical potential of air is independent of height:

$$\begin{aligned} \mu(z) &= \mu_0 = \mu_0 + kT \ln \frac{P(z)}{P_0} + mgz \\ \Rightarrow \frac{P(z)}{P_0} &= e^{-mgz/kT} \end{aligned} \quad (9)$$

For ions in an electrical field  $\varepsilon$  the potential energy is  $U(x) = -q\varepsilon x$  and thus  $\mu_{ext} = U(x)$ .

## 3 Osmotic flow

The simplistic derivation of osmotic pressure was done for constant  $N$  and  $V$  and we only found the equilibrium pressure. We would like to know how the pressure, chemical potentials, concentrations and particle flux over the membrane evolve with time when the two sides start at the same pressure and the right hand side is open.

### 3.1 Formalism of irreversible thermodynamics

We will introduce the formalism of irreversible thermodynamics which concerns linear transport. The basic idea is that the flux of particles,  $J_p$ , and heat,  $J_q$  are linearly dependent on the thermodynamic driving forces  $K$  that are  $\nabla\mu$  and  $\nabla T$ :

$$J_i = - \sum_{ij} l_{ij} K_j$$

For an isothermal 2 component system this can be written:

$$\begin{aligned} J_1 &= -l_{11}\nabla\mu_1 - l_{12}\nabla\mu_2 \\ J_2 &= -l_{21}\nabla\mu_1 - l_{22}\nabla\mu_2 \end{aligned} \quad (10)$$

The  $l_{ij}$  are called linear transport coefficients. The transport coefficients with equal indices  $l_{11} = D \left( \frac{\partial\mu}{\partial c} \right)$  are proportional to the diffusion coefficients we know from Fick's law of diffusion  $J = -D\nabla c$ . The off-diagonal transport coefficients are related to non-ideal solutions where different species attract or repel and tend to be affected by each other's gradients. Onsager showed that the coefficient matrix is symmetric:  $l_{ij} = l_{ji}$ .

### 3.2 General derivation of osmotic flux and pressure

For osmosis we want to calculate the fluxes across the semipermeable membrane. We will therefore only use differences  $\Delta$  instead of gradients  $\nabla$ .

$$\begin{aligned} J_1 &= -l_{11}\Delta\mu_1 - l_{12}\Delta\mu_2 \\ J_2 &= -l_{21}\Delta\mu_1 - l_{22}\Delta\mu_2, \end{aligned} \quad (11)$$

where water is species 1 and solute particles are species 2. Since species 2 cannot traverse the membrane  $l_{22} = l_{2,1} = 0$  and because of the Onsager symmetry relation  $l_{12} = l_{21} = 0$ . This shows that even though there is a difference in concentration of species 2 that will not affect the flow or equilibrium condition of species 1: only the chemical potential of species 1 matters. We already assumed as much for the ideal case, but now it is proven in general.

The flux equation reduces to

$$J_1 = -l_{11}\Delta\mu_1 \quad (12)$$

Now we would like to relate  $\Delta\mu_1$  to the concentration of solute particles. In order to do so we use the Gibbs-Duhem relation which for isothermal changes can be written:

$$\sum_i c_i \Delta\mu_i = \Delta P \quad (13)$$

or

$$\Delta\mu_1 = \frac{1}{c_1}(\Delta P - c_2\Delta\mu_2) \quad (14)$$

We insert this into equation (12):

$$J_1 = -\frac{l_{11}}{c_1}(\Delta P - c_2\Delta\mu_2) \quad (15)$$

Now we will simplify assuming that the solutions are ideal:

$$\begin{aligned}\mu_2 &= \mu_{2,0} + RT \ln c_2 \\ \frac{d\mu_2}{dc_2} &= RT \frac{d \ln c_2}{dc_2} = RT \frac{1}{c_2} \\ \Rightarrow \Delta\mu_2 &= RT \frac{\Delta c_2}{c_2}\end{aligned}\tag{16}$$

With this we can find a version of equation (15) for ideal solutions:

$$J_1 = -\frac{l_{11}}{c_1}(\Delta P - RT\Delta c_2)\tag{17}$$

which has the same equilibrium state ( $J_1 = 0$ ) as before:

$$\Delta P = RT\Delta c_2.\tag{18}$$