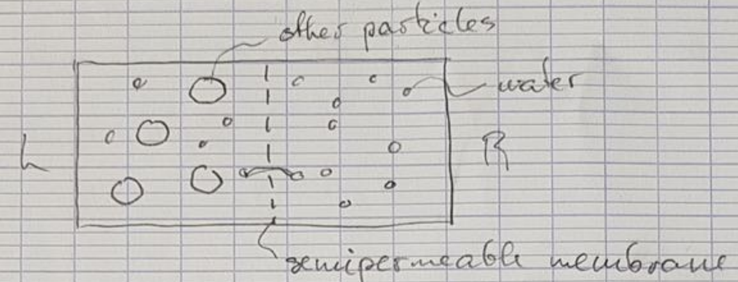
Osmosis ①



What will happen ?

How can we model this ?

$N_{w,l}$ $\quad$ $N_{w,r}$

$N_{p,l} > 0$ $\quad$ $N_{p,r} = 0$

$V_l = V_r = \frac{V}{2}$

P_l $\quad$ P_r $\quad$ Initially equal

* Only water molecules are free to move. How do they distribute ? S or R ?

From intuition & ideal gas :
Largest S when equal distribution in the volume

=> Equilibrium of water on right & left side
$P_{w,L} = P_{w,R}$

* Particles not in equilibrium on L & R

What is the effect ?

* Dilute solution => non interacting particles

Osmosis (2)

* Non-interacting particles : Ideal gas model

Left side :

$\Rightarrow \quad P_p V_L = N_p kT$

$$P_L - P_R = \Delta P = P_p = c_p kT \,, \quad c_p = \frac{N_p}{V_L}$$

Can this shockingly simple argument be true ?

Van't Hoff equation

$$\Delta P = \varphi_i c_i kT$$

c_i = solute concentration

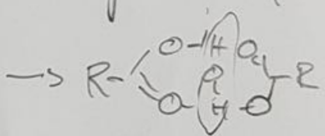
φ_i - dimless number

φ_i = how many particles in solution from one solute particle

$$c_p = \varphi_i c_i$$

NaCl → $Na^+ + Cl^-$ $\varphi = 2$

glucose → glucose $\varphi = 1$

carboxylic acid → 

2 → 1 $\varphi = \frac{1}{2}$

It is actually the number of "ideal gas" particles that count!!!

Numbers : Physiological saline solution : Eyes, blood ....

$$c = \frac{9\,g\ NaCl}{\ell\ H_2O}$$ How do I calculate c_p ?

Periodic table : Na: 23, Cl: 35 What units ? $\boxed{g/mol}$

$$P = \frac{nRT}{V}$$

$R = 8{,}3\ J/K\,mol$

Osmosis ③

$$C = \frac{9\,g}{(23+35)\,g/mol \cdot l} = 15{,}5\ \frac{mol}{l}$$

NaCl → (Na^+) + (Cl^-)

$$C_p = 2C = 0{,}31\ \frac{mol}{l}$$

$$P = CRT = 0{,}31 \cdot 8{,}3 \cdot 300\ \frac{mol}{l}\,\frac{J}{K\,mol}\,K$$

$l = 10^{-3}\,m^3$

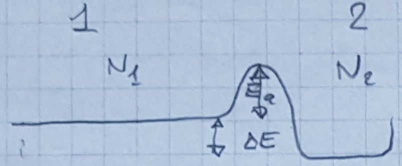
$$\approx 9 \cdot 8\ 10^{-1+2+3}\ Pa$$

$$\approx 7{,}2 \cdot 10^5\ Pa = 7{,}2\ bar$$

more than in tyres of a racing bike!

(1)

Reaction rates



Boltzm. factors $\frac{P_1}{P_2} = \frac{e^{-E_1/kT}}{e^{-E_2/kT}} = e^{-\Delta E/kT} = \frac{N_{1,eq}}{N_{2,eq}}$

Rate $\Gamma_{1\to 2} = A N_1 e^{-E_a/kT}$ $\propto$ how many can jump over the E_a

$\Gamma_{2\to 1} = B N_2 e^{-(E_a+\Delta E)/kT}$

$\Gamma_{1\to 2} = \Gamma_{2\to 1}$

$\frac{A N_1}{B N_2} = \frac{e^{-(E_a+\Delta E)/kT}}{e^{-E_a/kT}} = e^{-\Delta E/kT}$

$\Rightarrow A = B$

$\dot{N}_1 = N_1\Gamma_{12} - N_2\Gamma_{21}$

$\dot{N}_2 = -N_1\Gamma_{12} + N_2\Gamma_{21}$

Fixed N_{tot}

$\dot{N}_1 = N_1\Gamma_{12} - (N_t - N_1)\Gamma_{21}$

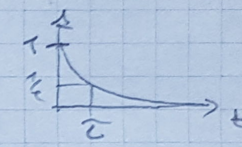
eq $\dot{N}_1 = 0 \Rightarrow N_{1eq}(\Gamma_{12}+\Gamma_{21}) - N_t\Gamma_{21} = 0$

$N_1(\Gamma_{12}+\Gamma_{21}) - N_t\Gamma_{21} = \dot{N}_1$

-4 $(N_1 - N_{1eq})(\Gamma_{12}+\Gamma_{21}) = \frac{dN_1}{dt} = \frac{d(N_1-N_{1eq})}{dt}$

(2)

$\Rightarrow \frac{N_1(t) - N_{1,eq}}{N_1(0) - N_{1,eq}} = e^{-(\Gamma_{12}+\Gamma_{21})t}$



$\tau = (\Gamma_{12}+\Gamma_{21})^{-1}$

NVT : natural free energy?

NVE $dE = TdS - pdV + \mu dN$ TD1

for NVT $dX = (\ )dT + (\ )dV + (\ )dN$

$d(TS) = TdS + SdT$

$\Rightarrow dE - d(TS) = SdT - pdV + \mu dN$

Helmholtz $\Rightarrow dF$, $F = E - TS$