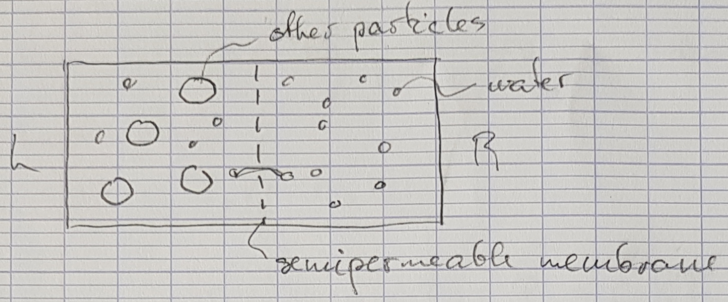
Osmosis ①



What will happen ?

How can we model this ?

$N_{w,l}$ $N_{w,r}$
$N_{p,l} > 0$ $N_{p,r} = 0$
$V_l = V_r = \frac{V}{2}$
P_l P_r Initially equal

* Only water molecules are free to move. How do they distribute ? $S_{or}\Omega$?

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

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

* 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

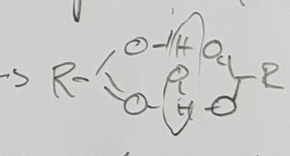
φ_i = how many particles in solution from one solute particle

$$c_p = \varphi_i c_i$$

$NaCl \rightarrow Na^+ + Cl^-$ $\quad \varphi = 2$

glucose $\rightarrow$ glucose $\quad \varphi = 1$

carboxylic acid $\rightarrow$



$2 \rightarrow 1 \quad \varphi = \frac{1}{2}$

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 ? $\boxed{g/mol}$

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

$R = 8{,}3\ J/Kmol$

Osmosis (3)

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

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

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

$$P = CRT = 0{,}31 \cdot 8{,}3 \cdot 300\ \frac{\cancel{mol}}{\underset{10^{-3}\,m^3}{l}}\,\frac{J}{\cancel{K}\,\cancel{mol}}\,\cancel{K}$$

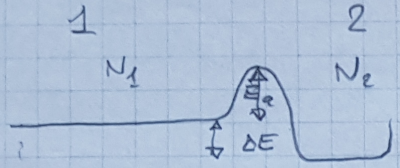
$$\approx 9 \cdot 8\ 10^{-1+2+3}\ Pa$$

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

more than in tyres of a racing bike!

1

Reaction rates



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

Rate $\quad \Gamma_{1\to 2} = A N_1 e^{-E_A/kT}$ $\quad \propto$ 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}

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

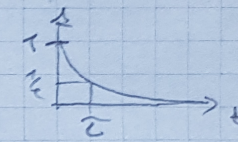
eq $\quad \dot N_1 = 0 \Rightarrow N_{1eq}(\Gamma_{12} + \Gamma_{21}) - N_t\Gamma_{21} = 0$

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

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

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 $\quad dE = TdS - pdV + \mu dN$ $\quad$ TDI

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

$d(TS) = TdS + \underline{\underline{SdT}}$

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

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