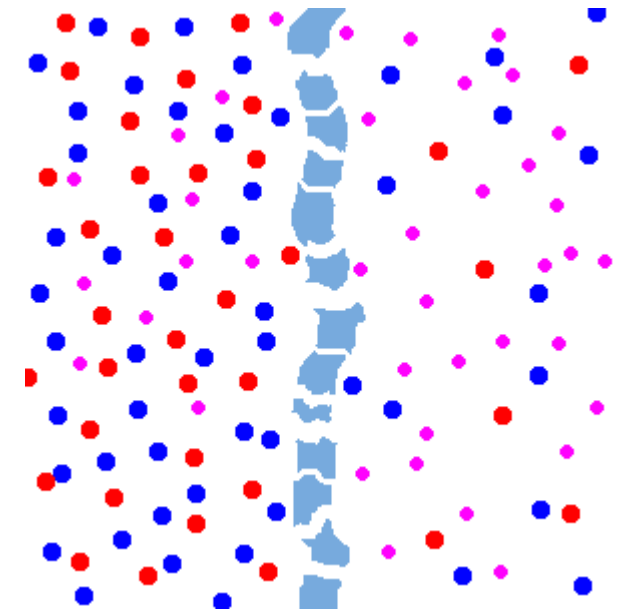


# Membranes and ions

Semipermeable membrane; glass frit; diaphragm

- concentrations of ions on both sides differ
- different permeabilities of ions
- mechanisms:
  - ion channels (in cell membrane)
  - pores (wider, permeability  $\propto$  diffusivity)
  - sorption+diffusion (polymer membrane), ...

“ $\propto$ ” = “is proportional”



E.g.: cell membrane, kidneys, dialysis, fuel cells, liquid junction (between electrolytes)  
[cf. osmotic pressure]

- We are interested in the membrane potential **in equilibrium**:
  - one ion permeates through the membrane – zero diffusion (fast!)
  - some ions permeate, other do not – Donnan equilibrium
- We are interested in the membrane potential during diffusion (**irreversible!**):
  - thin membrane (e.g., cell): (bio)membrane potential (Goldman)
  - electrolysis separated by a (thick) membrane:
    - liquid junction (diffusion) potential

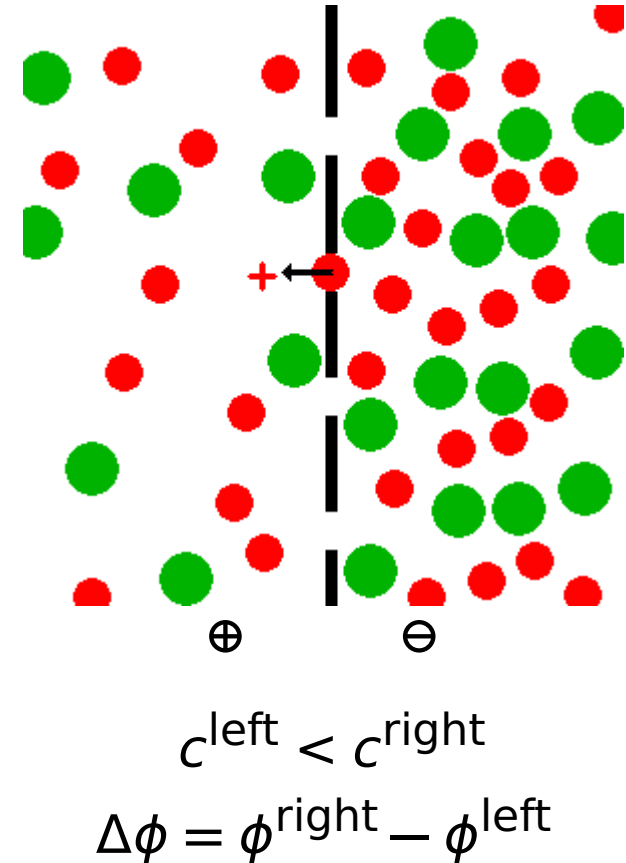
## Simple start: one ion permeates

- ⊙ HCl, different concentrations at both sides of a membrane (glass, Nafion, ...)
- only cations  $H^+$  can permeate

Cations try to diffuse to places with a lower concentration. Since the anions cannot follow them, a **membrane potential** arises. In equilibrium, the difference in the chemical potentials is compensated by the electric potential,  $\Delta\phi$  (also  $E$ ,  $\mathcal{E}$ ):

$$\mu_{H^+}^{\text{right}} - \mu_{H^+}^{\text{left}} + zF\Delta\phi = 0$$

$$\Delta\phi = \phi^{\text{right}} - \phi^{\text{left}} = -\frac{RT}{zF} \ln \frac{a_{H^+}^{\text{right}}}{a_{H^+}^{\text{left}}} \approx -\frac{RT}{zF} \ln \frac{c_{H^+}^{\text{right}}}{c_{H^+}^{\text{left}}}$$



Equivalently: the **electrochemical potentials**  $\tilde{\mu}_i = \mu_i + z_i F \phi$  ( $z_i$  includes sign) of ions  $H^+$  left and right are the same.

Macroscopic concentrations of  $H^+$  (HCl) are unchanged (electroneutrality), only concentrations close to surfaces (within double-layer) are affected.

left	:	right
NaX	:	NaCl
NaCl	:	

anion  $X^-$  does not permeate

The difference of the electrochemical potentials:

$$\tilde{\mu}_{\text{Na}^+}^{\text{right}} - \tilde{\mu}_{\text{Na}^+}^{\text{left}} = RT \ln \frac{c_{\text{Na}^+}^{\text{right}}}{c_{\text{Na}^+}^{\text{left}}} + F\Delta\phi \stackrel{\text{equilibrium}}{=} 0$$

$$\tilde{\mu}_{\text{Cl}^-}^{\text{right}} - \tilde{\mu}_{\text{Cl}^-}^{\text{left}} = RT \ln \frac{c_{\text{Cl}^-}^{\text{right}}}{c_{\text{Cl}^-}^{\text{left}}} - F\Delta\phi \stackrel{\text{equilibrium}}{=} 0$$

Sum of both equations  $\Rightarrow$

$$c_{\text{Na}^+}^{\text{left}} c_{\text{Cl}^-}^{\text{left}} = c_{\text{Na}^+}^{\text{right}} c_{\text{Cl}^-}^{\text{right}}$$

Generally for salt  $K\nu_{\oplus}A\nu_{\ominus}$ :

$$(c_{\oplus}^{\text{left}})^{\nu_{\oplus}} (c_A^{\text{left}})^{\nu_{\ominus}} = (c_{\oplus}^{\text{right}})^{\nu_{\oplus}} (c_A^{\text{right}})^{\nu_{\ominus}}$$

# Donnan equilibria—membrane hydrolysis

In the left compartment, there is  $n = 0.01$  mol of sodium *p*-toluensulfonate (NaTsO) in  $V^{\text{left}} = 100$  ml of water; in the right compartment, there is  $V^{\text{right}} = 1$  L of pure water. The membrane is impermeable for  $\text{TsO}^-$ . Calculate pH in both compartments in equilibrium at 25 °C.

balance [mol]	start		equilibrium	
	left	: right	left	: right
$\text{TsO}^-$	$n$	:	$n$	:
$\text{Na}^+$	$n$	:	$n - x$	: $x$
$\text{OH}^-$	:	:	$\approx 0$	: $x$
$\text{H}^+$	:	:	$x$	: $\approx 0$

$$\begin{aligned} \Delta\phi &= -\frac{RT}{F} \ln \frac{c_{\text{Na}^+}^{\text{right}}}{c_{\text{Na}^+}^{\text{left}}} \\ &= -\frac{RT}{F} \ln \frac{x/V^{\text{right}}}{(n-x)/V^{\text{left}}} \\ &= 0.256 \text{ V} \end{aligned}$$

$$\begin{aligned} c_{\text{Na}^+}^{\text{left}} c_{\text{OH}^-}^{\text{left}} &= c_{\text{Na}^+}^{\text{right}} c_{\text{OH}^-}^{\text{right}} \quad (\text{or } c_{\text{Na}^+}^{\text{right}}/c_{\text{Na}^+}^{\text{left}} = c_{\text{H}^+}^{\text{right}}/c_{\text{H}^+}^{\text{left}}) \\ \frac{n-x}{V^{\text{left}}} \cdot \frac{K_w}{x/V^{\text{left}}} &= \frac{x}{V^{\text{right}}} \cdot \frac{x}{V^{\text{right}}} \end{aligned}$$

Numerically (in mol,  $\text{dm}^{-3}$ ; more accurately by iterations)

$$x = \sqrt[3]{K_w(n-x)(V^{\text{right}})^2} \quad x \ll n \quad \approx \sqrt[3]{1 \times 10^{-14} \times 0.01 \text{ mol}} = 4.64 \times 10^{-6} \text{ mol}$$

$$\text{pH}^{\text{left}} = 4.3, \text{pH}^{\text{right}} = 8.7$$

E.g., cell membrane (lipid double layer with ion channels)

- we know ion concentrations  $c_i^{\text{left}}$  and  $c_i^{\text{right}}$
- stationary diffusion—zero total current  
(after establishing voltage  $\Delta\phi$ , which is much faster)
- size of molecules neglected, membrane = dielectric continuum
- electric field intensity  $\mathcal{E} = -\frac{d}{dx}\phi$  across the membrane is homogeneous follows from the Poisson equation

$$\Delta\phi = \phi^{\text{right}} - \phi^{\text{left}}$$

$$d^2\phi/dx^2 = -\rho/\epsilon : E(L) = E(0) + L\rho/\epsilon \approx E(0) \text{ pro } L \ll \lambda$$

Nonzero diffusion flux = irreversible phenomenon

$$u_i = D_i|z_i|F/RT$$
$$\lambda_i = |z_i|Fu_i$$

**Permeability** of the membrane for ion  $i$ :  $P_i = D_iK_{Ni}/L$

$D_i$  = diffusivity **in the membrane material**;  $D_i$  in a frit =  $D_i$  in  $\odot$ .

“Nernst distribution coefficient”  $K_{Ni}$  here = sorption coefficient, dimensionless for sorption from liquid  $\Rightarrow J_i = P_i(c_i^{\text{right}} - c_i^{\text{left}})$

For univalent ions:  $P_i \propto D_i \propto u_i \propto \lambda_i$ . This is enough: we shall see that the voltage depends only on the ratio of permeabilities.

# Thin membrane: Goldman equation

Flux of ions  $i$  at  $x$  (left  $x = 0$ , right  $x = L$ );  $[J_i] = \text{mol m}^{-2} \text{s}^{-1}$

$$\begin{aligned} J_i &= -D_i \text{grad } c_i + \frac{\lambda_i c_i \mathcal{E}}{z_i F} = -\frac{D_i}{RT} c_i \text{grad } [\mu_i + z_i F \phi] = -\frac{D_i}{RT} c_i \text{grad } \tilde{\mu}_i \\ &= -D_i \frac{dc_i}{dx} + \frac{D_i c_i z_i F \mathcal{E}}{RT} \end{aligned}$$

$J_i$  does not depend on  $x$  (stationary flux—nothing accumulates). Equation can be integrated (separation of variables):

$$\int_0^L dx = \int_{c_i^{\text{left}}}^{c_i^{\text{right}}} \frac{D_i}{c_i z_i F \mathcal{E} D_i / RT - J_i} dc_i$$

better  $\int_{K_{Ni} c_i^{\text{left}}}^{K_{Ni} c_i^{\text{right}}}$   
( $K_{Ni}$  cancel out)

We calculate  $J_i$  from concentrations and  $\mathcal{E}$ . After several steps:

$$J_i RT = D_i z_i F \mathcal{E} \frac{\epsilon^{z_i} c_i^{\text{left}} - c_i^{\text{right}}}{\epsilon^{z_i} - 1}, \quad \text{where } \epsilon = \exp\left(\frac{FL\mathcal{E}}{RT}\right) = \exp\left(-\frac{F\Delta\phi}{RT}\right)$$

Zero total current:

NB signs:  $\Delta\phi = \phi^{\text{right}} - \phi^{\text{left}} = -L\mathcal{E}$

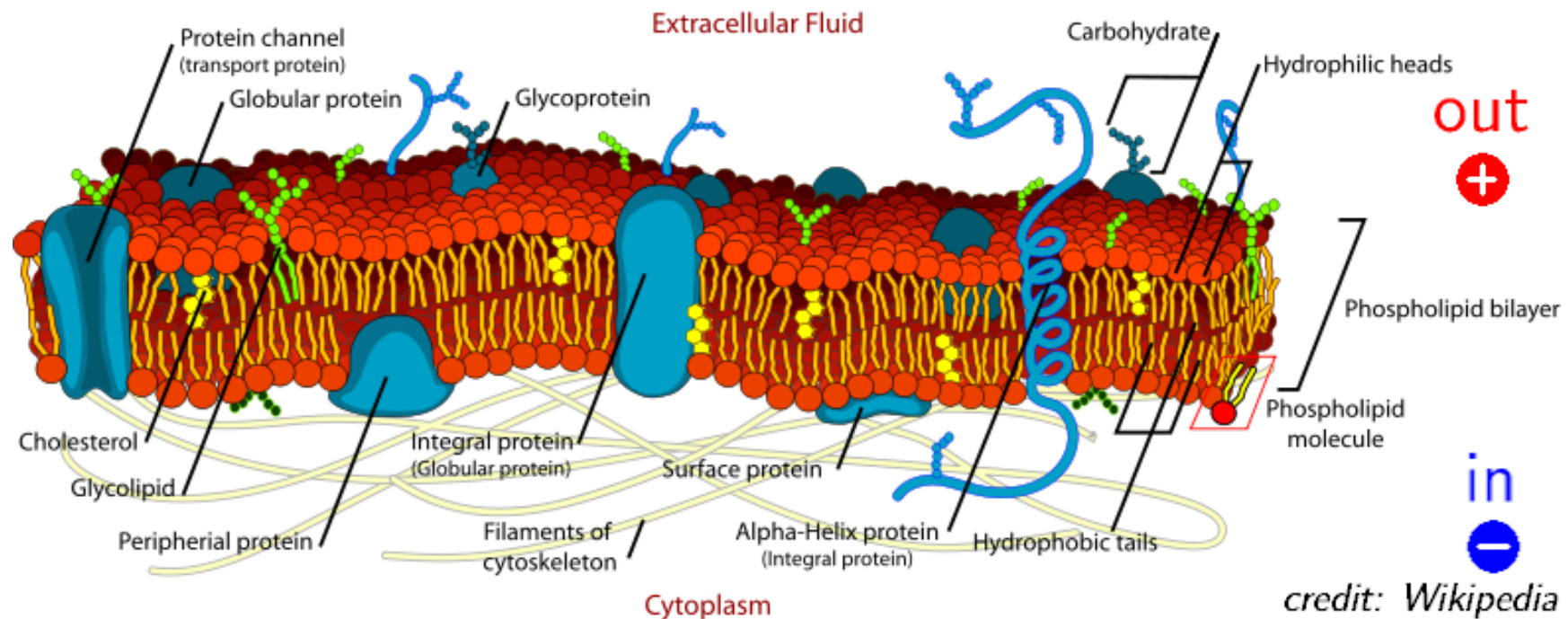
$$0 = \sum_i z_i J_i$$

# Thin membrane: Goldman equation

Additional simplification: only univalent ions ( $|z_i| = 1$ )

Let's sum anions and cations separately, replacing  $D_i \propto P_i$   
 $\Rightarrow$  linear equation for  $\epsilon$ , after rearranging:

$$\Delta\phi = -\frac{RT}{F} \ln \frac{\sum_{\text{cations}} P_i C_i^{\text{right}} + \sum_{\text{anions}} P_i C_i^{\text{left}}}{\sum_{\text{cations}} P_i C_i^{\text{left}} + \sum_{\text{anions}} P_i C_i^{\text{right}}}$$



# Goldman equation: example

8/22  
col09

Relative permeabilities of main ions in the mammalian plasmatic membrane are:

$$P(\text{K}^+) = 1, P(\text{Na}^+) = 0.04, P(\text{Cl}^-) = 0.45$$

Concentrations inside the cell (in  $\text{mmol dm}^{-3}$ ):

$$[\text{K}^+]^{\text{right}} = 400, [\text{Na}^+]^{\text{right}} = 50, [\text{Cl}^-]^{\text{right}} = 50$$

Concentrations outside the cell (in  $\text{mmol dm}^{-3}$ ):

$$[\text{K}^+]^{\text{left}} = 20, [\text{Na}^+]^{\text{left}} = 500, [\text{Cl}^-]^{\text{left}} = 560$$

The resting potential of the membrane:

$$\Delta\phi = -\frac{RT}{F} \ln \frac{\sum_{\text{cations}} P_i C_i^{\text{right}} + \sum_{\text{anions}} P_i C_i^{\text{left}}}{\sum_{\text{cations}} P_i C_i^{\text{left}} + \sum_{\text{anions}} P_i C_i^{\text{right}}}$$
$$\Delta\phi = \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 310 \text{ K}}{96485 \text{ C mol}^{-1}} \times \ln \frac{1 \times 400 + 0.04 \times 50 + 0.45 \times 560}{1 \times 20 + 0.04 \times 500 + 0.45 \times 50}$$
$$= -0.063 \text{ V}$$

The inside of the cell (“right”) is negative, because  $\text{K}^+$  faster escape from the cell



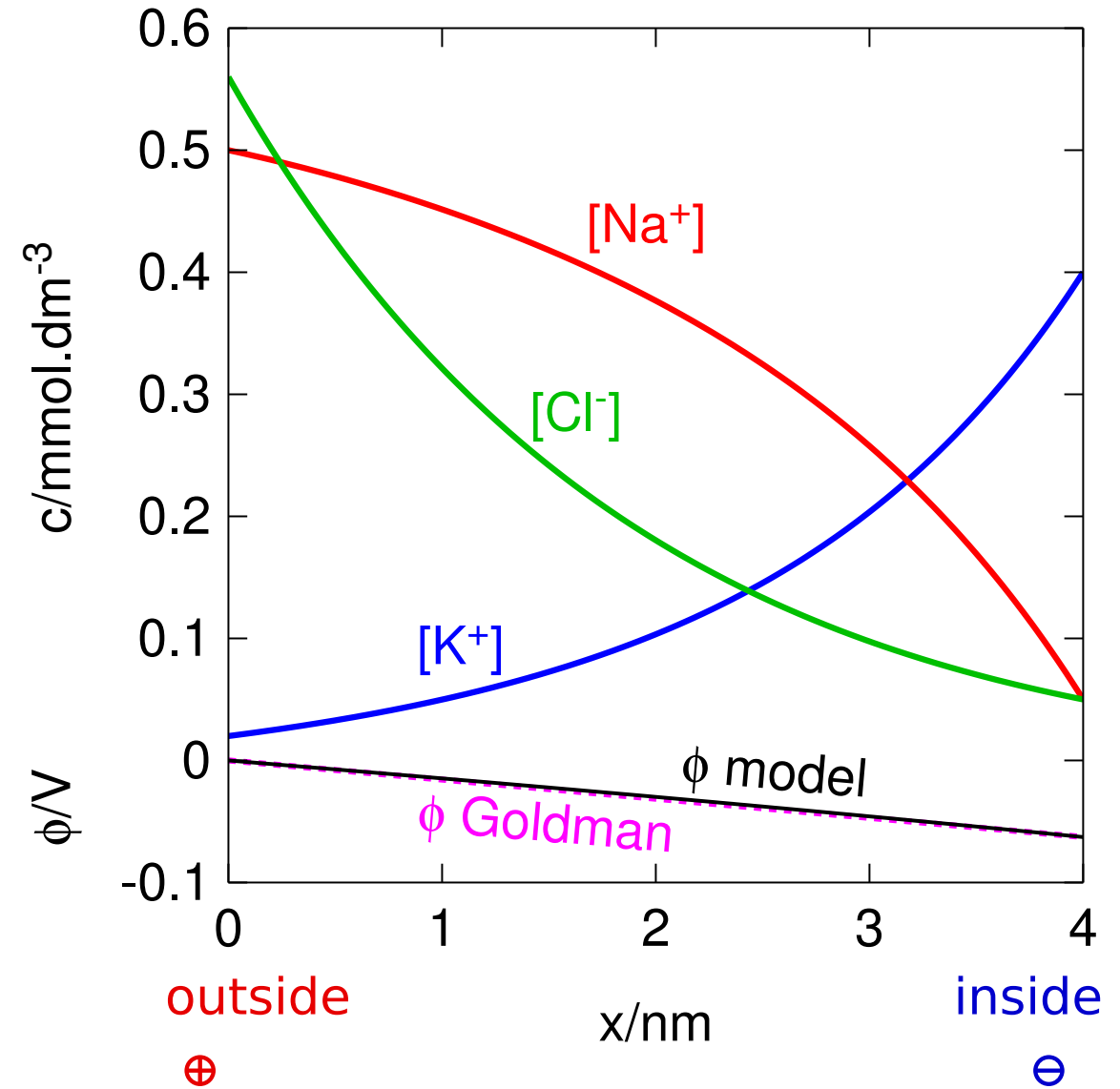
# Cell membrane—continued

Numerical solution for:

$$L = 4 \text{ nm}$$

$$\epsilon_r = 4$$

$K_{N_i} = 0.001$  (membrane concentration is 1000× smaller)



# Thick membrane (frit, liquid junction)

Irreversible process, complex problem (partial differential equation).

Simplification:

● solution of a uni-univalent salt at both sides, conc.  $c^{\text{left}}$  and  $c^{\text{right}}$

● the membrane is thick  $\Rightarrow \text{grad } c_{\oplus} = \text{grad } c_{\ominus} = \text{const}$

It follows from the Poisson equation  $d^2\phi/dx^2 = -\sum_i z_i F c_i / \epsilon$  – every layer is electroneutral, small difference will curve  $\phi(x)$  as needed

Formulas:  $\tilde{\mu}_i = \mu_i + z_i F \phi$ ,  $\vec{j}_i = -c_i u_i \vec{\nabla} \tilde{\mu}_i$ ,  $\vec{J}_i = -\frac{c_i D_i}{RT} \vec{\nabla} \tilde{\mu}_i$ ,  $u_i RT = D_i z_i F$ ,  $z_{\ominus} < 0$

$$\text{flux of cations: } J_{\oplus} = -D_{\oplus} \frac{d}{dx} c_{\oplus} - \frac{D_{\oplus} F}{RT} c_{\oplus} \frac{d}{dx} \phi$$

$$\text{flux of anions: } J_{\ominus} = -D_{\ominus} \frac{d}{dx} c_{\ominus} + \frac{D_{\ominus} F}{RT} c_{\ominus} \frac{d}{dx} \phi$$

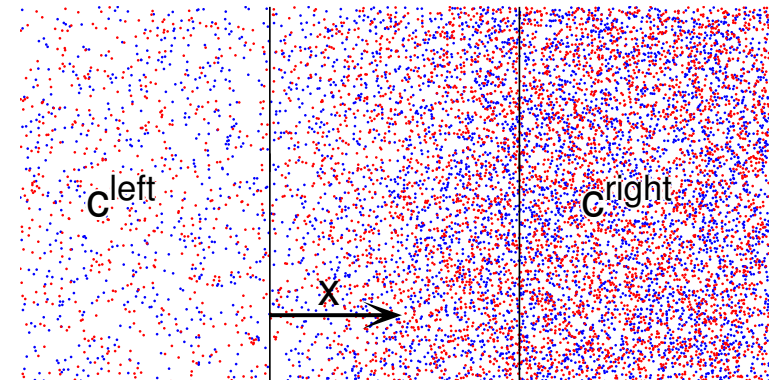
Steady state:  $j = \sum_i z_i j_i = J_{\ominus} - J_{\oplus} = 0$ ,  $c_{\oplus} = c_{\ominus} = c \Rightarrow$

$$(D_{\ominus} - D_{\oplus}) \frac{dc}{dx} = (D_{\ominus} + D_{\oplus}) \frac{F}{RT} c \frac{d\phi}{dx}, \quad \text{separation of variables } c, \phi:$$

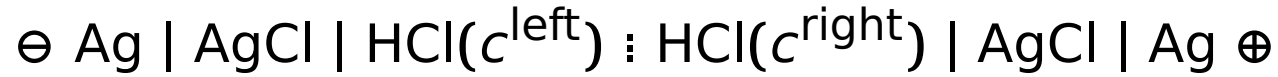
$$\frac{D_{\ominus} - D_{\oplus}}{D_{\ominus} + D_{\oplus}} \ln \frac{c^{\text{right}}}{c^{\text{left}}} = \frac{F}{RT} \Delta\phi$$

$$\Delta\phi = (t_{\ominus} - t_{\oplus}) \frac{RT}{F} \ln \frac{c^{\text{right}}}{c^{\text{left}}}$$

$$t_{\pm} = \frac{D_{\pm}}{D_{\ominus} + D_{\oplus}}$$



Applications: voltage loss at a liquid junction (diffusion potential), e.g.:



For uni-univalent salt and  $t_{\ominus} = t_{\oplus}$  it holds  $\Delta\phi = 0$ . Therefore in salt bridges there are solutions with  $t_{\ominus} \approx t_{\oplus}$  (e.g., KCl:  $t_{\oplus} = 0.49$ ,  $t_{\ominus} = 0.51$ )

Generalization for salt  $\text{K}_{\nu_{\ominus}}^{z_{\ominus}} \text{A}_{\nu_{\oplus}}^{z_{\oplus}}$ :

$$\Delta\phi = \left( \frac{t_{\ominus}}{|z_{\ominus}|} - \frac{t_{\oplus}}{z_{\oplus}} \right) \frac{RT}{F} \ln \frac{c^{\text{right}}}{c^{\text{left}}}$$

Inaccurate “derivation” (for uni-univalent salt):

Let 1 mole of charge ( $1F$ ) flows from left to right.

This is  $t_{\ominus}$  anions migrating left and  $t_{\oplus}$  cations migrating right:



$$\Delta G = -t_{\ominus} RT \ln \frac{c_{\ominus}^{\text{right}}}{c_{\ominus}^{\text{left}}} + t_{\oplus} RT \ln \frac{c_{\oplus}^{\text{right}}}{c_{\oplus}^{\text{left}}} \stackrel{?}{=} -zF\Delta\phi \Rightarrow \Delta\phi = (t_{\ominus} - t_{\oplus}) \frac{RT}{F} \ln \frac{c^{\text{right}}}{c^{\text{left}}}$$

But  $\Delta G \neq$  work for an irreversible process – fails for a thin membrane

1:1 electrolyte

$c^{\text{right}} : c^{\text{left}} = 10$

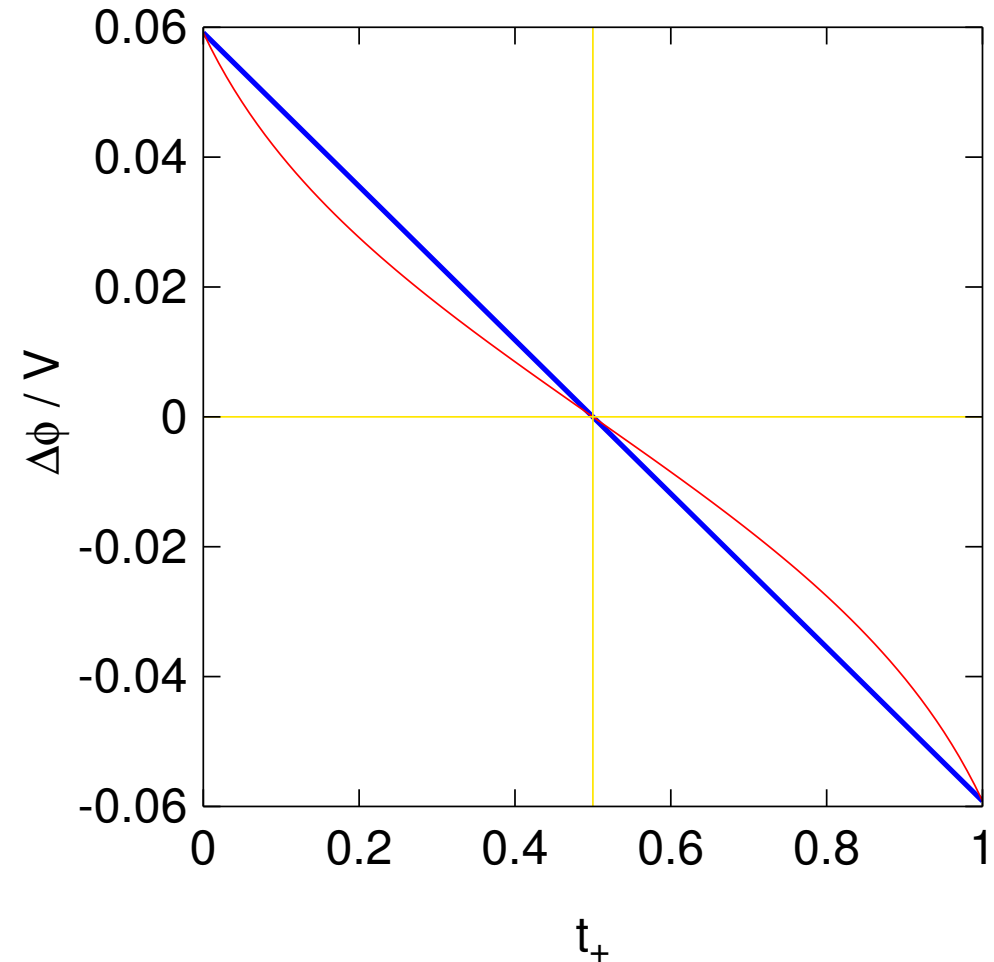
— **thin membrane** ( $L \ll \lambda$ )

Controlled by electric forces (they determine the local concentrations)

The simplified reasoning (previous slide) fails!

— **thick membrane** ( $L \gg \lambda$ )

Controlled by diffusion (electric forces screened off)



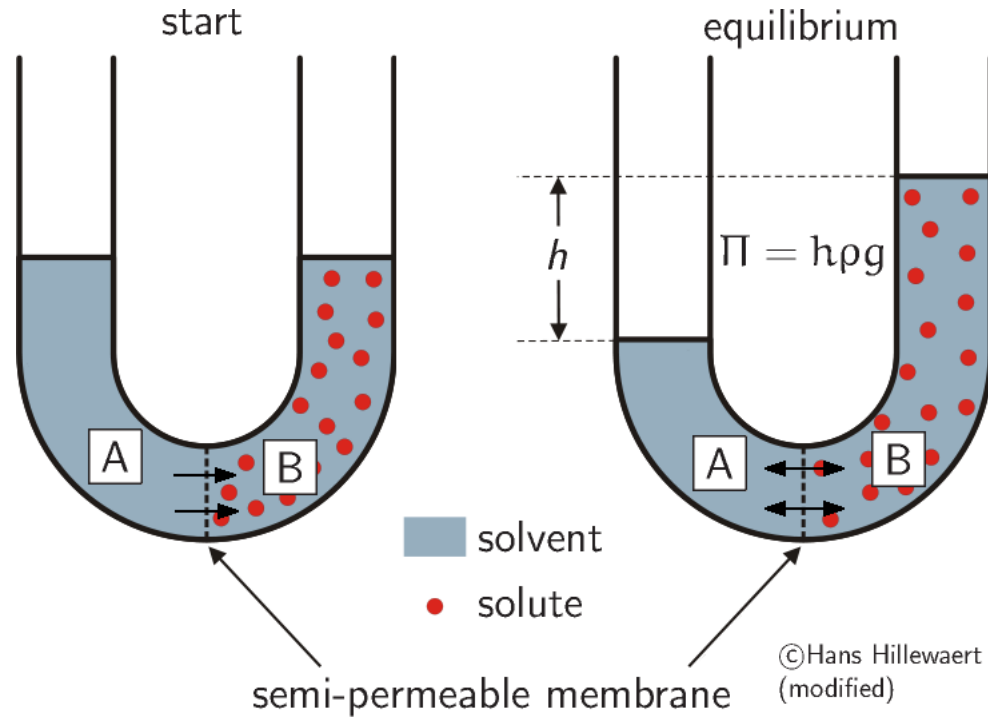
For  $t_{\oplus} = 1$  (only cations permeate), both equations give

$$\Delta\phi = -\frac{RT}{zF} \ln \frac{c^{\text{right}}}{c^{\text{left}}}$$

For  $t_{\oplus} = \frac{1}{2}$ , we have  $\Delta\phi = 0$  (symmetry cations:anions)

The membrane lets through **solvent** (optionally with small molecules). The solvents tries to permate to the place with a lower chemical potential  $\Rightarrow$  **osmotic pressure**

1 = solvent



$$\mu_1^\bullet(p_A) \equiv \mu_1(p_A, 1)$$

$$\mu_1^\bullet(p_A) \stackrel{!}{=} \mu_{1B}(p_B, x_{1B}) \stackrel{\text{id.}\odot}{=} \mu_1^\bullet(p_B) + RT \ln x_{1B} = \mu_1^\bullet(p_B) + RT \ln(1 - x_{2B})$$

$$\stackrel{V_{1m}=\text{const}, x_2 \ll 1}{=} \mu_1^\bullet(p_A) + V_{1m} \underbrace{(p_B - p_A)}_{\Pi} - RT x_{2B} \Rightarrow V_{1m} \Pi = RT \frac{n_2}{n}$$

$$\Rightarrow \Pi = \frac{n_2}{nV_{1m}} RT = \frac{n_2}{V} RT = c_2 RT$$

J. H. **van 't Hoff**, H. N. Morse  
 $n_2, c_2$  are incl. dissociation

The osmotic pressure is a **colligative property** – it depends on the number of particles (amount of substance)

**Osmolarity** = amount of substance (not permeating through the membrane) in unit volume

**Osmolality** = amount of substance (not permeating through the membrane) per unit mass of the solvent

**Example.** Calculate the osmolality of 0.15 mol of NaCl in 1 kg of water.

0.3 mol of ions in 1 kg of water, osmolality =  $0.3 \text{ osmol kg}^{-1}$

Approximately  $\rho = 1 \text{ kg dm}^{-3} \Rightarrow \text{osmolarity} \doteq 0.3 \text{ osmol dm}^{-3}$

Loosely  $0.15 \text{ M } \odot \text{ NaCl} = 0.3 \text{ Osm } \odot \text{ NaCl}$

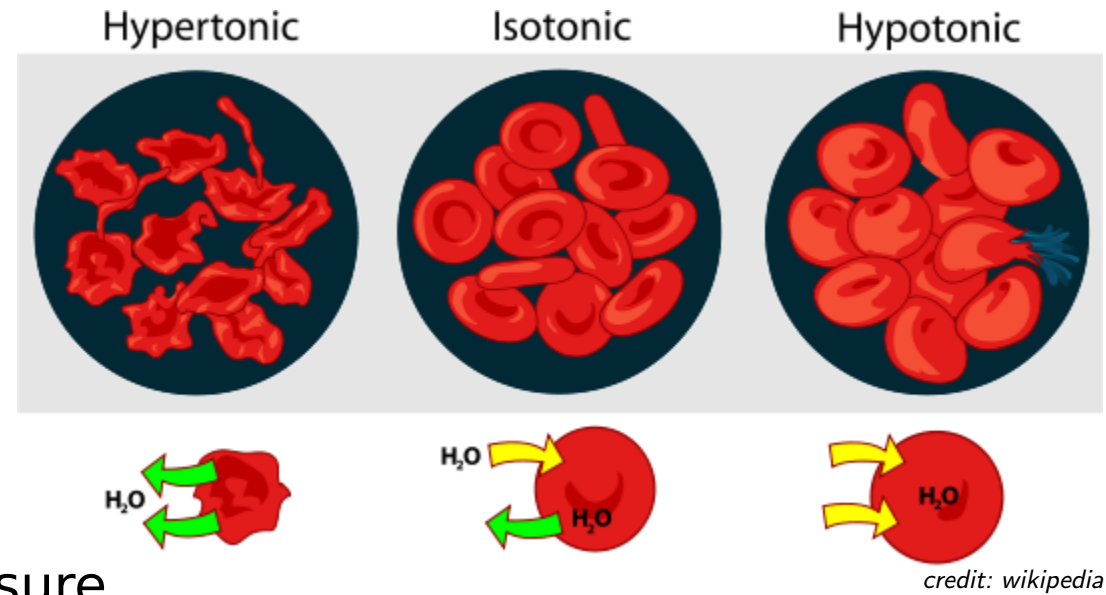
**Osmotic pressure more accurately:**  $\Pi = c_2RT(1 + Bc_2 + \delta c_2^{3/2} + Cc_2^2 + \dots)$

$B$ : second osmotic virial coefficient – interaction of a pair of solutes  
for colloid particles determined mainly by the excluded volume

$\delta$ : ionic interactions (Debye-Hückel)

$C$ : triples of solutes

- extra/intracellular solutions are isotonic
- ultrafiltrate (primary urine) is produced in glomeruli (sg. glomerulus) by reverse osmosis (ultrafiltration) of blood; macromolecules do not pass, osmotic pressure 30–60 mmHg (according to the source) > diastolic pressure
- dialysis
- sea water desalination by reverse osmosis
- determining molar masses



**Example.** Calculate the minimum pressure needed to desalinate sea water by reverse osmosis at 300 K, and the minimum energy needed to produce 1 m<sup>3</sup> of fresh water. The total concentration of ions in sea water is 1.12 mol dm<sup>-3</sup>.

28 bar; 2.8 MJ

The osmotic pressure of a solution of an enzyme in water (25 °C) is

$\frac{c_w}{\text{g dm}^{-3}}$	1	2	3	4	5	6
$\frac{\Pi}{\text{Pa}}$	25	54	83	118	152	191

Calculate the molar mass.

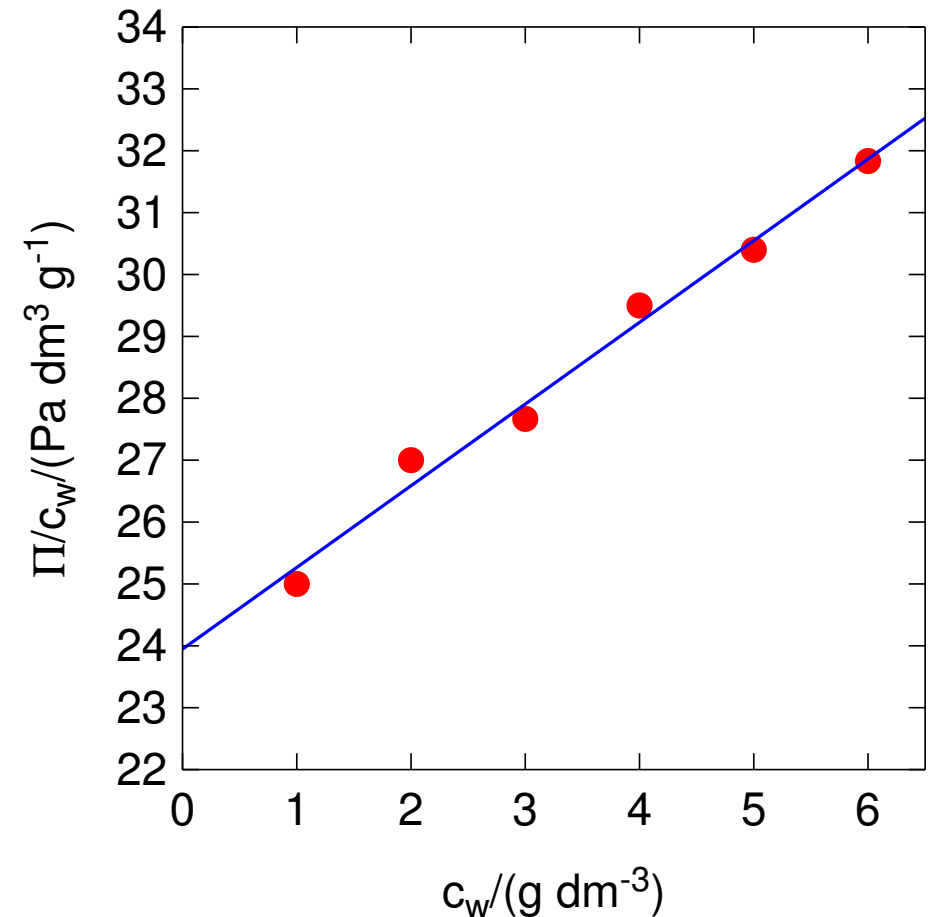
$$c_w = c_2 M$$

After dividing by  $M$ :

$$\frac{\Pi}{c_w} = \frac{RT}{M} + \frac{RTB}{M^2} c_w$$

From the plot:  $\frac{RT}{M} \doteq 24 \text{ Pa g}^{-1} \text{ dm}^3 = 24 \text{ Pa kg}^{-1} \text{ m}^3$

$$M = \frac{8.314 \text{ Pa m}^3 \text{ K}^{-1} \times 298 \text{ K}}{24 \text{ Pa g}^{-1} \text{ dm}^3} = 103 \text{ kg mol}^{-1} \equiv 103 \text{ kDa}$$





Eq.  $\Pi = c_2RT$  is sometimes written as

$$\Pi = ic_2RT$$

where  $c_2$  is the analytic (formal) concentration and  $i$  is the **van 't Hoff factor**, i.e., the average number of molecules (not permeating) the compound dissociates to.

Examples:

$$i(\text{glucose}) = 1$$

$$i(\text{NaCl}) = 2$$

$$i(\text{CH}_3\text{COOH}) = 1 + \alpha$$

## Raoult + Dalton law

$$p_i = py_i = x_i p_i^S, \quad p = \sum_i p_i = \sum_i x_i p_i^S$$

Apply to:

1 = solvent

2 = non-volatile solute ( $x_2 \approx 0$  or  $n_2 \ll n_1$ )

if dissociated in  $\odot$ , the fragments are counted in  $n_2$  and  $x_2$

$$p_1 = x_1 p_1^S = p_1^S - x_2 p_1^S$$

or

$$\Delta p = -x_2 p_1^S = -p_1^S \frac{n_2}{n_1 + n_2} \stackrel{n_2 \ll n_1}{\approx} -p_1^S \frac{n_2}{n_1}$$

The saturated pressure of a solution is lower than that of a pure solvent at the same temperature.

1 = solvent

2 = solute (incl. dissociation)

At constant  $p$ ,  $\Delta p$  is compensated ( $\rightarrow -\Delta p$ ) by increasing the boiling point of the solution by  $\Delta T$ . Using the Clausius–Clapeyron equation:

$$\frac{1}{p} \frac{\Delta p}{\Delta T} \approx \frac{\Delta_{\text{vap}}H_m}{RT^2}$$

$\Rightarrow$

$$\Delta T \approx \frac{-\Delta p}{p_1^s} \frac{RT_{\text{boil},1}^2}{\Delta_{\text{vap}}H_{1,m}} = \frac{p_1^s \frac{n_2}{n_1}}{p_1^s} \frac{RT_{\text{boil},1}^2}{\Delta_{\text{vap}}H_{1,m}} = K_E \underline{m}_2$$

where

$$K_E = \frac{RT_{\text{boil},1}^2 M_1}{\Delta_{\text{vap}}H_{1,m}} = \text{ebullioscopic constant}$$

The boiling temperature of a solution is higher than that of a pure solvent at the same pressure.

**Example.** Calculate the boiling point of a soup (1% wt. NaCl) at normal pressure.  $K_E(\text{water}) = 0.513 \text{ K kg mol}^{-1}$ .

alternative derivation:  
see next slide

Or  $\Delta T = K_E i \underline{m}_2$ , where  $\underline{m}_2$  is the chemical-formula-based molality and  $i$  is the van 't Hoff's factor

A compound dissolves in a liquid solvent, but there is no mixed crystal in the solid phase  $\Rightarrow$  melting (fusion) temperature decreases.

**Derivation:** 1 = solvent, 2 = solute

$$x_1 = 1, T = T_{\text{fus}} : \quad \mu_1^s(T_{\text{fus}}) = \mu_1^l(T_{\text{fus}}) \quad n_2 \ll n_1$$

$$\mu_1^{\bullet s}(T_{\text{fus}}) = \mu_1^{\bullet l}(T_{\text{fus}}) \quad x_1 \approx 1$$

$$x_1 < 1, T = T_{\text{fus}} + \Delta T : \mu_1^s(T_{\text{fus}} + \Delta T) = \mu_1^l(T_{\text{fus}} + \Delta T)$$

$$\mu_1^{\bullet s}(T_{\text{fus}} + \Delta T) = \mu_1^{\bullet l}(T_{\text{fus}} + \Delta T) + RT \ln x_1$$

$$\Delta T \left( \frac{\partial \mu_1^{\bullet s}}{\partial T} \right) = \Delta T \left( \frac{\partial \mu_1^{\bullet l}}{\partial T} \right) + RT \ln(1 - x_2)$$

$$\Delta T \frac{\partial(\mu_1^{\bullet l} - \mu_1^{\bullet s})}{\partial T} = \Delta T(-\Delta_{\text{fus}} S_m) = \Delta T \frac{-\Delta_{\text{fus}} H_m^{\bullet}}{T} = -RT \ln(1 - x_2) \approx RT x_2 \approx RT M_1 \underline{m}_2$$

$$\Delta T = -K_K \underline{m}_2 \quad K_K = \frac{M_1 R T_{\text{fus}}^2}{\Delta_{\text{fus}} H_m^{\bullet}} = \text{cryoscopic constant}$$

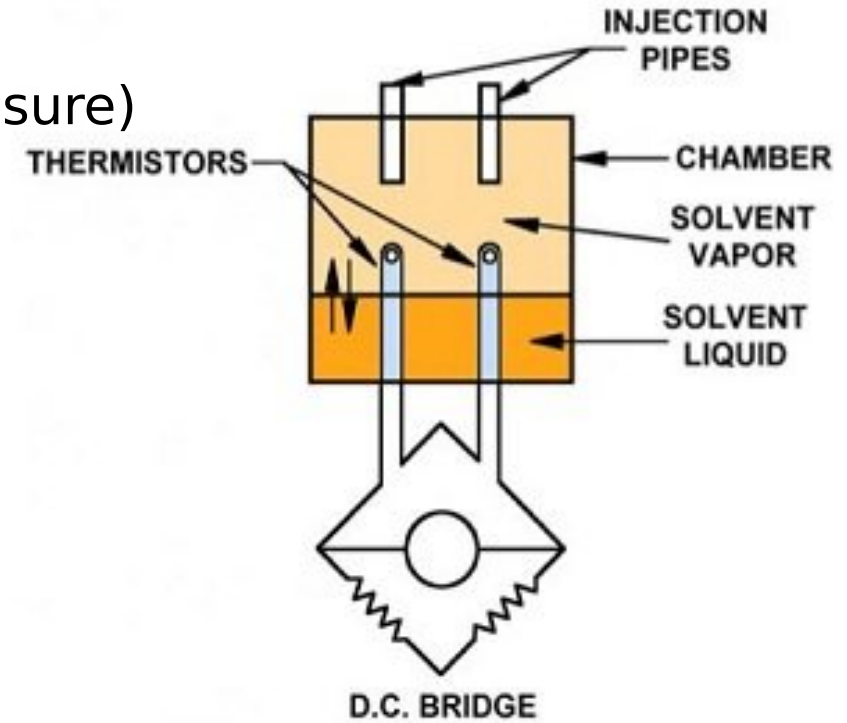
$$\text{or } K_f = -K_K$$

$$\Delta T = K_f \underline{m}_2^{\text{non-dissoc.}}$$

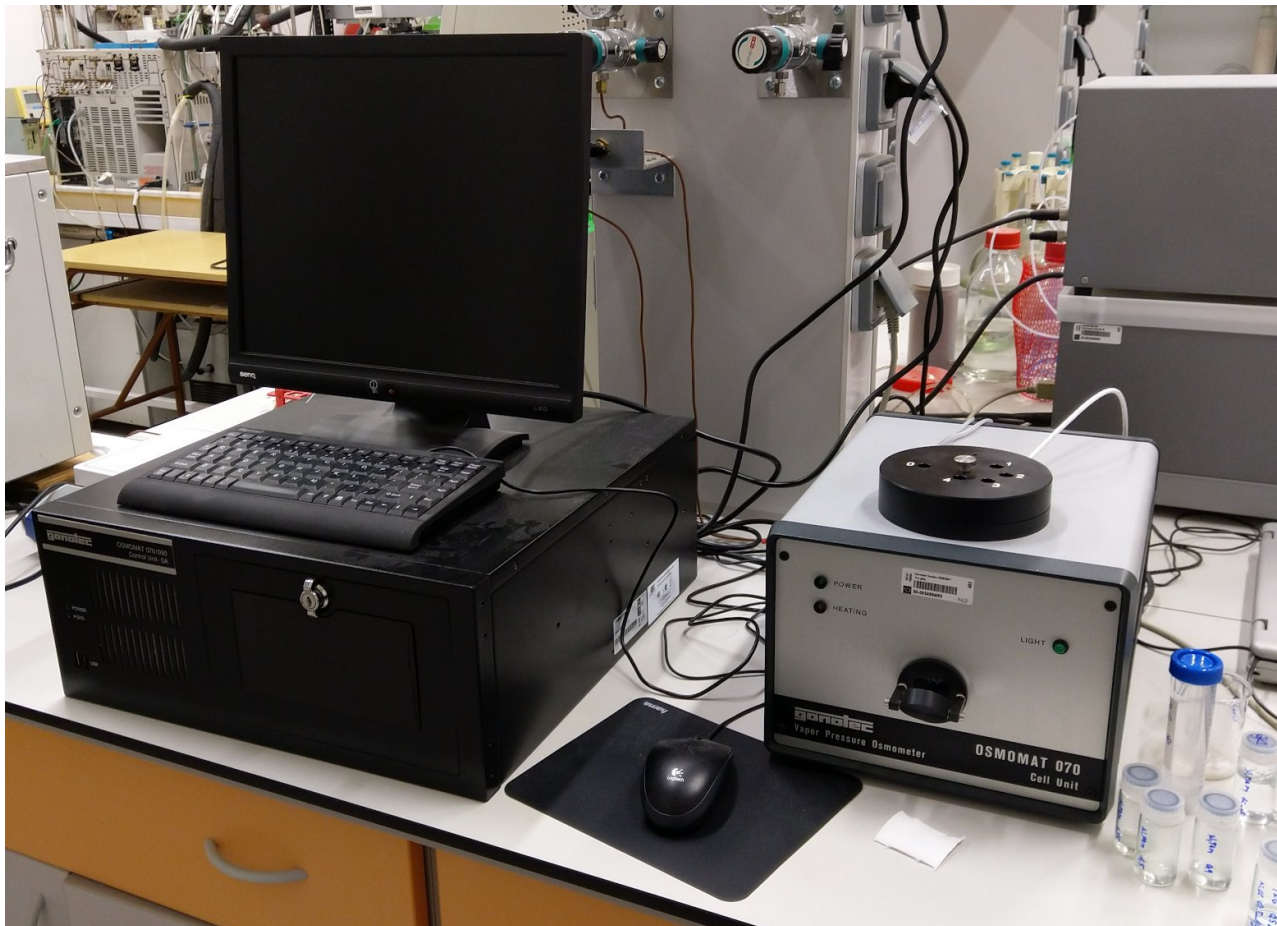
**Example.** Calculate the freezing temperature of beer (4.5 vol.% alcohol, density of alcohol =  $0.8 \text{ g cm}^{-3}$ ).  $K_{K, \text{water}} = 1.85 \text{ K kg mol}^{-1}$ .

# Vapor pressure osmometry

- pure solvent evaporates
- vapor condenses on a solution (lower vapor pressure)
- $\Rightarrow$  pure solvent cools down, solution heats up
- $\Delta T \propto$  concentration (colligative property)



credit: <http://www.uicinc.com/model-833/>



... depend on the **number of molecules** (moles) dissolved.

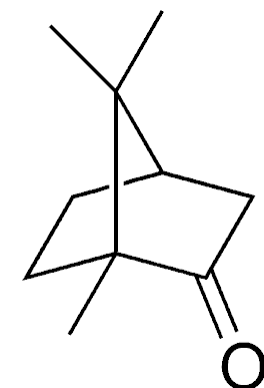
● boiling temperature increase (ebullioscopy),  $\Delta T = K_E \underline{m}_2 = K_E \frac{m_2}{m_1 M_2}$

● melting temperature decrease (cryoscopy),  $\Delta T = -K_K \underline{m}_2 \Delta T = -K_K \frac{m_2}{m_1 M_2}$

e.g., camphor  $K_K = 40 \text{ K kg mol}^{-1}$ ,  $t_{\text{fus}} = 176 \text{ }^\circ\text{C}$ .

● osmotic pressure,  $\Pi = c_2 RT = \frac{m_2}{V M_2} RT$

● pressure of (ideal) gas,  $p = nRT/V = cRT = \frac{m}{V M_2} RT$



Usage: determining molar masses

Accuracy: ebullioscopy < cryoscopy < vapor pressure osmometry < membrane osmometry