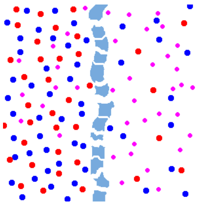
Membranes and ions

Semipermeable membrane; glass frit; diaphragm

- concentrations of ions on both sides differ
- different permeabilities of ions
- mechanisms: "∝" = "is proportional"
  - ion channels (in cell membrane)
  - pores (wider, permeability ∝ diffusivity)
  - sorption+diffusion (polymer membrane), ...

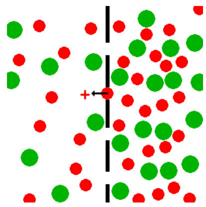


E.g.: cell membrane, kidneys, dialysis, fuel cells, liquid junction (between electrolytes) [cf. osmotic pressure]

- 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



⊕ ⊖

$c^{\rm left} < c^{\rm right}$

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

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, $\mathcal{E}$):

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

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

Equivalently: the **electrochemical potentials** $\tilde\mu_i = \mu_i + z_iF\phi$ (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.

Donnan equilibria

left	:	right
NaX	:	NaCl
NaCl	:	

anion X^- does not permeate

The difference of the electrochemical potentials:

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

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

Sum of both equations ⇒

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

Generally for salt $K_{\nu_\oplus}A_{\nu_\ominus}$:

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

Donnan equilibria—membrane hydrolysis

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

balance	start			equilibrium		
[mol]	left	:	right	left	:	right
TsO^-	n	:		n	:	
Na^+	n	:		$n-x$	:	x
OH^-		:		≈ 0	:	x
H^+		:		x	:	≈ 0

$$\Delta\phi = -\frac{RT}{F}\ln\frac{c_{Na^+}^{\rm right}}{c_{Na^+}^{\rm left}} = -\frac{RT}{F}\ln\frac{x/V^{\rm right}}{(n-x)/V^{\rm left}} = 0.256\,{\rm V}$$

$$c_{Na^+}^{\rm left}c_{OH^-}^{\rm left} = c_{Na^+}^{\rm right}c_{OH^-}^{\rm right} \quad \left(\text{or } c_{Na^+}^{\rm right}/c_{Na^+}^{\rm left} = c_{H^+}^{\rm right}/c_{H^+}^{\rm left}\right)$$

$$\frac{n-x}{V^{\rm left}}\cdot\frac{K_W}{x/V^{\rm left}} = \frac{x}{V^{\rm right}}\cdot\frac{x}{V^{\rm right}}$$

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

$$x = \sqrt[3]{K_W(n-x)(V^{\rm right})^2} \stackrel{x\ll n}{\approx} \sqrt[3]{1\times10^{-14}\times0.01}\,{\rm mol} = 4.64\times10^{-6}\,{\rm mol}$$

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

Diffusion potential at a thin membrane

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

- we know ion concentrations $c_i^{\rm left}$ and $c_i^{\rm right}$

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

- 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

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

Nonzero diffusion flux = irreversible phenomenon

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

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

D_i = diffusivity **in the membrane material**; D_i in a frit = D_i in ⊙.

"Nernst distribution coefficient" K_{Ni} here = sorption coefficient, dimensionless for sorption from liquid ⇒ $J_i = P_i(c_i^{\rm right} - c_i^{\rm left})$

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 $x = L$); $[J_i] = {\rm mol\,m^{-2}\,s^{-1}}$

$$J_i = -D_i\,{\rm grad}\,c_i + \frac{\lambda_ic_i\mathcal{E}}{z_iF} = -\frac{D_i}{RT}c_i\,{\rm grad}\,[\mu_i + z_iF\phi] = -\frac{D_i}{RT}c_i\,{\rm grad}\,\tilde\mu_i$$
$$= -D_i\frac{dc_i}{dx} + \frac{D_ic_iz_iF\mathcal{E}}{RT}$$

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

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

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

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

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

Zero total current:

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

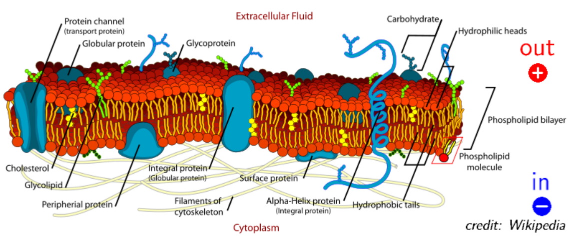
$$0 = \sum_i z_iJ_i$$

Thin membrane: Goldman equation

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

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

$$\Delta\phi = -\frac{RT}{F}\ln\frac{\sum_{\rm cations}P_ic_i^{\rm right} + \sum_{\rm anions}P_ic_i^{\rm left}}{\sum_{\rm cations}P_ic_i^{\rm left} + \sum_{\rm anions}P_ic_i^{\rm right}}$$



credit: Wikipedia

Goldman equation: example

Relative permeabilities of main ions in the mammalian plasmatic membrane are:
$P(K^+) = 1$, $P(Na^+) = 0.04$, $P(Cl^-) = 0.45$

Concentrations inside the cell (in ${\rm mmol\,dm^{-3}}$):
$[K^+]^{\rm right} = 400$, $[Na^+]^{\rm right} = 50$, $[Cl^-]^{\rm right} = 50$

Concentrations outside the cell (in ${\rm mmol\,dm^{-3}}$):
$[K^+]^{\rm left} = 20$, $[Na^+]^{\rm left} = 500$, $[Cl^-]^{\rm left} = 560$

The resting potential of the membrane:

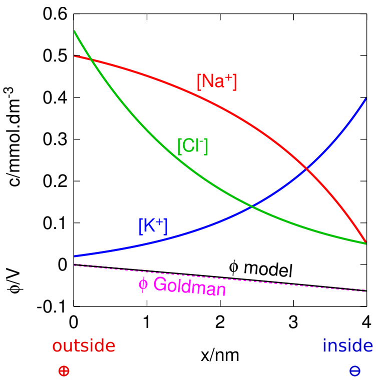
$$\Delta\phi = -\frac{RT}{F}\ln\frac{\sum_{\rm cations}P_ic_i^{\rm right} + \sum_{\rm anions}P_ic_i^{\rm left}}{\sum_{\rm cations}P_ic_i^{\rm left} + \sum_{\rm anions}P_ic_i^{\rm right}}$$

$$\Delta\phi = -\frac{8.314\,{\rm J\,mol^{-1}\,K^{-1}}\times310\,{\rm K}}{96485\,{\rm C\,mol^{-1}}}\times\ln\frac{1\times400 + 0.04\times50 + 0.45\times560}{1\times20 + 0.04\times500 + 0.45\times50}$$
$$= -0.063\,{\rm V}$$

The inside of the cell ("right") is negative, because K^+ faster escape from the cell

Cell membrane—continued

Numerical solution for:
$L = 4$ nm
$\epsilon_r = 4$
$K_{\mathrm{N}_i} = 0.001$ (membrane concentration is 1000× smaller)



Thick membrane (frit, liquid junction)

Irreversible process, complex problem (partial differential equation).

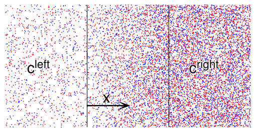
Simplification:

- solution of a uni-univalent salt at both sides, conc. $c^{\rm left}$ and $c^{\rm right}$
- the membrane is thick ⇒ grad $c_\oplus$ = grad $c_\ominus$ = const
  It follows from the Poisson equation $\mathrm{d}^2\phi/\mathrm{d}x^2 = -\sum_i z_i F c_i/\varepsilon$ – every layer is electroneutral, small difference will curve $\phi(x)$ as needed

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

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

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



Steady state: $j = \sum_i z_i J_i = J_\ominus - J_\oplus = 0$, $c_\oplus = c_\ominus = c$ ⇒

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

$$\frac{D_\ominus - D_\oplus}{D_\ominus + D_\oplus}\ln\frac{c^{\rm right}}{c^{\rm left}} = \frac{F}{RT}\Delta\phi \qquad \boxed{\Delta\phi = (t_\ominus - t_\oplus)\frac{RT}{F}\ln\frac{c^{\rm right}}{c^{\rm left}}} \qquad t_\pm = \frac{D_\pm}{D_\ominus + D_\oplus}$$

Thick membrane II

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

$$\ominus\ \mathrm{Ag}\mid\mathrm{AgCl}\mid\mathrm{HCl}(c^{\rm left}) \,\vdots\, \mathrm{HCl}(c^{\rm right})\mid\mathrm{AgCl}\mid\mathrm{Ag}\ \oplus$$

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 $\mathrm{K}^{z_\ominus}_{\nu_\oplus}\mathrm{A}^{z_\oplus}_{\nu_\ominus}$:

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

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:

$+t_\ominus$ anions ($c^{\rm left}$)	::	$-t_\ominus$ anions ($c^{\rm right}$)
$-t_\oplus$ cations ($c^{\rm left}$)	::	$+t_\oplus$ cations ($c^{\rm right}$)

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

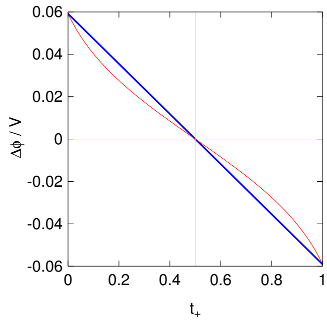
But $\Delta G \neq$ work for an irreversible process – fails for a thin membrane

Comparison of thin and thick membranes

1:1 electrolyte
$c^{\rm right} : c^{\rm left} = 10$

— 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

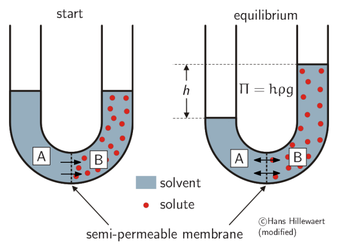
$$\Delta\phi = -\frac{RT}{zF}\ln\frac{c^{\rm right}}{c^{\rm left}}$$

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

Osmosis

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

1 = solvent



$$\mu_1^\bullet(p_{\rm A}) \equiv \mu_1(p_{\rm A}, 1)$$

$$\mu_1^\bullet(p_{\rm A}) \overset{!}{=} \mu_{1\rm B}(p_{\rm B}, x_{1\rm B}) \overset{\rm id.\odot}{=} \mu_1^\bullet(p_{\rm B}) + RT\ln x_{1\rm B} = \mu_1^\bullet(p_{\rm B}) + RT\ln(1 - x_{2\rm B})$$

$$\overset{V_{1\rm m}=\text{const},\ x_2\ll 1}{=} \mu_1^\bullet(p_{\rm A}) + V_{1\rm m}(\underbrace{p_{\rm B} - p_{\rm A}}_{\Pi}) - RTx_{2\rm B} \quad\Rightarrow V_{1\rm m}\Pi = RT\frac{n_2}{n}$$

$$\Rightarrow\ \boxed{\Pi} = \frac{n_2}{nV_{1\rm m}}RT = \frac{n_2}{V}RT\ \boxed{= c_2RT}$$

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

Osmosis

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) par unit mass of the solvent

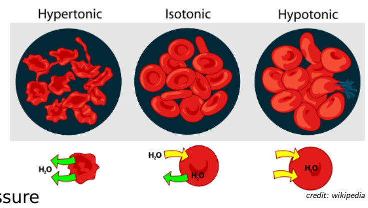
Example. Calculate the osmolality of 0.15 mol of NaCl in 1 kg of water.

0.3 mol of ions in 1 kg of water, osmolality = 0.3 osmol kg^{-1}
Approximately $\rho = 1\,\mathrm{kg\,dm^{-3}}$ ⇒ osmolarity ≐ 0.3 osmol dm^{-3}
Loosely 0.15 M ⊙ NaCl = 0.3 Osm ⊙ NaCl

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

B: second osmotic virial coefficient – interaction of a pair of solutes
for colloid particles determined mainly by the excluded volume
δ: ionic interactions (Debye-Hückel)
C: triples of solutes

Osmosis



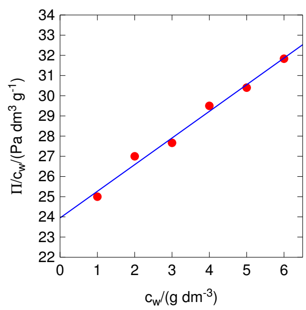
- extra/intracellular solutions are isotonic
- ultrafiltrate (primary urine) is produces in glomeruli (sg. glomerulus) by reverse osmosis (ultrafiltration) of blood; macromolecules do not pass, osmotic pressure 30–60 mm Hg (according to the source) > diastolic pressure
- dialysis
- sea water desalination 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^3 of fresh water. The total concentration of ions in sea water is 1.12 mol dm^{-3}. [28 bar; 2.8 MJ]

Example

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

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



Calculate the molar mass.

$$c_w = c_2M$$

After dividing by M:

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

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

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

Van't Hoff factor

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:

$$\begin{aligned} i(\text{glucose}) &= 1 \\ i(\text{NaCl}) &= 2 \\ i(\text{CH}_3\text{COOH}) &= 1+\alpha \end{aligned}$$

Saturated vapor pressure of a solution

Raoult + Dalton law

$$p_i = py_i = x_i p_i^{\mathrm{s}}, \quad p = \sum_i p_i = \sum_i x_i p_i^{\mathrm{s}}$$

Apply to:
1 = solvent
2 = non-volatile solute ($x_2 \approx 0$ or $n_2 \ll n_1$)
if disociated in ⊙, the fragments are counted in n_2 and x_2

$$p_1 = x_1 p_1^{\mathrm{s}} = p_1^{\mathrm{s}} - x_2 p_1^{\mathrm{s}}$$

or

$$\Delta p = -x_2 p_1^{\mathrm{s}} = -p_1^{\mathrm{s}} \frac{n_2}{n_1+n_2} \overset{n_2 \ll n_1}{\approx} -p_1^{\mathrm{s}} \frac{n_2}{n_1}$$

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

Ebulliscopy

alternative derivation: see next slide

1 = solvent
2 = solute (incl. dissociation)
At constant p, Δp is compensated ($\to -\Delta p$) by increasing the boiling point of the solution by ΔT. Using the Clausius–Clapeyron equation:

$$\frac{1}{p}\frac{\Delta p}{\Delta T} \approx \frac{\Delta_{\mathrm{vap}} H_{\mathrm{m}}}{RT^2}$$

$\Rightarrow$

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

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

where

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

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. $K_{\mathrm{E}}(\text{water}) = 0.513\,\mathrm{K\,kg\,mol^{-1}}$.

100.18 °C

Cryoscopy

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

Derivation: 1 = solvent, 2 = solute

$$\begin{aligned} x_1 = 1,\ T = T_{\mathrm{fus}}: \quad \mu_1^{\mathrm{s}}(T_{\mathrm{fus}}) &= \mu_1^{\mathrm{l}}(T_{\mathrm{fus}}) \\ \mu_1^{\bullet\mathrm{s}}(T_{\mathrm{fus}}) &= \mu_1^{\bullet\mathrm{l}}(T_{\mathrm{fus}}) \\ x_1 < 1,\ T = T_{\mathrm{fus}} + \Delta T: \quad \mu_1^{\mathrm{s}}(T_{\mathrm{fus}}+\Delta T) &= \mu_1^{\mathrm{l}}(T_{\mathrm{fus}}+\Delta T) \\ \mu_1^{\bullet\mathrm{s}}(T_{\mathrm{fus}}+\Delta T) &= \mu_1^{\bullet\mathrm{l}}(T_{\mathrm{fus}}+\Delta T) + RT\ln x_1 \\ \Delta T\left(\frac{\partial \mu_1^{\bullet\mathrm{s}}}{\partial T}\right) &= \Delta T\left(\frac{\partial \mu_1^{\bullet\mathrm{l}}}{\partial T}\right) + RT\ln(1-x_2) \end{aligned}$$

$n_2 \ll n_1$
$x_1 \approx 1$

$$\Delta T \frac{\partial(\mu_1^{\bullet\mathrm{l}} - \mu_1^{\bullet\mathrm{s}})}{\partial T} = \Delta T(-\Delta_{\mathrm{fus}} S_{\mathrm{m}}) = \Delta T \frac{-\Delta_{\mathrm{fus}} H_{\mathrm{m}}^{\bullet}}{T} = -RT\ln(1-x_2) \approx RTx_2 \approx RTM_1\underline{m}_2$$

$$\Delta T = -K_{\mathrm{K}} \underline{m}_2 \qquad K_{\mathrm{K}} = \frac{M_1 RT_{\mathrm{fus}}^2}{\Delta_{\mathrm{fus}} H_{\mathrm{m}}^{\bullet}} = \text{cryoscopic constant}$$

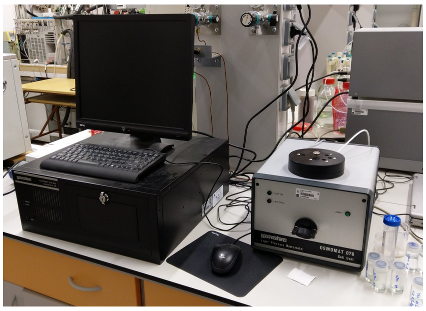
or $K_{\mathrm{f}} = -K_{\mathrm{K}}$
$\Delta T = K_{\mathrm{f}} i \underline{m}_2^{\text{non-dissoc.}}$

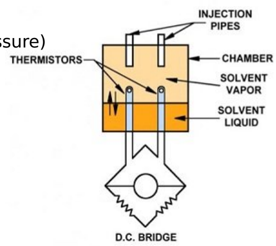
Example. Calculate the freezing temperature of beer (4.5 vol.% alcohol, density of alcohol=0.8 g cm^{-3}). $K_{\mathrm{K,water}} = 1.85\,\mathrm{K\,kg\,mol^{-1}}$.

−1.5 °C

Vapor pressure osmometry

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



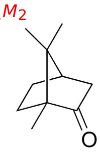


credit: http://www.uicinc.com/model-833/

Colligative properties – summary

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

- boiling temperature increase (ebullioscopy), $\Delta T = K_{\mathrm{E}} \underline{m}_2 = K_{\mathrm{E}} \frac{m_2}{m_1 M_2}$
- melting temperature decrease (cryoscopy), $\Delta T = -K_{\mathrm{K}} \underline{m}_2 \Delta T = -K_{\mathrm{K}} \frac{m_2}{m_1 M_2}$
  e.g., camphor $K_{\mathrm{K}} = 40\,\mathrm{K\,kg\,mol^{-1}}$, $t_{\mathrm{fus}} = 176\,°\mathrm{C}$.
- osmotic pressure, $\Pi = c_2 RT = \frac{m_2}{VM_2} RT$
- pressure of (ideal) gas, $p = nRT/V = cRT = \frac{m}{VM_2} RT$



Usage: determining molar masses

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