Lecture 2: Simple Mixtures

20-10-2009

- Lecture:
  - partial molar quantities
  - thermodynamics of mixing
  - ideal solutions
  - colligative properties
  - activities
  - Debye-Hückel limiting law
  - problems

Partial molar quantities

- we know how to describe phase equilibrium in the case of a single substance.
How it can be done in the case of mixtures?

- partial molar quantities: contribution of each component to the properties of mixtures
our final goal is chemical potential, but let's start with some simpler ones…

- Example: partial gas pressures (Dalton's Law): The pressure exerted by mixture of gases if the sum of partial pressures of the gases.

$p = p_A + p_B + \ldots,$, where $p_i = x_i p$ and $x_i = n_i / n$

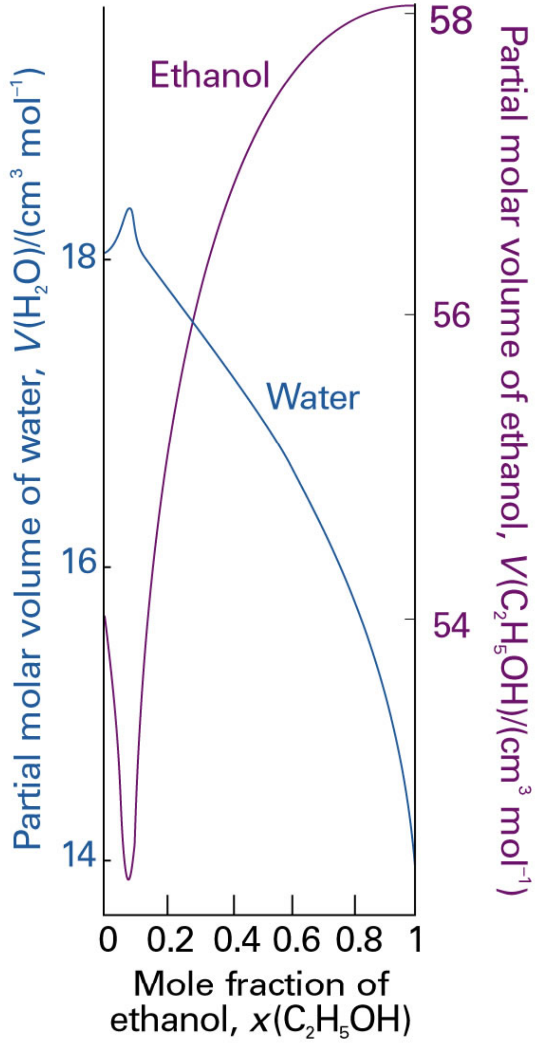
Partial molar volume

- How the total volume changes when we change the amount of one of the components
- Observation: If we add say 18 cm^3 of water to water the total volume increase will be exactly 18cm^3, but if we add it to ethanol the increase would be just 14 cm^3 .

  Partial molar volume depends on composition.
- Partial molar volume:

$$V_j = \left(\frac{\partial V}{\partial n_j} \right)_{p,T,n'}$$

Everything else is constant!



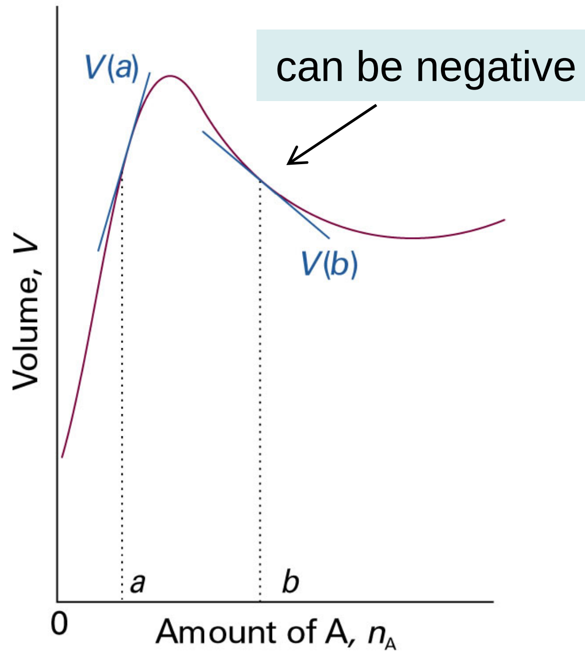
Partial molar volume

$$V_j = \left(\frac{\partial V}{\partial n_j}\right)_{p,T,n'}$$

Total volume

number of moles of j

the partial volume is a slope of the total volume graph vs. amount of moles.



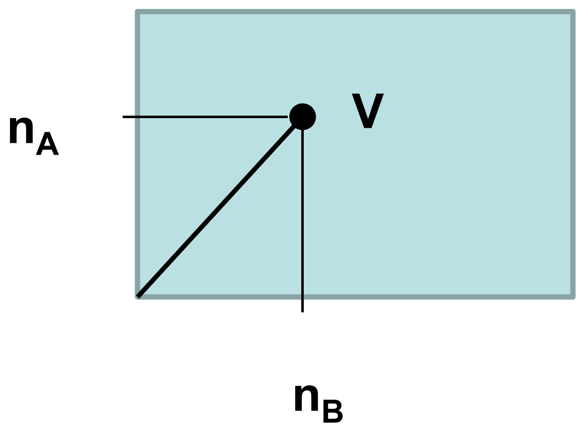
Volume change for a binary mixture:

$$dV = \left(\frac{\partial V}{\partial n_A}\right)_{p,T,n_B} dn_A + \left(\frac{\partial V}{\partial n_B}\right)_{p,T,n_A} dn_B = V_A dn_A + V_B dn_B$$

How we can calculate the total volume at a given concentration?

- Let's follow a path of constant cocentration:

$$V = V_A n_A + V_B n_B$$



Partial molar Gibbs energy

- The concept of partial molar quantity can be extended to any extensive state function:

$$\mu_j = \left(\frac{\partial G}{\partial n_j}\right)_{p,T,n'}$$

Chemical potential **definition**

- Fixing the composition the same we can prove that:

$$G = n_A \mu_A + n_B \mu_B$$

- Fundamental equation of chemical thermodynamics:

$$dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \dots$$

- At p, T=const

$$dG = \mu_A dn_A + \mu_B dn_B + \dots$$

$$dw_{add,\max} = \mu_A dn_A + \mu_B dn_B + \dots$$

Differential form of thermodynamic functions

$$U = G + TS - PV \quad \Rightarrow \quad dU = TdS - PdV + \sum_j \mu_j dn_j$$

$-PdV$ VdP

U

$$dU = TdS - PdV + \sum_j \mu_j dn_j$$

$$\mu_j = \left(\frac{\partial U}{\partial n_j}\right)_{S,V,n'}$$

H

$$dH = TdS + VdP + \sum_j \mu_j dn_j$$

$$\mu_j = \left(\frac{\partial H}{\partial n_j}\right)_{S,P,n'}$$

TdS

$-SdT$

A

$$dA = -SdT - PdV + \sum_j \mu_j dn_j$$

$$\mu_j = \left(\frac{\partial A}{\partial n_j}\right)_{T,V,n'}$$

G

$$dG = -SdT + VdP + \sum_j \mu_j dn_j$$

$$\mu_j = \left(\frac{\partial G}{\partial n_j}\right)_{T,P,n'}$$

Partial molar quantities

- **The Gibbs-Duhem equation**

Let's find change in Gibbs energy with infinitesimally change in composition:

$$G = \mu_A n_A + \mu_B n_B \quad \Rightarrow \quad dG = \mu_A dn_A + \mu_B dn_B + n_A d\mu_A + n_B d\mu_B$$

At P, T=const $\quad dG = \mu_A dn_A + \mu_B dn_B$

Thus, as G is state function: $\quad n_A d\mu_A + n_B d\mu_B = 0$

Gibbs-Duhem equation:

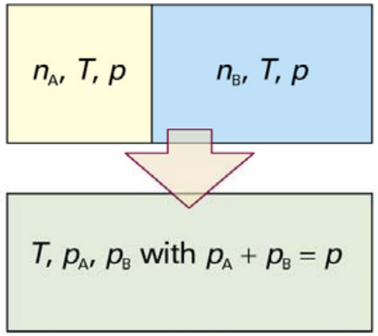
$$\boxed{\sum_J n_J d\mu_J = 0}$$

The same is true for all partial molar quantities

Gibbs-Duhem equation shows that chemical potential of one compound cannot be changed indepentently of the other chemical potentials.

Thermodynamics of mixing

- **The Gibbs energy of mixing**



Let's consider mixing of 2 perfect gases at constant pressure p:

For each of them: $\mu = \mu^{\theta} + RT \ln \frac{p}{p^{\theta}}$

and $G = \mu_A n_A + \mu_B n_B$

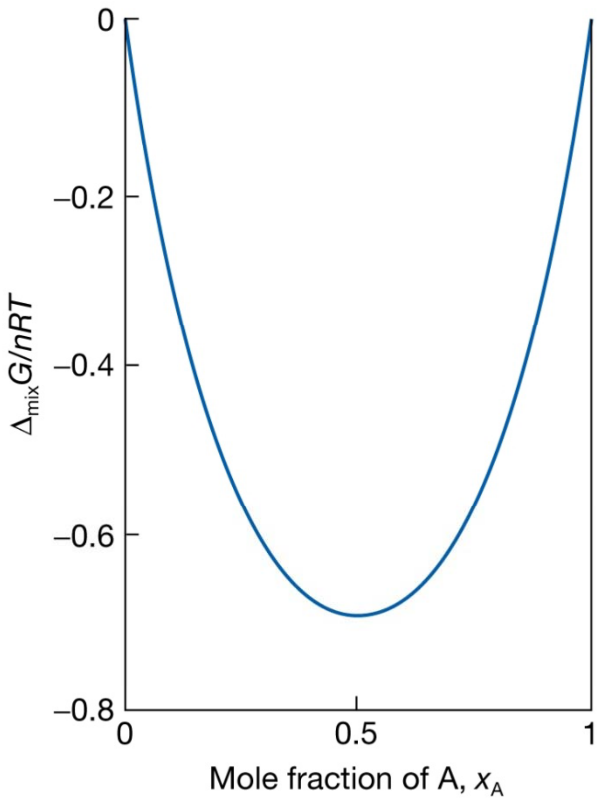
After mixing the energy difference:

$$\Delta_{mix} G = n_A RT \ln \frac{p_A}{p} + n_B RT \ln \frac{p_B}{p}$$

Using Dalton's law:

$$\Delta_{mix} G = nRT(x_A \ln x_A + x_B \ln x_B)$$

as $x_{A,B} < 1$, $\Delta_{mix} G < 0$



Thermodynamics of mixing

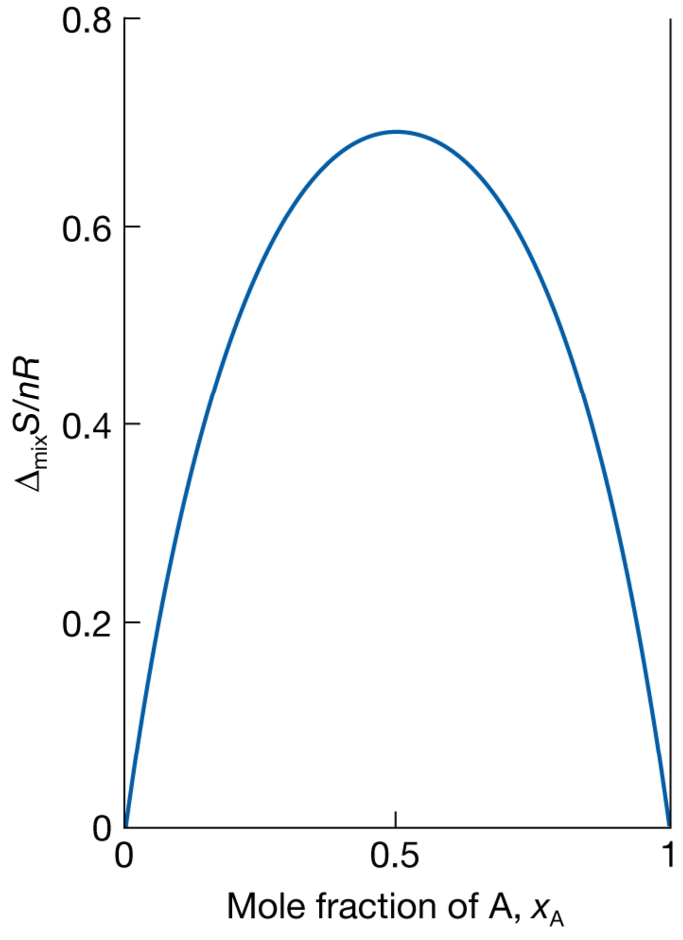
- **entropy of mixing**

$$\Delta_{mix} S = -\left(\frac{\partial \Delta_{mix} G}{\partial T} \right) = -nR(x_A \ln x_A + x_B \ln x_B)$$

- **enthalpy of mixing**

$$\Delta_{mix} H = \Delta_{mix} G + TdS = 0$$

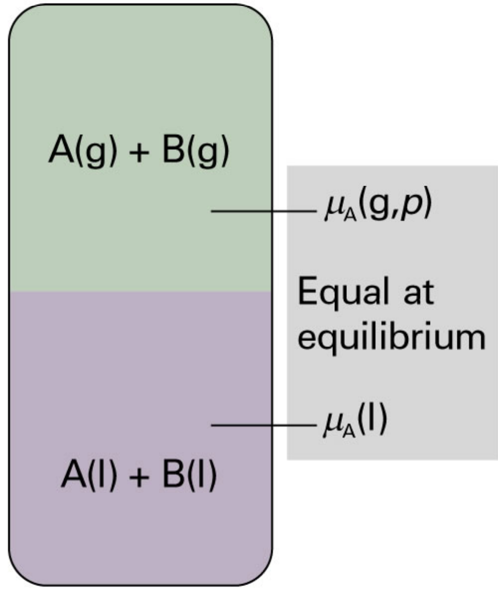
The driving force of mixing is a purely entropic one!



Chemical potential of liquid

- **Ideal solutions**

Let's consider vapour (treated as perfect gas) above the solution. At equilibrium the chemical potential of a substance in vapour phase must be equal to its potential in the liquid phase



For pure substance: $$\mu_A^* = \mu_A^\theta + RT \ln p_A^*$$

In solution: $$\mu_A = \mu_A^\theta + RT \ln p_A$$

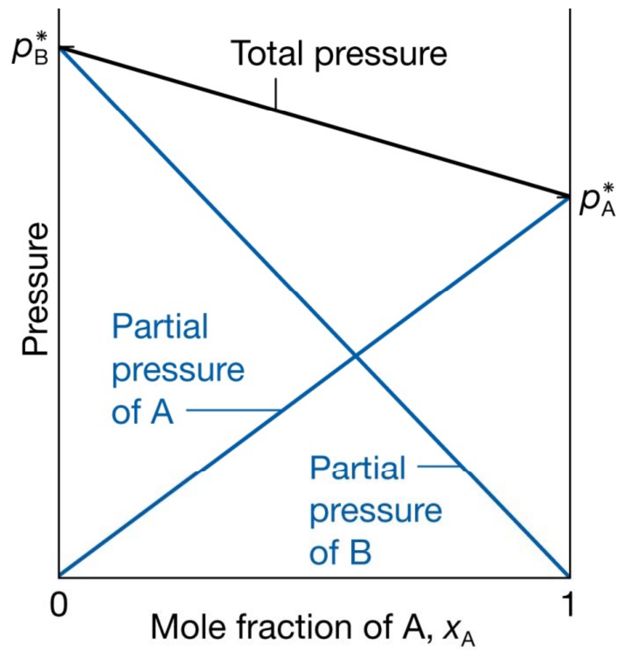
$$\mu_A = \mu_A^* + RT \ln \frac{p_A}{p}$$

Francouis Raoult experimentally found that:

$$p_A = x_A p_A^*$$ Raoult's law:

$$\mu_A = \mu_A^* + RT \ln x_A$$

Mixtures obeying Raoult's law called ideal solutions



Chemical potential of liquid

- Molecular interpretation of Raoult's law

rate of condensation

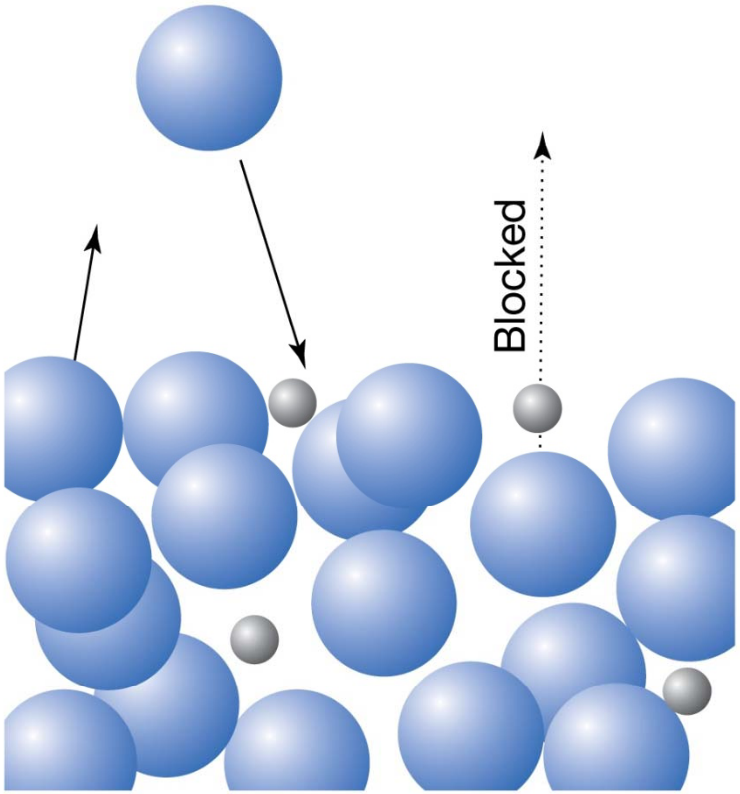
$$k' p_A = k x_A$$

rate of evaporation

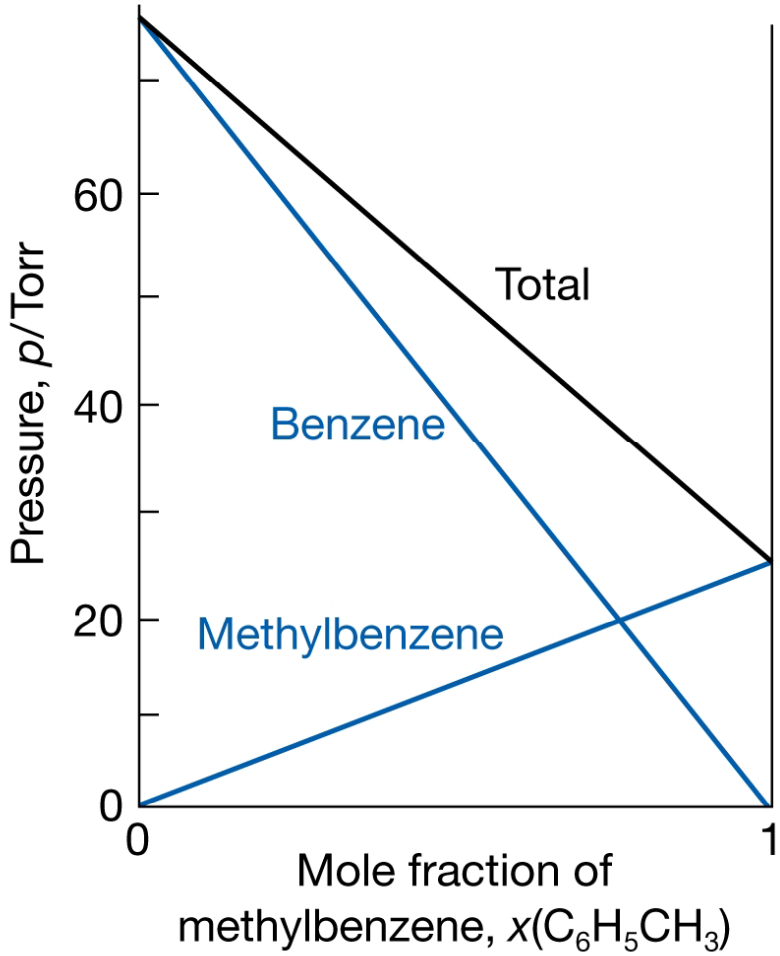
$$p_A = \frac{k}{k'} x_A$$

and in case of pure liquid ($x_A = 1$):

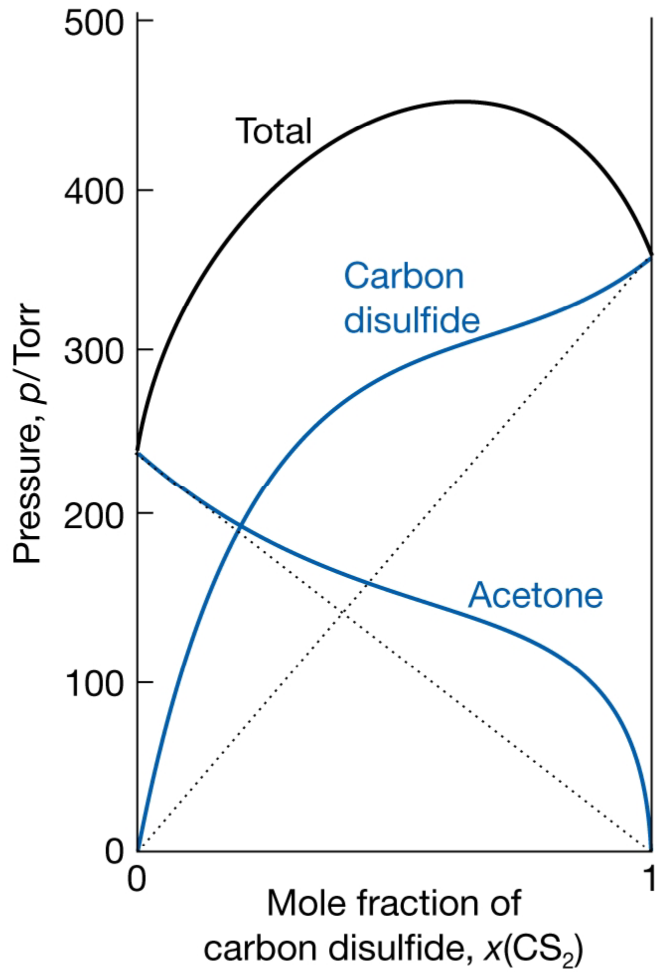
$$p^*_A = \frac{k}{k'}$$



Chemical potential of liquid



Similar liquid



Dissimilar liquid often show strong deviation

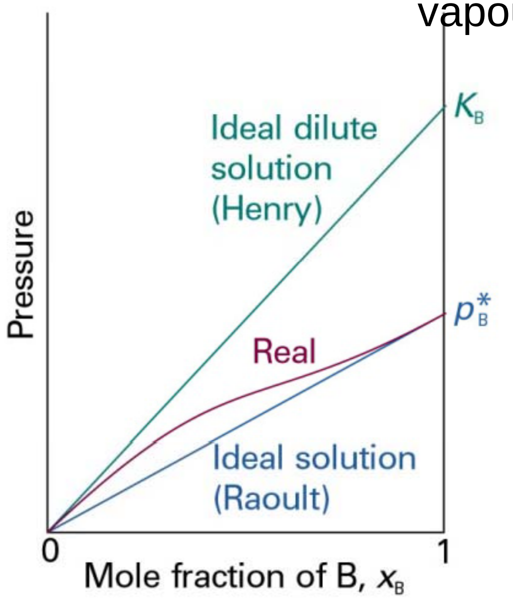
Chemical potential of liquid

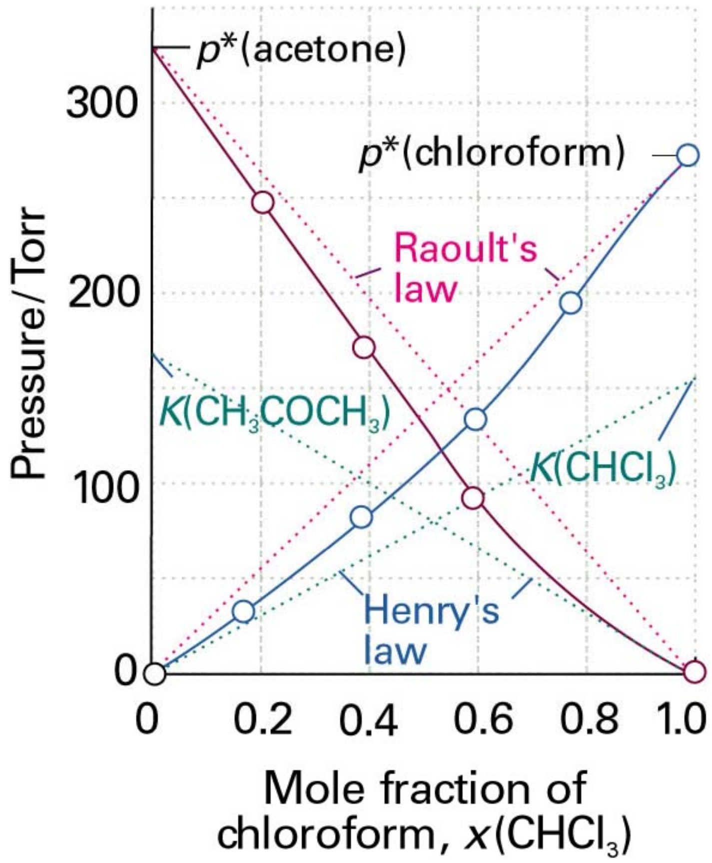
- **Ideal-dilute solutions: Henry's law**

In a dilute solution the molecule of solvent are in an environment similar to a pure liquid while molecules of solute are not!

$$p_A = x_A K_A$$

empirical constant, not the vapour pressure





Chemical potential of liquid

- **Using Henry's law**

Example: Estimate molar solubility of oxygen in water at 25 ^{0}C at a partial pressure of 21 kPa.

$$p_A = x_A K_A$$

$$x_A = \frac{p_A}{K_A} = \frac{21\,\text{kPa}}{7.9\times10^4\ \text{kPa kg mol}^{-1}} = 2.9\times10^{-4}\ \text{mol kg}^{-1}$$

molality

$$[\mathrm{O_2}] = x_A \rho_{\mathrm{H_2O}} = 0.29mM$$

Synoptic Table 5.1* Henry's law constants for gases in water at 298 K

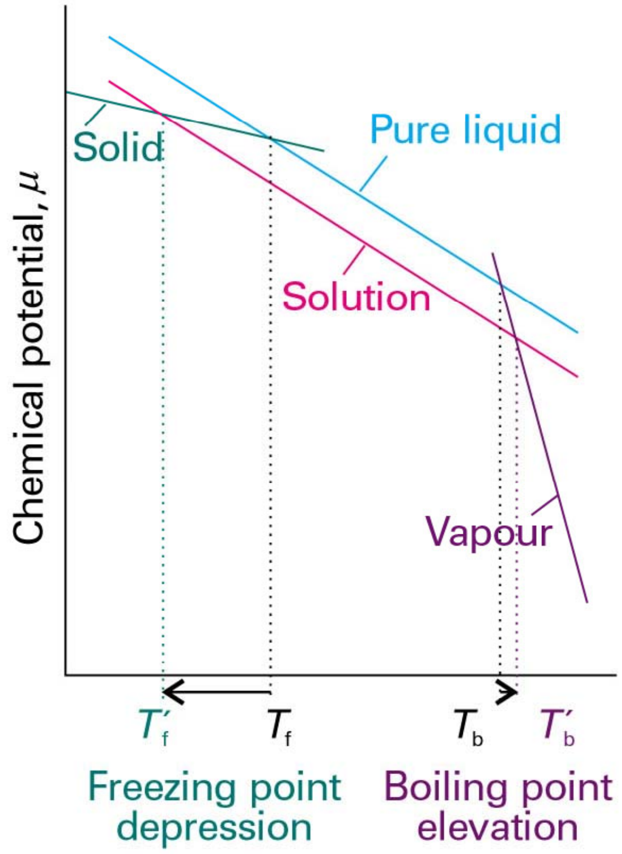
	$K/(\text{kPa kg mol}^{-1})$
CO_2	3.01×10^3
H_2	1.28×10^5
N_2	1.56×10^5
O_2	7.92×10^4

* More values are given in the *Data section*.

Colligative properties

- Elevation of boiling point
- Depression of freezing point
- Osmotic pressure phenomenon

All stem from lowering of the chemical potential of the solvent due to presence of solute (even in ideal solution!)



Larger

Colligative properties

- **Elevation of boiling point**

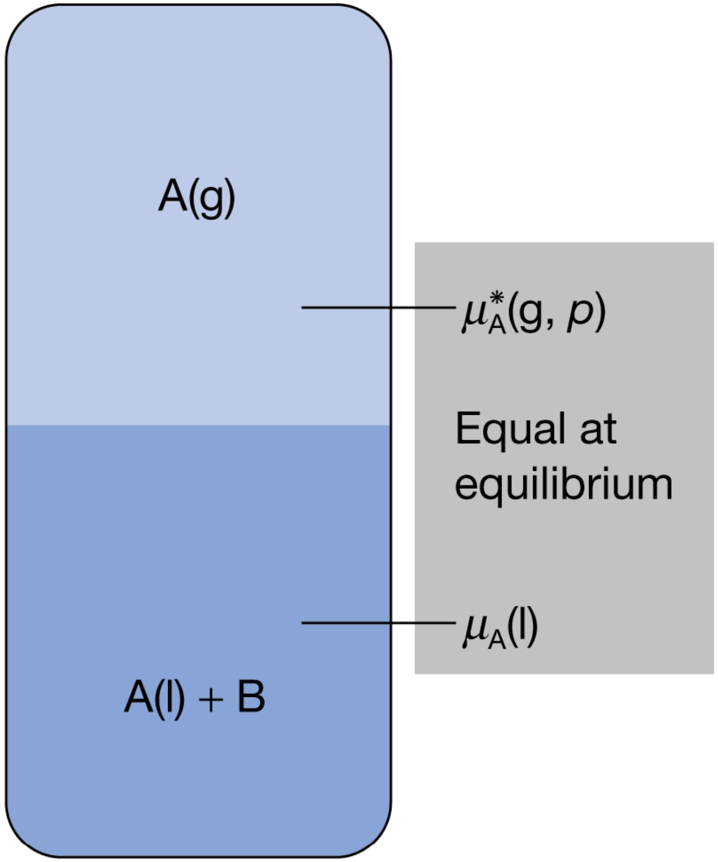
$$\mu_A^*(g) = \mu_A^*(l) + RT \ln x_A$$

$$\ln(1 - x_B) = \frac{\mu_A^*(l) - \mu_A^*(g)}{RT} = \frac{\Delta G_{vap}}{RT}$$

$$\Delta G_{vap} = \Delta H_{vap} - T\Delta S_{vap}$$

(Here we neglect temperature dependence)

For pure liquid: $$\ln 1 = \frac{\Delta H_{vap}}{RT^*} - \frac{\Delta S_{vap}}{R}$$



$$\ln(1 - x_B) = \frac{\Delta H_{vap}}{RT^*}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

$$x_B = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T^*} - \frac{1}{T}\right) \approx \frac{\Delta H_{vap}}{R}\frac{\Delta T}{T^{*2}} \Rightarrow \Delta T = \frac{RT^{*2}}{\Delta H_{vap}} x_B$$

Colligative properties

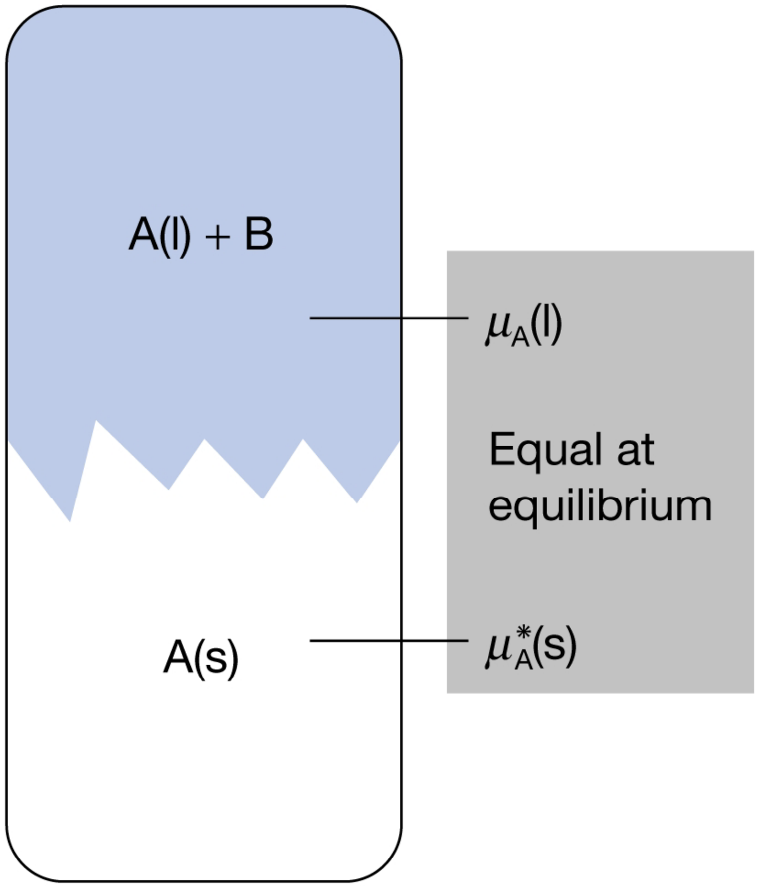
- **Depression of freezing point**

$$\mu_A^*(s) = \mu_A^*(l) + RT \ln \kappa_A$$

$$\Delta T = \frac{RT^{*2}}{\Delta H_{vap}} \kappa_B$$

$$\Delta T = K_f \kappa_B$$

Cryoscopic constant



Can be used to measure molar mass of a solute

Colligative properties

- **Solubility**

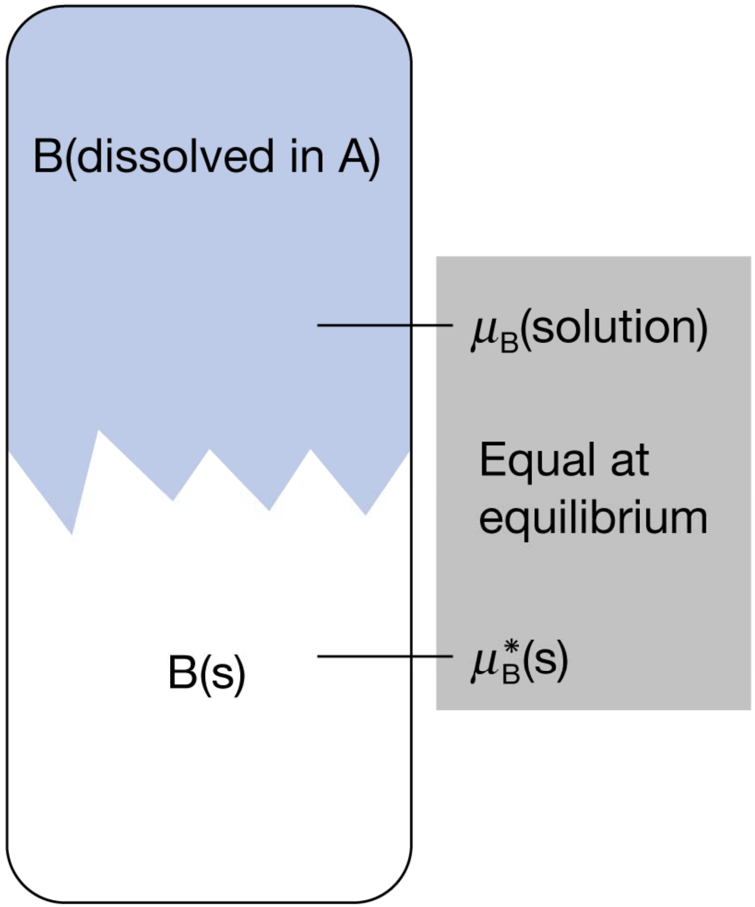
$$\mu_B^*(s) = \mu_B^*(l) + RT \ln \kappa_B$$

$$\ln \kappa_B = \frac{\mu_B^*(s) - \mu_B^*(l)}{RT} = \frac{-\Delta G_{fus}}{RT}$$

$$\Delta G_{fus} = \Delta H_{fus} - T\Delta S_{fus}$$

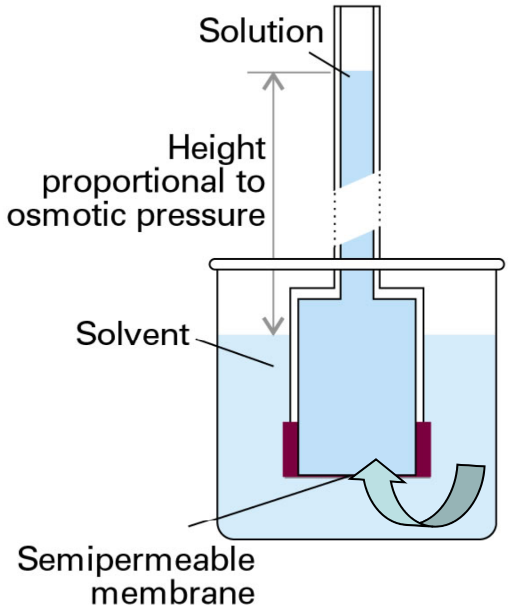
$$\Delta G_{fus}(T^*) = \Delta H_{fus} - T^*\Delta S_{fus} = 0$$

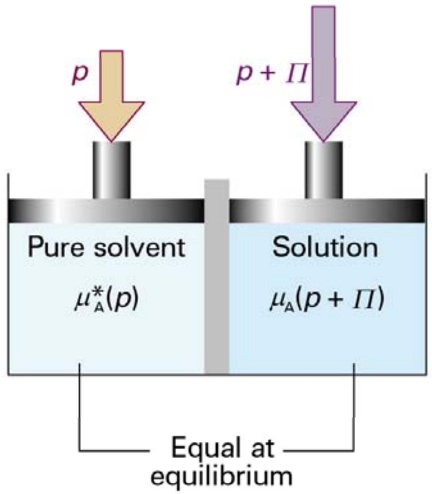
$$\ln \kappa_B = \frac{\Delta H_{fus}}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$



Colligative properties: Osmosis

- **Osmosis – spontaneous passage of pure solvent into solution separated by semipermeable membrane**





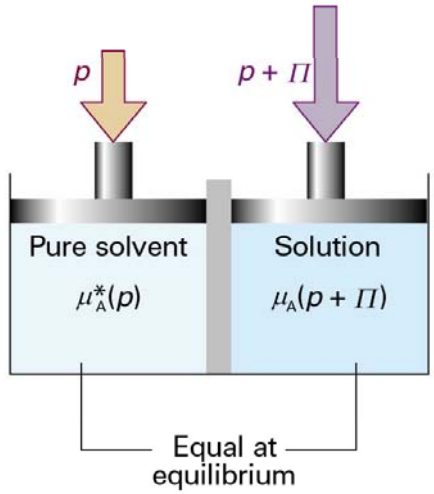
Van't Hoff equation: $\Pi = [B]RT, \quad [B] = n_B / V$

Osmosis

$$\mu_A^{*}(p) = \mu_A^{*}(p+\Pi) + RT\ln \kappa_A$$

$dG = -SdT + Vdp$

$$\mu_A^{*}(p+\Pi) = \mu_A^{*}(p) + \int_{p}^{p+\Pi} V_m dp$$



For dilute solution: $RT\kappa_{\mathbf{B}} = \Pi V_m$

$\boxed{V/n_A}$

$\boxed{n_B/n_A}$

Van't Hoff equation: $\Pi = [B]RT, \quad [B] = n_B/V$

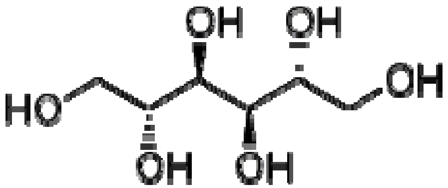
More generally: $\Pi = [B]RT(1 + b[B] + \ldots)$

Osmotic virial coefficients

Osmosis: Examples

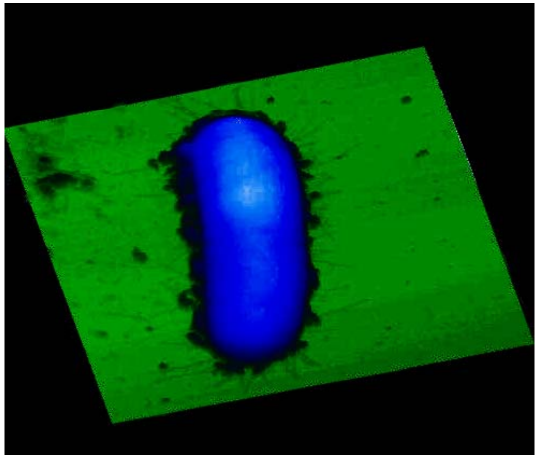
- Calculate osmotic pressure exhibited by 0.1M solutions of mannitol and NaCl.

$$\Pi = [B]RT, \qquad [B] = n_B / V$$



Mannitol ($C_6H_8(OH)_6$)

Osmosis: Examples



Isotonic conditions

Decreasing salt concentration

Hypotonic conditions:
cells burst and dye
haemolysis (for blood)

Increasing salt concentration

Hypertonic conditions:
cells dry and dye

Internal osmotic pressure keeps the cell “inflated”

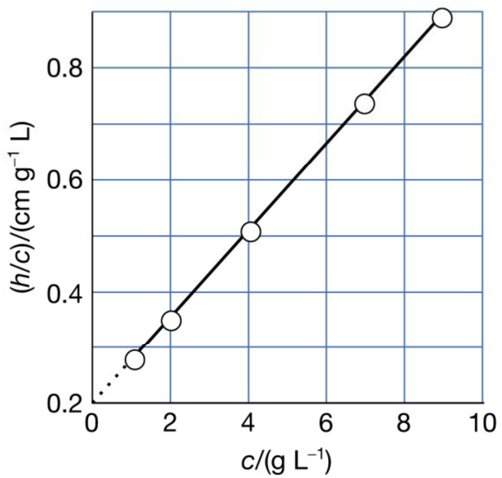
Application of Osmosis

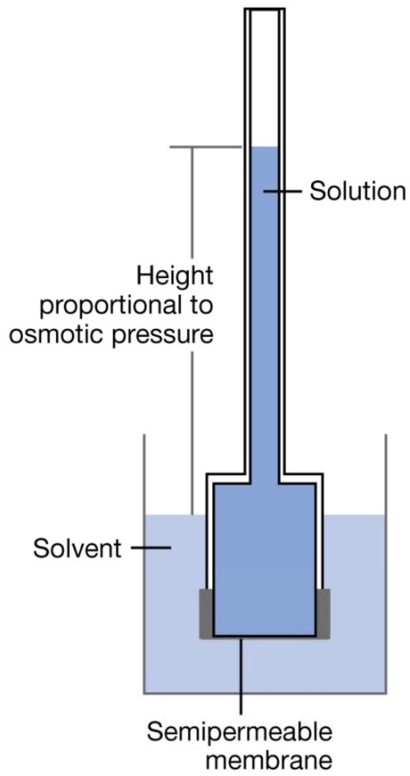
- **Using osmometry to determine molar mass of a macromolecule**

Osmotic pressure is measured at a series of mass concentrations ***c*** and a plot of Π / c vs. ***c*** is used to determine molar mass.

$$\underbrace{\Pi}_{\rho g h} = \underbrace{[B]}_{c/M} RT(1 + b[B] + \ldots)$$

$$\frac{h}{c} = \frac{RT}{\rho g M} + \frac{bRT}{\rho g M^2} c + \ldots$$

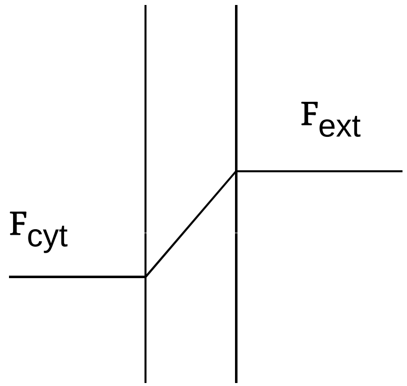




Membrane potential

- Electrochemical potential

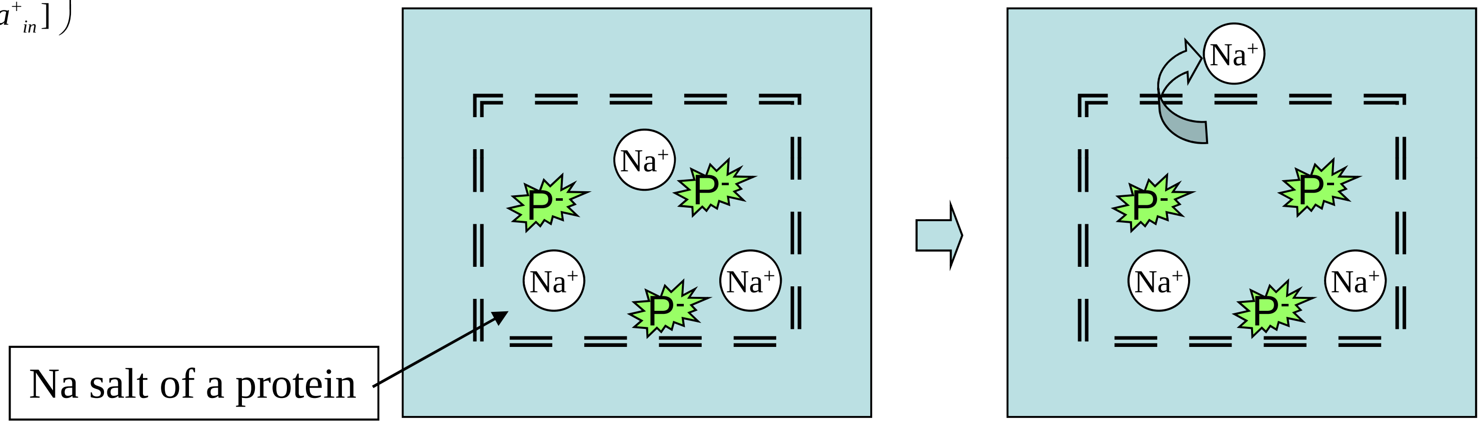
$$\bar{\mu}_j = \mu_j + z_j N_A e\Phi = \mu_j^{\theta} + RT\ln[j] + z_j F\Phi$$



- Example: membrane potential

$$\mu_{Na^+}^{\theta} + RT\ln[Na^+{}_{in}] + z_{Na^+}F\Phi_{in} = \mu_{Na^+}^{\theta} + RT\ln[Na^+{}_{out}] + z_{Na^+}F\Phi_{out}$$

$$\Delta\Phi = \frac{RT}{F}\ln\left(\frac{[Na^+{}_{out}]}{[Na^+{}_{in}]}\right)$$



Activities

- the aim: to modify the equations to make them applicable to real solutions

Generally:

vapour pressure of A above solution

$$\mu_A^{*} = \mu_A^{*} + RT\ln\frac{p_A}{p_A^{*}}$$

vapour pressure of A above pure A

For ideal solution

$$\mu_A^{*} = \mu_A^{*} + RT\ln\kappa_A$$

(Raoult’s law)

For real solution

$$\mu_A^{*} = \mu_A^{*} + RT\ln a_A$$

activity of A

$$a_A \to \kappa_A \quad \text{as} \quad \kappa_A \to 1$$

$$\mu_A^{*} = \mu_A^{*} + RT\ln\kappa_A + RT\ln\gamma_A$$

activity coefficient of A

Activities

- Ideal-dilute solution: Henry's law $p_B = K_B \kappa_B$

$$\mu_B^{\,*} = \mu_B^{*} + RT\ln\frac{p_B}{p^{*}_{\,B}} = \underbrace{\mu_B^{*} + RT\ln\frac{K_B}{p^{*}_{\,B}}}_{\mu_B^{\ominus}} + RT\ln\kappa_B$$

$$\mu_B^{\,*} = \mu_B^{\ominus} + RT\ln\kappa_B$$

- Real solutes

$$\mu_B^{\,*} = \mu_B^{\ominus} + RT\ln a_B \qquad a_B = \frac{p_B}{K_B}$$

Example: Biological standard state

- Biological standard state: let's define chemical potential of hydrogen at pH=7

$$\mu_{H^+} = \mu_{H^+}^{\theta} + RT \ln a_{H^+}$$

$$\mu_{H^+} = \mu_{H^+}^{\theta} - 7RT \ln(10) = \mu_{H^+}^{\theta} - 40kJ/mol$$

Ion Activities

$$\mu = \mu^{\theta} + RT \ln a$$

$$\boxed{a = \gamma \frac{b}{b^{\theta}}}$$

standard state: ideal solution at molality b^0=1mol/kg

Alternatively:

$$\mu = \mu^{\theta} + RT \ln b + RT \ln \gamma = \mu^{ideal} + RT \ln \gamma$$

ideal solution of the same molality b

In ionic solution there is no experimental way to separate contribution of cations and anions

$$G_m = \mu_+ + \mu_- = \mu_+^{ideal} + \mu_-^{ideal} + RT \ln \gamma_+ \gamma_-$$

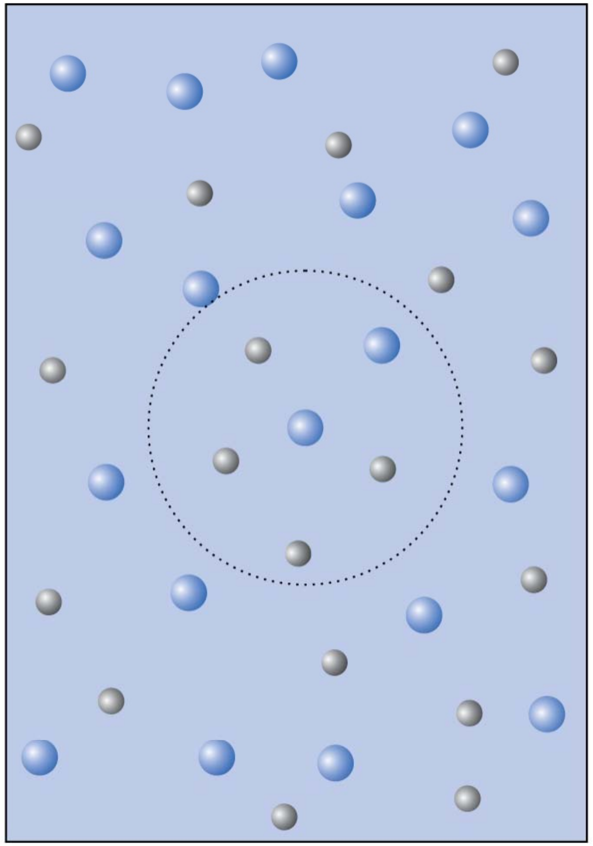
$$\boxed{\gamma_\pm^{\ 2}}$$

$$\mu_+ = \mu_+^{ideal} + RT \ln \gamma_\pm ; \ \mu_- = \mu_-^{ideal} + RT \ln \gamma_\pm$$

In case of compound M_pX_q: $G_m = p\mu_+ + q\mu_- = G_m^{ideal} + RT \ln \gamma_+^{\ p} \gamma_-^{\ q}$

Debye-Hückel limiting law

- Coulomb interaction is the main reason for departing from ideality
- Oppositely charged ions attract each other and will form shells (***ionic atmosphere***) screening each other charge
- The energy of the screened ion is lowered as a result of interaction with its atmosphere



Debye-Hückel limiting law

In a limit of low concentration the activity coefficient can be calculated as:

$$\boxed{\log \gamma_{\pm} = -|z_{+} z_{-}| A I^{1/2},} \quad A = -0.509 \text{ for water}$$

where: $I = \frac{1}{2}\sum_i z_i^{2}(b_i / b^{\ominus})$ Ionic strength of the solution

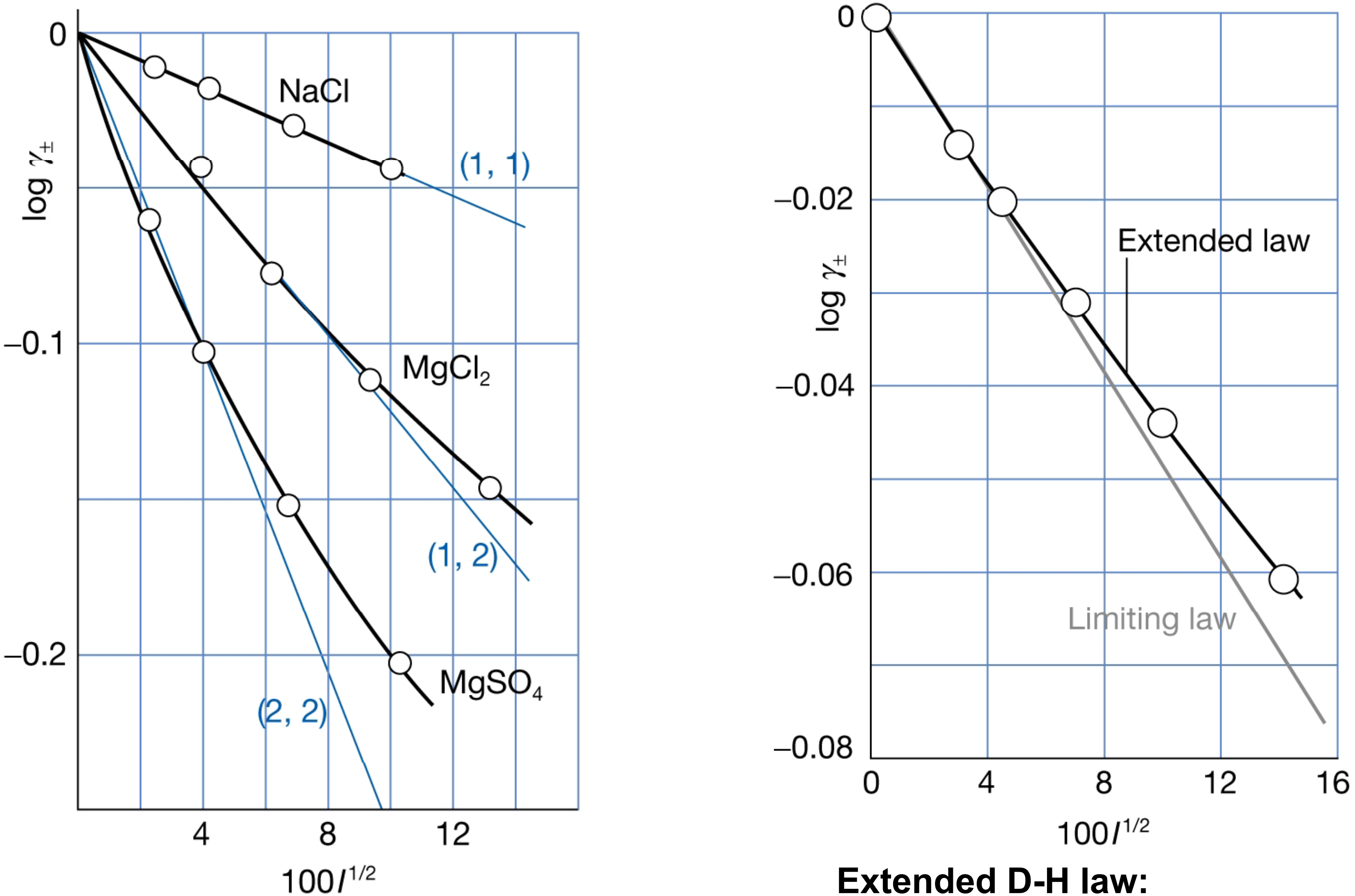
Example: calculate mean activity coefficient of 5 mM solution of KCL at 25C.

$$I = \frac{1}{2}(b_{+} + b_{-})/b^{\ominus} = b/b^{\ominus} = 5 \bullet 10^{-3}$$

$$\log \gamma_{\pm} = -|z_{+} z_{-}| A I^{1/2} = -0.509 * (5 \bullet 10^{-3})^{1/2} = -0.036$$

$$\gamma_{\pm} = 0.92$$

Debye-Hückel limiting law



$$\log \gamma_{\pm} = -\left|z_+ z_-\right| A I^{1/2}$$

Extended D-H law:

$$\log \gamma_{\pm} = -\frac{\left|z_+ z_-\right| A I^{1/2}}{1 + B I^{1/2}}$$

Problems (to solve in class)

- **5.2a** At 25°C, the density of a 50 per cent by mass ethanol–water solution is 0.914 g cm^{-3}. Given that the partial molar volume of water in the solution is 17.4 cm^3 mol^{-1}, calculate the partial molar volume of the ethanol
- **5.6a** The addition of 100 g of a compound to 750 g of CCl_4 lowered the freezing point of the solvent by 10.5 K. Calculate the molar mass of the compound.
- **5.14a** The osmotic pressure of solution of polystyrene in toluene were measured at 25 °C and the pressure was expressed in terms of the height of the solvent of density 1.004g/cm^3. Calculate the molar mass of polystyrene:

c [g/dm3]	2.042	6.613	9.521	12.602
h [cm]	0.592	1.910	2.750	3.600

- **5.20(a)** Estimate the mean ionic activity coefficient and activity of a solution that is 0.010 mol kg^{-1} $CaCl_2$(aq) and 0.030 mol kg^{-1} NaF(aq).

Assignment problems

- **E5.16b** Benzene and toluene form nearly ideal solutions. The boiling point of pure benzene is 80.1 °C. Calculate the chemical potential of benzene relative to that of pure benzene when $x_{benzene}$ =0.30 at its boiling point. If the activity coefficient of benzene in this solution were 0.93 rather than 1.00 what would be the vapour pressure?
- **P5.16** The main activity coefficients for aqueous solution of NaCl are given below. Confirm that they support Debye-Huckel law and that an improved fit can be obtained with the extended law.

$b/(\mathrm{mmol\ kg^{-1}})$	**1.0**	**2.0**	**5.0**	**10.0**	**20.0**
$\gamma_\pm$	0.9649	0.9519	0.9275	0.9024	0.8712

Use Excel (or other graphing software of your choice) to perform fit in the problem P5.16