Thermodynamics
remedial 5

March 17th 2022

Chemical potential, colligative properties and statistical thermodynamics

Course outline

- 5 sessions:
  - 1 Basics, (state) functions, ideal gas, internal energy, work, heat, Enthalpy
  - 2 Energy, Entropy
  - 3 Energy, chemical reactions
  - 4 Electrochemistry
  - **5 Colligative properties & statistical thermo**

Course today

- – Chemical potential
  - What is it and what is the function in thermodynamics
- – Colligative properties
- – Statistical thermodynamics

Study material

- Study guide (page 14-17 & 22-25)
- Atkins (see study guide)
- Relevant formulas on formula sheet

$$\Delta T = \left(\frac{RT^{*2}}{\Delta_{\text{trs}} H}\right) x_B$$

$$\Delta S = -nR\left(x_A \ln x_A + x_B \ln x_B\right)$$

$$\Pi = [B]RT = \frac{n_B}{V} RT$$

$$S = k \ln W$$

$$\mu_i = \mu_i^{\ominus} + RT \ln a_i = \mu_i^{\ominus} + RT \ln \frac{P_i}{P^{\ominus}}$$

$$G_{P,T} = \sum_i \mu_i n_i$$

$$\sum_j n_j \mathrm{d}\mu_j = 0$$

$$\frac{n_i}{N} = \frac{\exp \frac{-\epsilon_i}{kT}}{q} \quad \text{with} \quad q = \sum_i \exp \frac{-\epsilon_i}{kT} \quad \text{and} \quad < X >= N < x >= N \sum_i x_i \frac{n_i}{N}$$

Chemical potential:

Potential is the ability to perform work. Remember: being with low potential (impotent) you can’t perform action!

The more molecules of a certain type will be in a system, the more the ability to perform work (of that system) will depend on those molecules. That’s why the potential $\mu = G_{molar}$.
In other words, the "chemical potential ***μ***" is a measure of how much the Gibbs free energy of a system *changes* (by $\mathbf{d}\boldsymbol{G}_{\mathbf{i}}$) if you add or remove a number $\mathbf{d}\boldsymbol{n}_{\mathbf{i}}$ particles of the particle species **i** while keeping the number of the other particles (and the temperature ***T*** and the pressure ***p***) constant.

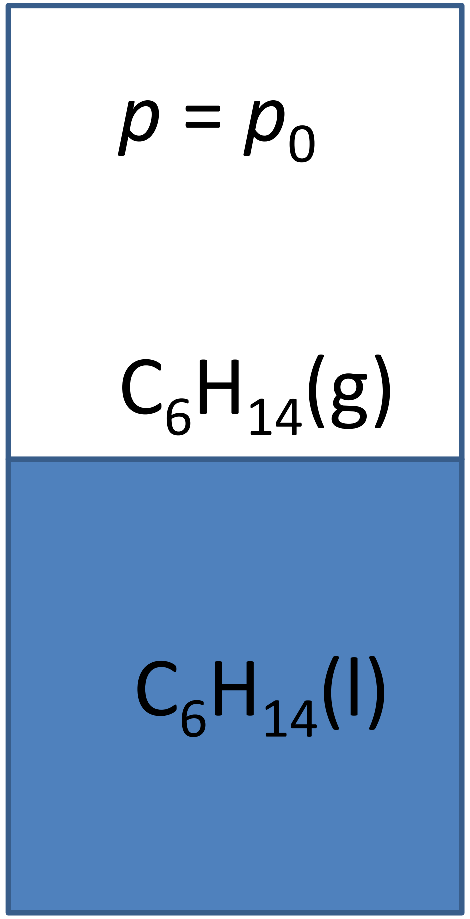
In equilibrium (nothing seems to happen, looking from a distance) the chemical potential of 2 systems connected to each other are equal! There is no driving force.

If there is a driving force (a spontaneous process), something happens and goes from high potential to low potential.

Use of chemical potential in this course

- Basis for the derivation of colligative properties
  - Equilibrium between liquid and vapour (boiling point elevation)
  - Equilibrium between liquid and solid (freezing point depression)
  - Osmotic pressure
- It is hard to see from the derived formulas that chemical potential is the basis…. But it is!

Elevation of boiling point



$p = p_0$

$C_6H_{14}(g)$

$C_6H_{14}(l)$

At equilibrium:

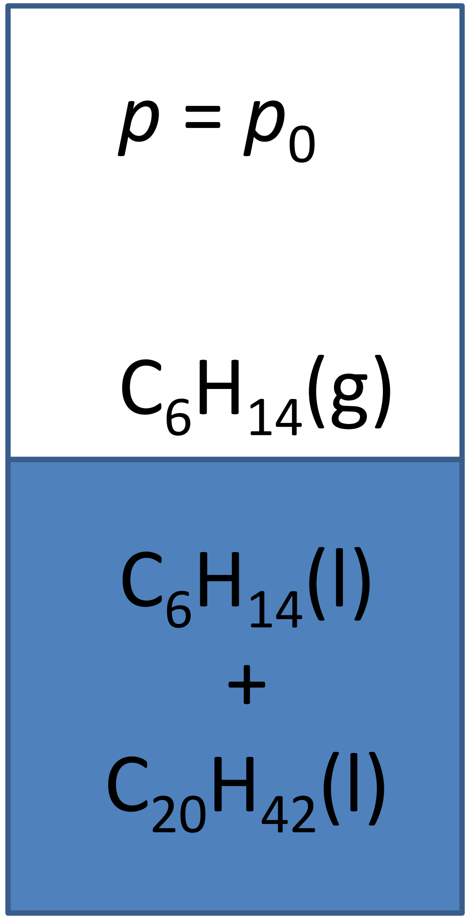
$\mu_{gas} = \mu_{liq}$

At $T = T^*_{boil}$ (69°C):

$\mu^*_{gas} = \mu^*_{liq}$

* means: pure substance!

Elevation of boiling point



$p = p_0$

$C_6H_{14}(g)$

$C_6H_{14}(l)$

+

$C_{20}H_{42}(l)$

At equilibrium:

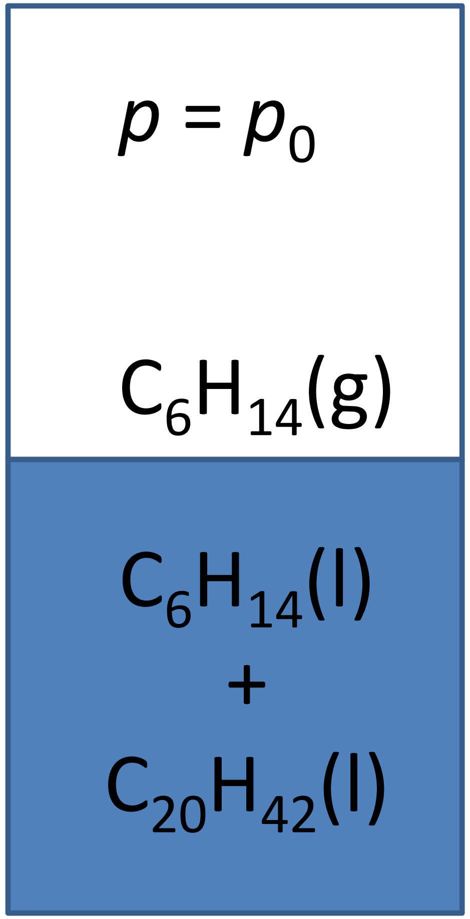
$\mu_{\mathrm{gas}} = \mu_{\mathrm{liq}}$

$\mu^*_{\mathrm{gas}} = \mu^*_{\mathrm{liq}}$ + correction for dissolving

$$\Delta T = \left(\frac{RT^{*2}_{boil}}{\Delta_{vap}H}\right)x_B$$

$p = p_0$, ideal dilute solution (low concentration)

Elevation of boiling point



$$\Delta T = \left(\frac{RT_{boil}^{*2}}{\Delta_{vap}H}\right)x_B$$

ΔT : elevation of boiling point

T_{boil}^{*} : boiling point of pure hexane

$\Delta_{vap}H$: enthalpy of vaporization of hexane

x_B : mole fraction of eicosane

$$x_B = \frac{\#\,\text{mol eicosane}}{\#\,\text{mol hexane} + \#\,\text{mol eicosane}}$$

$p = p_0$, ideal dilute solution

Boiling point **elevation** and freezing point **depression**

$$\Delta T = \left(\frac{RT_{vap}^{*2}}{\Delta_{vap} H}\right)\chi_B \qquad \Delta T = \left(\frac{RT_{fus}^{*2}}{\Delta_{fus} H}\right)\chi_B$$

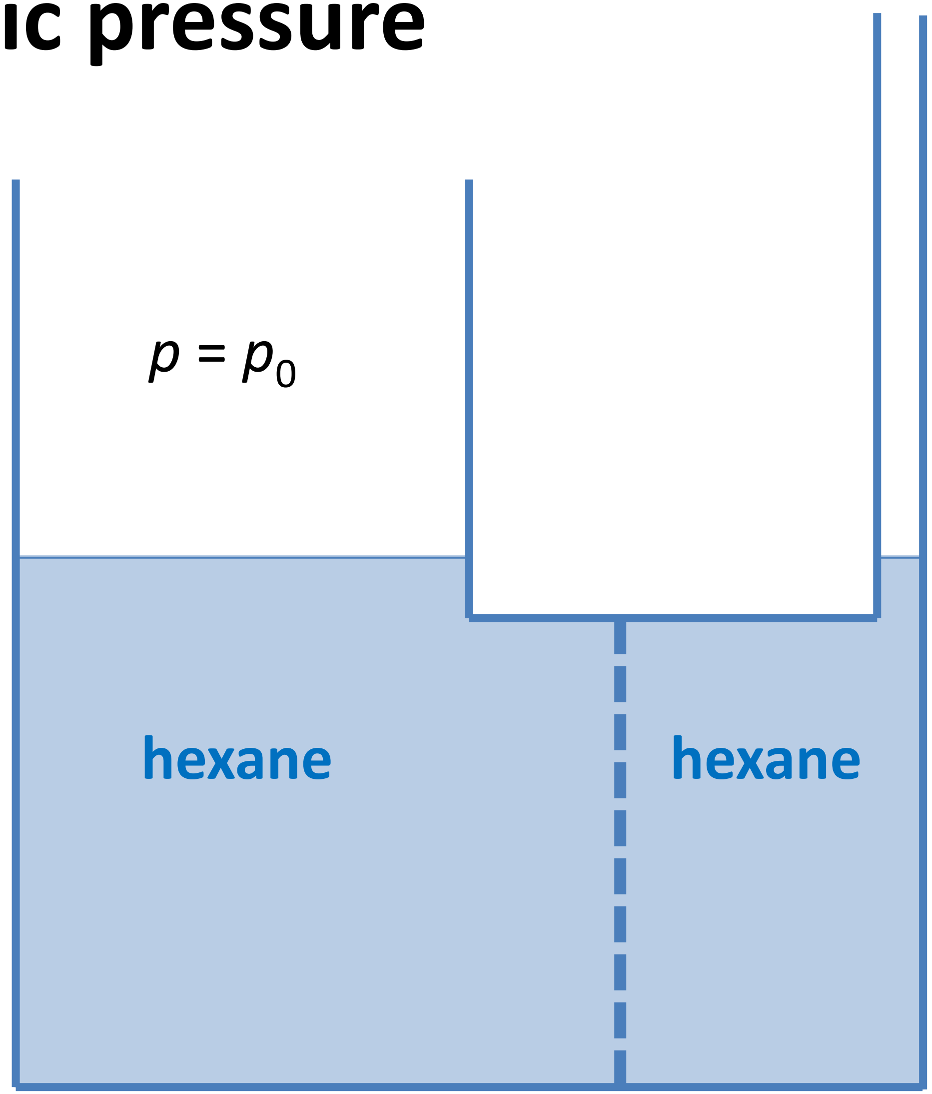
$$\Delta T = \left(\frac{RT^{*2}}{\Delta_{\mathrm{trs}} H}\right) x_B$$

See also the checklist of key equations

trs = transition

$p = p_0$, ideal dilute solution

Osmotic pressure

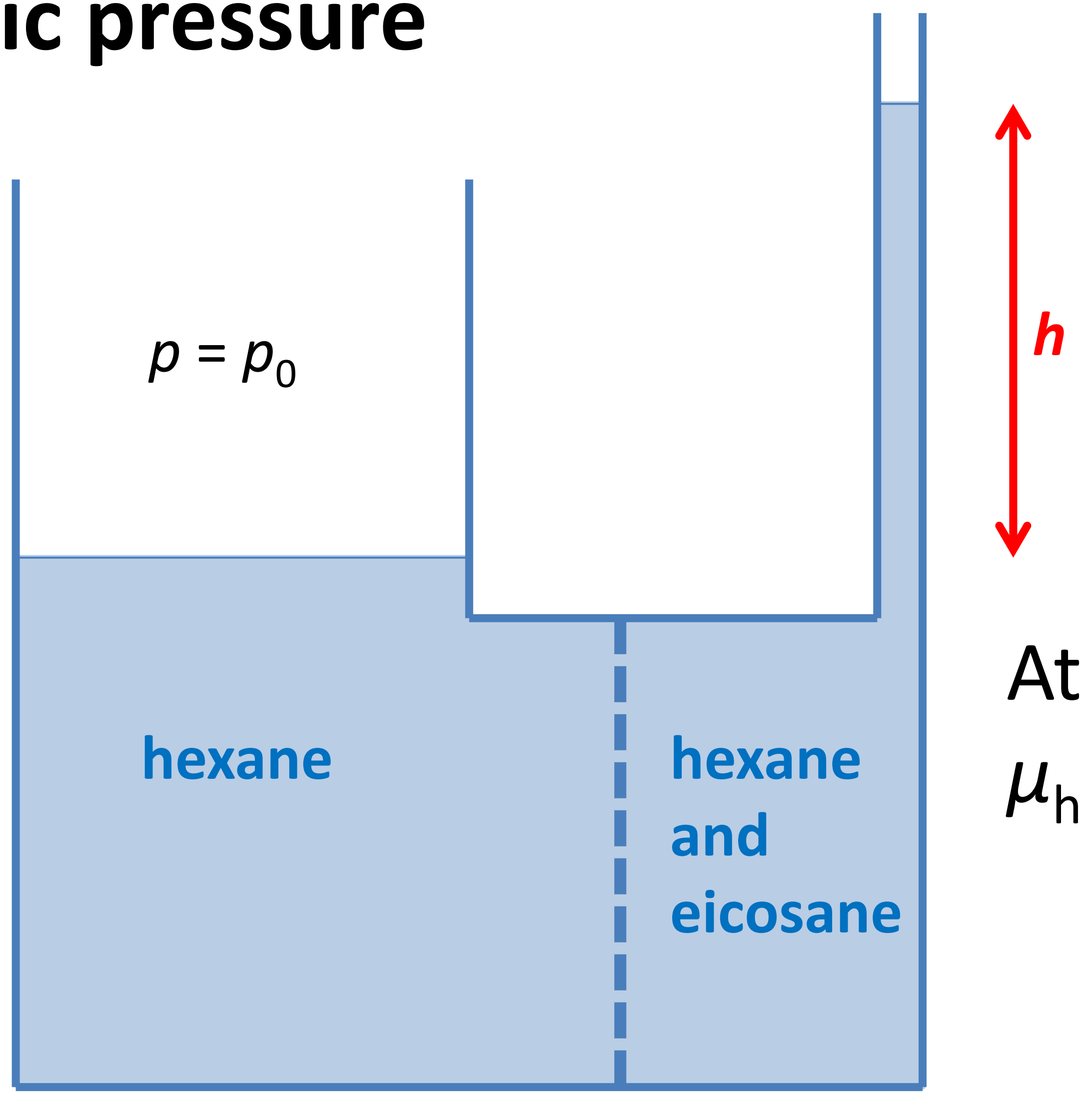


At equilibrium:

$$\mu_{\text{hexane,left}} = \mu_{\text{hexane,right}}$$

$$\mu^*_{\text{hexane}} = \mu^*_{\text{hexane}}$$

Osmotic pressure



additional pressure:

$p = p_0 + \Pi$

At equilibrium:

$\mu_{\text{hexane,left}} = \mu_{\text{hexane,right}}$

$\mu^*(p_0)_{\text{hexane}} = \mu(p_0+\Pi)_{\text{mixture}}$

$\mu^*(p_0)_{\text{hexane}} = \mu^*(p_0)_{\text{hexane}}$ + correction for dissolving + additional pressure

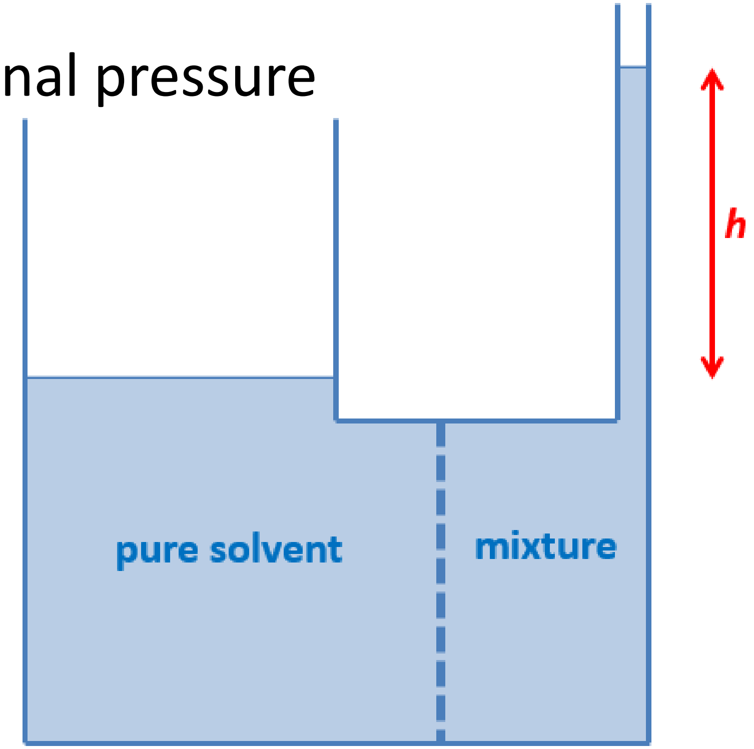
Osmotic pressure

$\mu^*(p_0)_{\text{hexane}} = \mu^*(p_0)_{\text{hexane}}$ + correction for dissolving + additional pressure

$p = p_0$, ideal dilute solution

$$\Pi = [B]RT = \frac{n_B}{V}RT$$

Note: [B] in **mol/m^3**



$$\Pi = \rho \cdot g \cdot h = [B]RT$$

Exercise 16

The boiling point of benzene is 80.15 °C. The heat of evaporation is 30.8 kJ/mol. The molar mass of benzene is 78.11 g/mol. 10 g of a solid is completely dissolved in 100 g benzene. Because of this, the boiling point of benzene increases to 80.95 °C. Calculate the molar mass of the dissolved substance.

Exercise 16

We substitute the measured temperature increase into the standard expression for boiling point elevation:

$$\Delta T = K x_B \quad \text{in which} \quad K = \frac{RT^{*2}}{\Delta_{vap}H},$$

or

$$0.80 = \Delta T = \frac{RT^{*2}}{\Delta_{vap}H} \cdot \frac{n_B}{n_{\text{benzene}} + n_B} = \frac{8.314 \cdot 353.30^2}{30.8 \cdot 10^3} \cdot \frac{\frac{10}{M_B}}{\frac{100}{78.11} + \frac{10}{M_B}} = \frac{8.314 \cdot 353.30^2}{30.8 \cdot 10^3 \cdot \left(\frac{10}{78.11} M_B + 1\right)}.$$

With this we find

$$M_B = 321 \text{ g/mol}.$$

Exercise add_12

The osmotic pressure of solutions of polystyrene in toluene at 25 °C is measured; see the table below (h is the pressure in terms of the height of a fluid column with density $\rho = 1.004$ g cm^{-3}).

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

Determine the molar mass of the polymer.

Exercise add_12

For very low concentrations of a dissolved compound (the solute) we can use the simple expression

$$\Pi = [B]RT \quad \text{with} \quad [B] = \frac{n_B}{V} = \frac{c_B}{M_B}$$

for the osmotic pressure. Here M_B is the molar mass and c_B is the mass concentration of the polystyrene. The osmotic pressure is measured as $\Pi = \rho g h$, such that

$$h = \left(\frac{RT}{\rho g M_B}\right) c_B.$$

When we plot $h(c_B)$, the expression between the brackets is the slope. For this plot we can incorporate the point $h(c_B = 0) = 0$; this increases the accuracy since the equation above is most accurate for $c_B \approx 0$. The slope of this plot is 0.29 cmL/g, or

$$\frac{RT}{\rho g M_B} = 0.29 \cdot 10^{-2}\ \text{m}^4/\text{kg}.$$

With that we find for the molar mass of the dissolved polystyrene ($g = 9.81$ m/s^2):

$$M_B = \frac{8.314 \cdot 298.15}{1.004 \cdot 10^3 \cdot 9.81 \cdot 0.29 \cdot 10^{-2}} = 87\ \text{kg/mol} = 87 \cdot 10^3\ \text{g/mol}.$$

Statistical Thermodynamics

- Based on statistics, chance
- Used in this course
    - to predict the chance that a particle is in a certain state
    - To calculate entropy, microstates

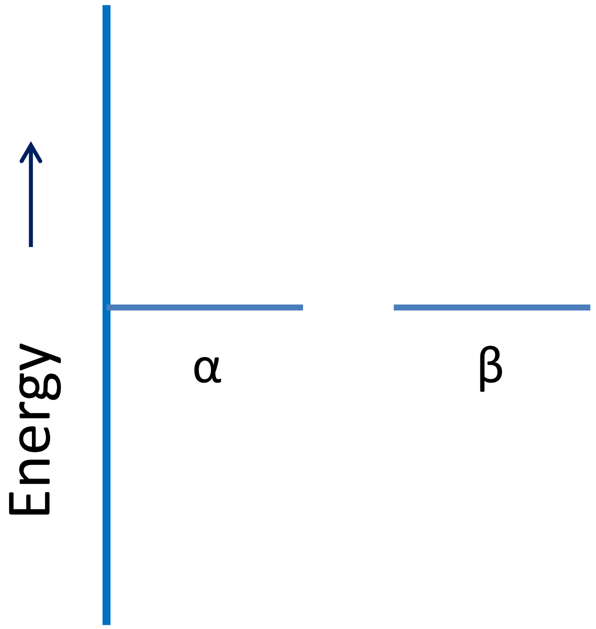
System of particles: Boltzmann factor

$$\exp \frac{-\varepsilon_i}{kT}$$

Checklist of key equations: $\frac{n_i}{N} = \frac{\exp \frac{-\varepsilon_i}{kT}}{q}$ with $q = \sum_i \exp \frac{-\varepsilon_i}{kT}$

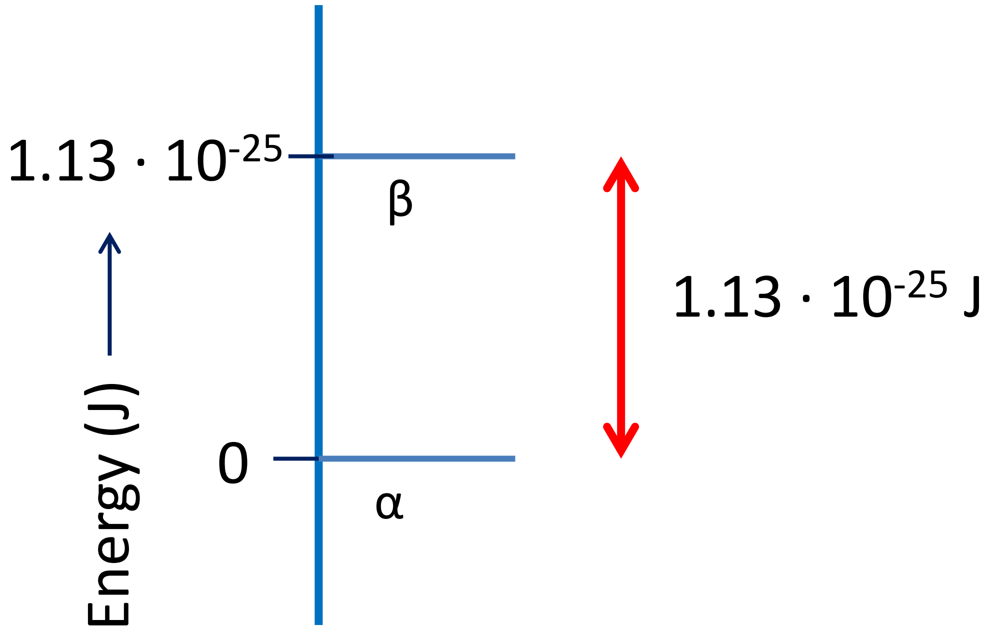
Equation for calculating the fraction of particles (p_i) present at energy level ε_i: $p_i = \frac{n_i}{N} = \frac{\exp \frac{-\varepsilon_i}{kT}}{q} = \frac{\exp \frac{-\varepsilon_i}{kT}}{\sum_i \exp \frac{-\varepsilon_i}{kT}}$

Nuclear spin H-atom: α and β



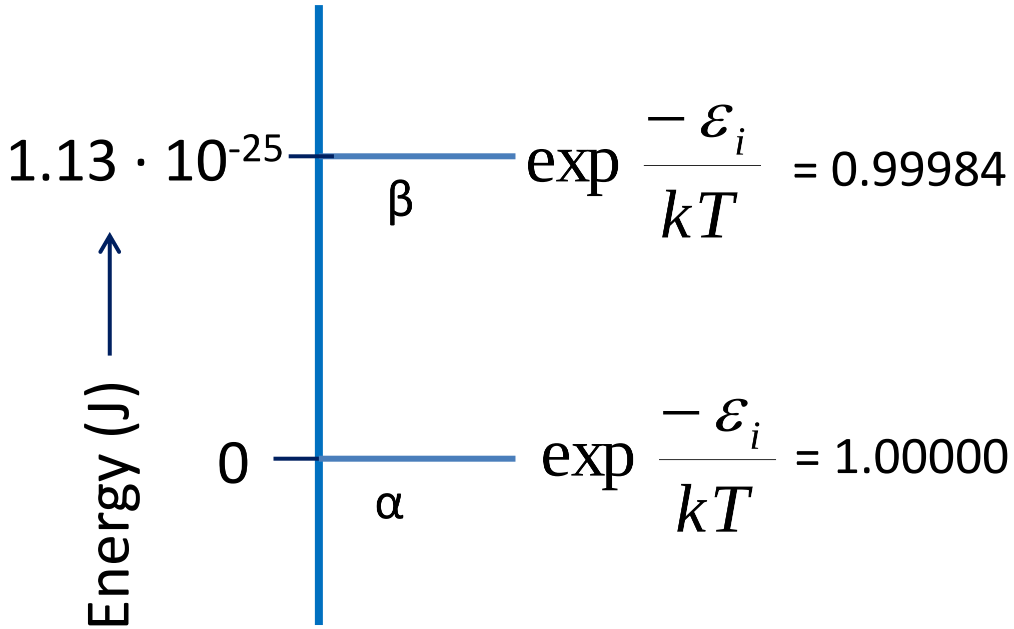
Nuclear spin α and β in a strong magnetic field

At T = 50 K and B = 4 Tesla



Nuclear spin α and β in a strong magnetic field

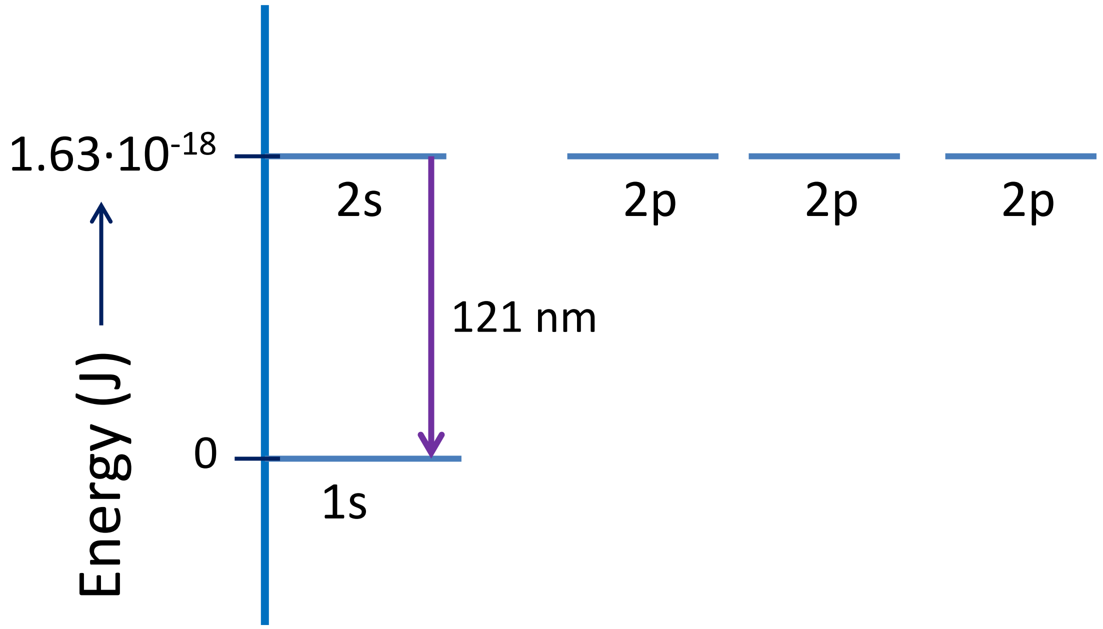
At T = 50 K and B = 4 Tesla



$$\text{Chance}(\boldsymbol{\beta}) = \frac{\mathbf{0.99984}}{\mathbf{1.00000 + 0.99984}} = \mathbf{0.49996}$$

simplified H atom (only 2 energy levels)

At T = 50000 K



$$\exp\frac{-\varepsilon_i}{kT} = 0.094$$

$$\exp\frac{-\varepsilon_i}{kT} = 1.000$$

$$\text{Chance}(\mathbf{1s}) = \frac{\mathbf{1.000}}{\mathbf{1.000 + 4 \times 0.094}} = \mathbf{0.727}$$

Particle system: Boltzmann factor

In this presentation:

$$p_i = \frac{n_i}{N} = \frac{\exp \frac{-\varepsilon_i}{kT}}{q} \qquad q = \sum_i \exp \frac{-\varepsilon_i}{kT}$$

Partition function:

This summation is hard to calculate in real systems

Entropy, statistical approach

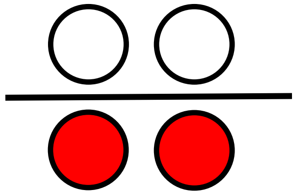
$$S = k \ln W$$

S = (absolute) entropy (the entropy of all particles in a system)
K = boltzmann constant
W = total amount of microstates of a system

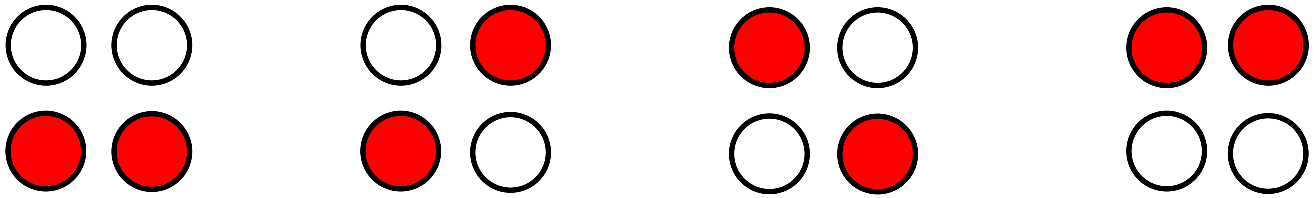
Microstates…. What does it mean?

Imagine a system with 4 molecules, 2 white ones and 2 red ones and only 4 places where the molecules can reside. The system is divided into 2 subsystems, so that the red molecules and the white ones will be divided. There is only 1 possible microstate for this system (picture 1). W = 1 here and S = 0.

If we connect both subsystems by removing the barrier and the new system has the opportunity to rearrange things, there can be found 4 possible microstates, W = 4 (picture 2).
If we imagine that a real system holds moles of molecules, we can imagine that the possible amounts of microstates increase enormously with increasing numbers of molecules.



Picture 1



Picture 2

Exercise 23

Given is a polypeptide with n amino acids.
We estimate the conformational entropy of a completely unfolded polypeptide compared to that in completely folded state. We assume that the difference is only determined by the difference in torsional degrees of freedom.
In unfolded state the peptide groups can rotate around the N-C$_\alpha$ and the C$_\alpha$-CO bond axes, namely over the two angles ϕ and ψ, respectively. These rotations each have three positions in which the torsion energy is minimal, therefore these three torsion angles occur often. For the conformations of the polypeptide molecule we limit ourselves to those torsion positions (see figure 1).

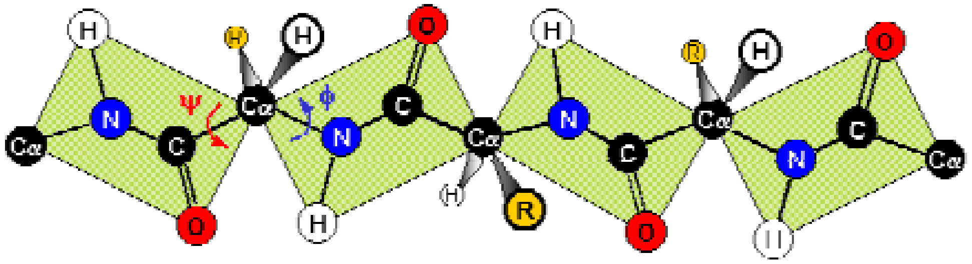


Figure 1: Completely unfolded polypeptide chain. The torsion angles ϕ and ψ each have 3 preferred states.

In the folded state there is one torsion position for both ϕ and ψ.

a) Determine the number of possible conformations N of the polypeptide molecule in the unfolded state.

b) Use the Boltmann definition of the entropy to calculate the molar entropy difference ΔS between all possible unfolded states on one hand and the completely folded state on the other hand for a polypeptide with $n = 100$ amino acids.

c) Make a similar estimation of the entropy as a consequence of the torsion freedom in an ethane molecule, again assuming that three torsion positions can be occupied.

d) How can you reconcile the results of parts b) and c)?

Exercise 23

a) There are n amino acids and thus $(n-1)$ peptide bonds in the polypeptide chain. Every peptide bond has two rotational degrees of freedom, the torsion angles ϕ and ψ, which each have three positions so there are $3^2 = 9$ torsional states per peptide bond (see figure 1).

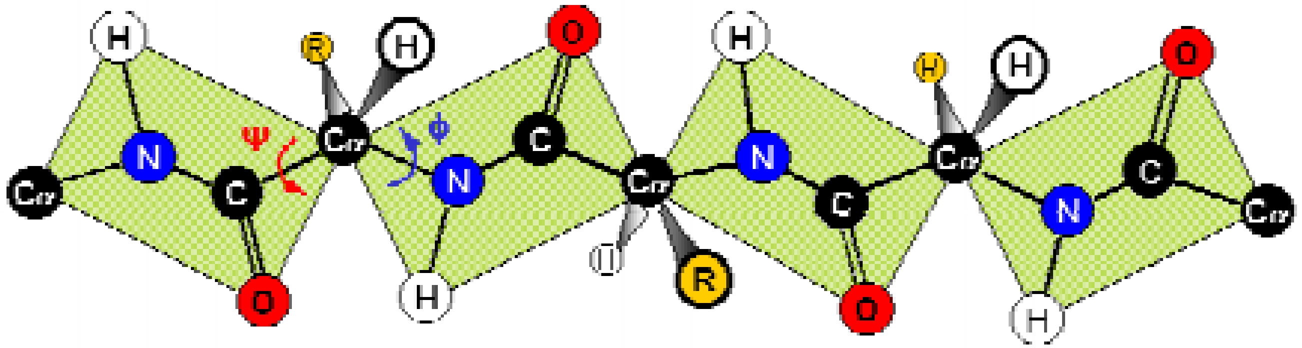


Figure 1: Completely unfolded polypeptide chain; ϕ and ψ each have 3 preferred states.

Thus for the n peptides of the entire molecule there are $N_c = 3^{2(n-1)} = 9^{(n-1)}$ conformations.

b) $\Delta S = k \ln W_u - k \ln W_n$, in which the number of conformations is $W_n = 1$ for the folded (native) state, whereas part a) shows that $W_u = N_c = 3^{2(n-1)}$ for all unfolded states. With this we find $\Delta S = k \ln 3^{2(n-1)} - k \ln 1 = k \ln 3^{2 \cdot 99} - 0 = 2 \cdot 99 k \ln 3 = 218k = 3.0 \cdot 10^{-21}$ J/K. This is the entropy per molecule. The molar entropy thus becomes $\Delta S_m = N_A \Delta S = 1.8$ kJ/mol K.

c) The torsional degrees of freedom in an ethane molecule result in an entropy gain per mol ethane of $\Delta S = N_A k \ln 3 = R \ln 3 = 9.1$ J/mol K.

d) The conformational torsional entropy per group in the molecule for the polypeptide molecule is $\frac{\Delta S}{100} = 18$ J/mol K, which is twice as much as for the ethane molecule. The factor two is a consequence of the number of torsion angles (ϕ and ψ). The huge difference between the two cases of part b) and c) is the result of the large difference in possible molecular conformations.

Exercise 17

The van 't Hoff expression for the osmotic pressure of very diluted ideal solutions is

$$\Pi = [B]RT.$$

a) Show that the osmotic pressure of a real (non-ideal) solution is given by

$$\Pi = -\frac{RT}{V_{m,A}} \ln a_A.$$

For an aqueous solution of sucrose ($C_{12}H_{22}O_{11}$) with a molality of 0.300 mol/kg the molarity is 0.282 mol/dm^3 at 20 °C and 1 atm. The density of pure water at 20 °C is $\rho_{H_2O} = 0.998$ g/cm^3.

b) Determine the osmotic pressure using the van 't Hoff expression for very diluted ideal solutions.

c) The measured osmotic pressure for this solution turns out to be 7.61 atm.
Determine the activity and the activity coefficient of the solvent.

Exercise 17

a) For a non-ideal solution the chemical potential of component A is $\mu_A = \mu_A^* + RT \ln a_A$ instead of the ideal solution approximation $\mu_A = \mu_A^* + RT \ln x_A$. This implies that in the derivation for the osmotic pressure we also have to replace $\ln x_A$ by $\ln a_A$, in which a_A is the activity of component A in the solution. So we can continue the original derivation for the osmotic pressure at the equation

$$-RT \ln x_A = V_{m,A}\Pi.$$

Replacing $\ln x_A$ by $\ln a_A$ immediately gives the accurate result for the osmotic pressure

$$\Pi = -\frac{RT}{V_{m,A}} \ln a_A.$$

Note that A represents the solvent, while in the approximated van 't Hoff equation the concentration of the solute B shows up.

b) The osmotic pressure of an ideal solution is given by the van 't Hoff equation
(use $R = 8.31447\ \mathrm{J/mol\,K} = 8.20574 \cdot 10^{-2}\ \mathrm{L\,atm/mol\,K}$)
$\Pi = [B]RT = 0.282\ \mathrm{mol/L} \cdot 8.20574 \cdot 10^{-2}\ \mathrm{L\,atm/mol\,K} \cdot 293.2\ \mathrm{K} = 6.78\ \mathrm{atm}.$

c) We use the result of a).
The molar volume of water at 20 °C and 1 atm is $V^*_{m,H_2O} = \frac{18.015\ \mathrm{g/mol}}{0.998\ \mathrm{g/cm^3}} = 18.05\ \mathrm{cm^3/mol}$. Using this result, we find for the activity of the water (component A)
$\ln a_A = -\frac{\Pi V_{m,A}}{RT} = -\frac{\Pi V^*_{m,H_2O}}{RT} = -\frac{7.61\ \mathrm{atm}\cdot 18.05\cdot 10^{-3}\ \mathrm{L/mol}}{8.20574\cdot 10^{-2}\ \mathrm{L\,atm/mol\,K}\cdot 293.2\ \mathrm{K}} = -5.71 \cdot 10^{-3}$, or $a_A = 0.9943$.
The activity coefficient γ_{H_2O} of the solvent follows with $a_i = \gamma_i x_i$ and is the easiest to determine using the molality b_i of the components, according to

$$\gamma_{H_2O} = \frac{a_{H_2O}}{x_{H_2O}} = a_{H_2O}\frac{n_{H_2O} + n_B}{n_{H_2O}} = a_{H_2O}\frac{b_{H_2O} + b_B}{b_{H_2O}} = 0.9943\frac{\frac{10^3}{18.015} + 0.300}{\frac{10^3}{18.015}} = \frac{0.9943}{0.9946} = 0.9997.$$