Chemical Potential in Focus – Osmosis and more

Regina Rüffler, Georg Job

JOO FOUNDATION

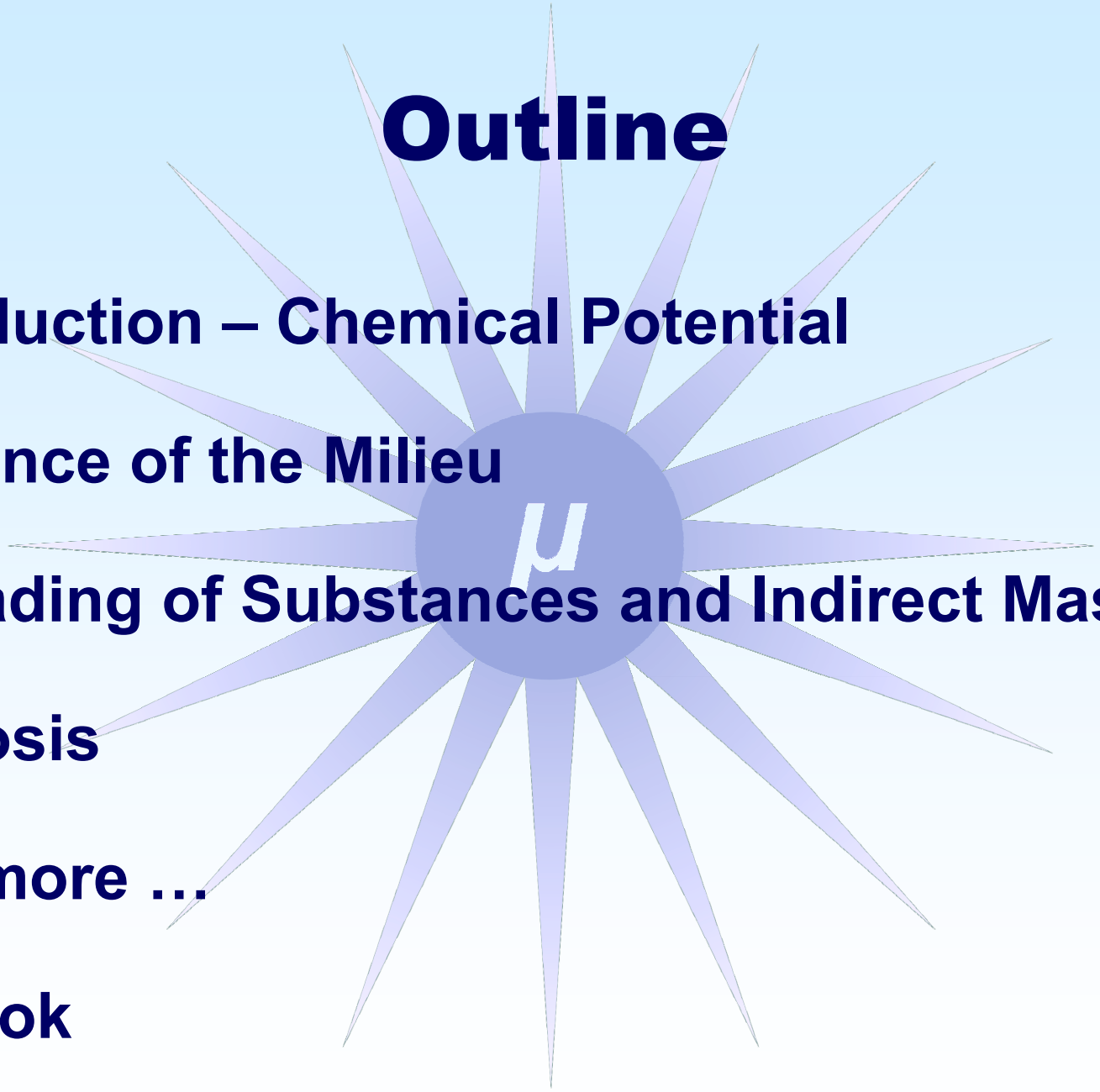
c/o. Institute of Physical Chemistry,

University of Hamburg

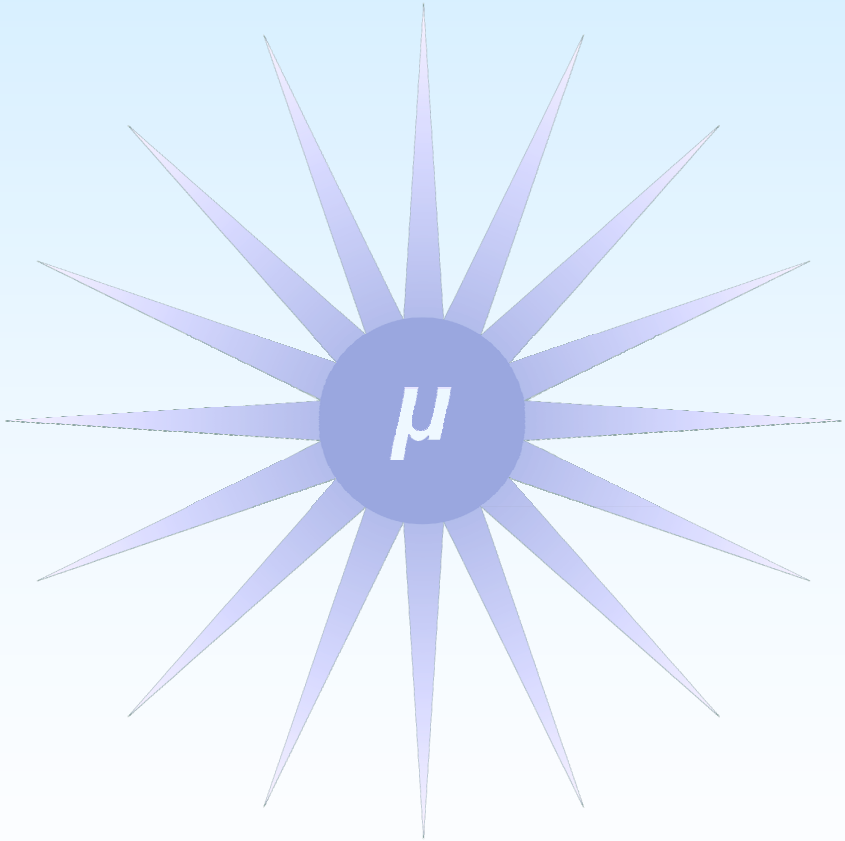
ChemEd 2013 Conference **Waterloo, Canada, 29th July 2013**

Outline

1. Introduction – Chemical Potential
2. Influence of the Milieu
3. Spreading of Substances and Indirect Mass Action
4. Osmosis
5. And more …
6. Outlook



1. Introduction – Chemical Potential

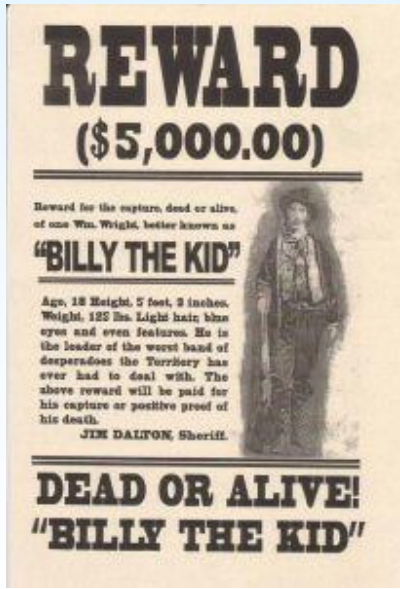


Basic Concept

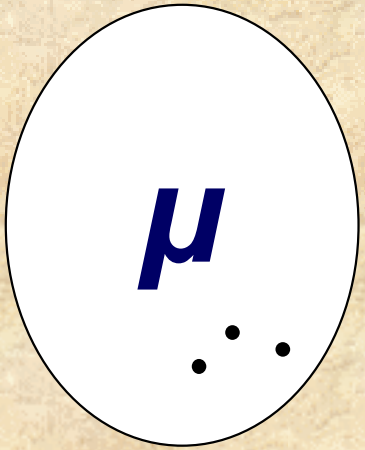
introduction of chemical potential μ in the class room *directly* as tendency to transform, i.e. without detour via other thermodynamic quantities

characterization of this tendency to transform by its most important and easily observable properties like a wanted person

phenomenological description may be supported by a direct measuring procedure

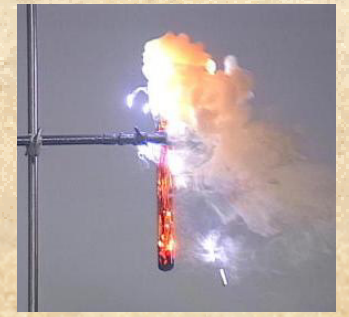


Wanted



- The tendency of a substance
  - to *react* with other substances,
  - to undergo a phase *transition*,
  - to *redistribute* in space,

  can be expressed by the same quantity – namely its chemical potential *μ*.



- The strength of this tendency, meaning the numerical value of *μ*
  - is determined by the *nature* of the substance, as well as
  - by its *milieu* (temperature, pressure, concentration, ...),
  - but not by the nature of reaction partners or the products.
- A *reaction*, *transition*, *redistribution* can only proceed spontaneously if the tendency for the process is more pronounced in the initial state than in the final state, i.e. it exists a potential drop: $\sum_{\text{initial}} \mu_i > \sum_{\text{final}} \mu_j$.

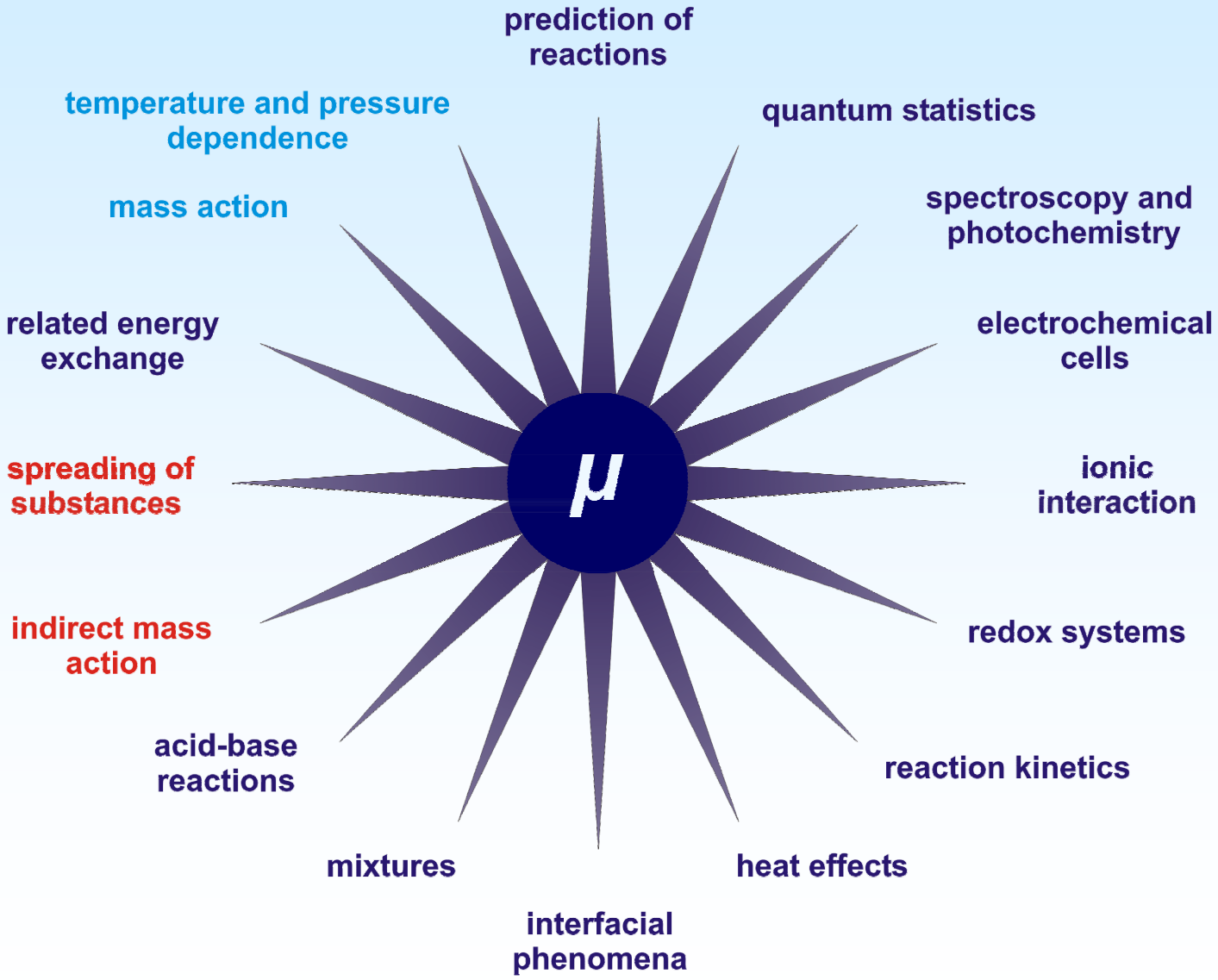
Application

proposed approach immediately leads to practical results meaning the qualitative and quantitative description of the behavior of substances

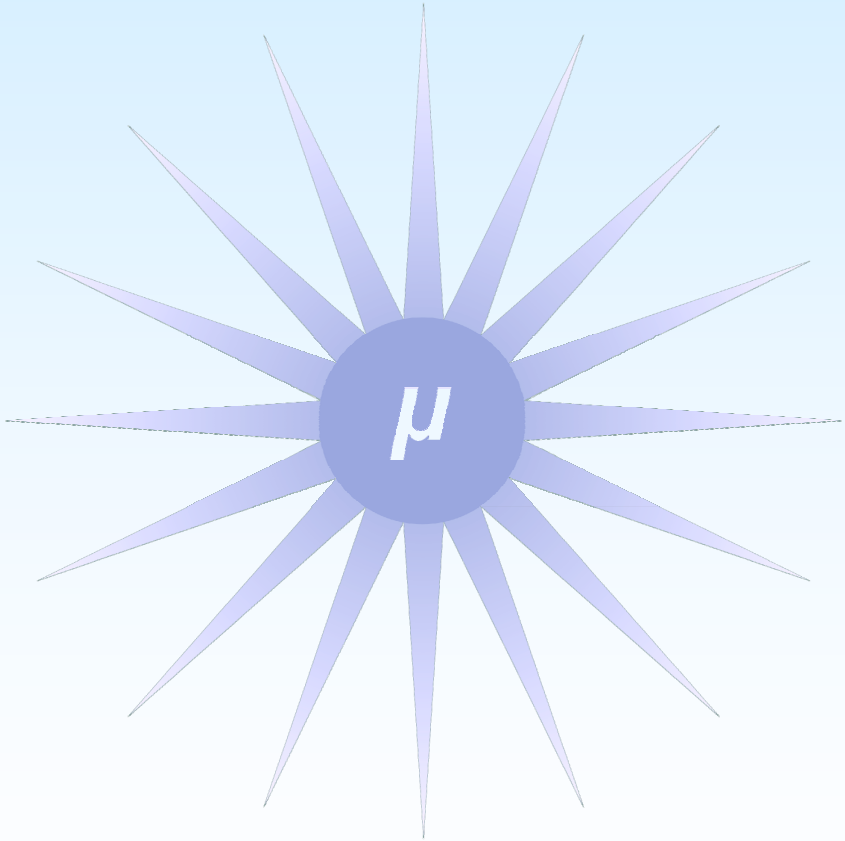
easy access allows to start teaching the subject even at introductory high school level

more than 100 selected demonstration experiments as link between textbook knowledge and everyday experiences

Chemical Potential μ as Central Concept in Chemical Dynamics



2. Influence of the Milieu



Temperature and Pressure Dependence

The numerical value of the chemical potential *μ*, as mentioned, is

- **not only determined by the *nature* of the substance, but also**
- **by its *milieu* (temperature, pressure, concentration, ...).**

A more detailed approach has to consider the *T* and *p* dependence of *μ*. Often *linear* approximations are sufficient:

$$\mu = \mu_0 + \alpha \cdot (T - T_0) \qquad \mu = \mu_0 + \beta \cdot (p - p_0)$$

μ_0: initial value

rules for *temperature coefficients α* and *pressure coefficients β* of the chemical potential of a substance B:

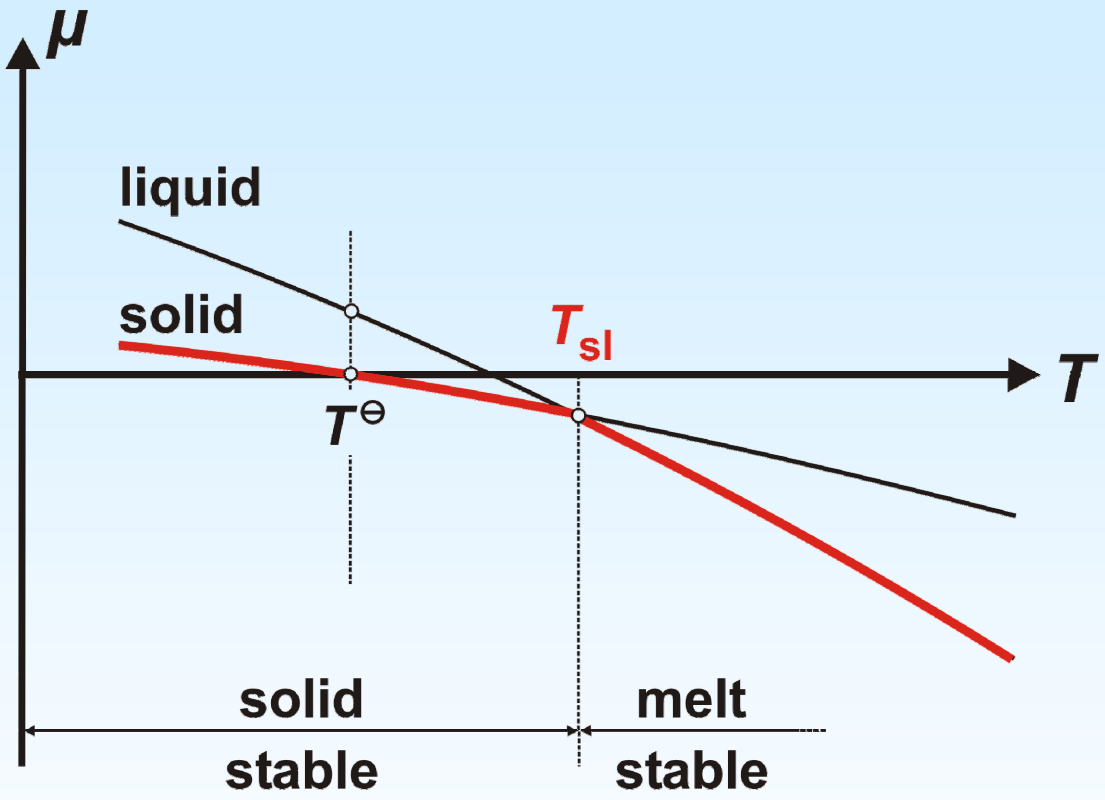
$$\alpha(\mathrm{B|g}) \ll \alpha(\mathrm{B|l}) < \alpha(\mathrm{B|s}) < 0$$

always negative!

always positive!

$$0 < \beta(\mathrm{B|s}) < \beta(\mathrm{B|l}) \lll \beta(\mathrm{B|g})$$

Melting Point



Determination of T_{sl}:

Condition for equilibrium:

$$\mu_s = \mu_l$$

Linear approach:

$$\mu_{s,0} + \alpha_s (T_{sl} - T_0) = \mu_{l,0} + \alpha_l (T_{sl} - T_0)$$

Calculation of T_{sl}:

$$T_{sl} = T_0 - \frac{\mu_{s,0} - \mu_{l,0}}{\alpha_s - \alpha_l}$$

e.g. Pb: $T_{sl} \approx 620$ K (meas. 601 K)

The chemical potentials decrease with warming and this happens more quickly in the liquid state than in the solid (α(B|l) < α(B|s) < 0).

$\Rightarrow$ The curves intersect at the *melting temperature T_{sl}*.

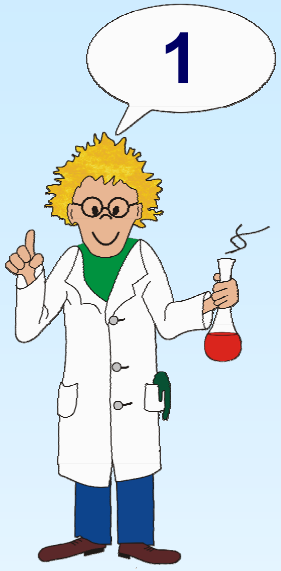
Influence of Pressure

Because of

$$0 < \beta(B|s) < \beta(B|l) <<< \beta(B|g)$$

an increase in pressure results in an increasing chemical potential, but the increase is different for the different states of aggregation with the smallest change in the solid state. Therefore, at high pressures the solid state is normally preferred compared to the others.

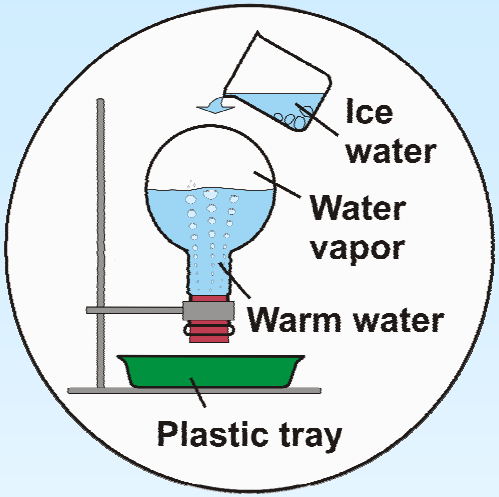
Conversely, a pressure reduction results in the preference of the gaseous state.

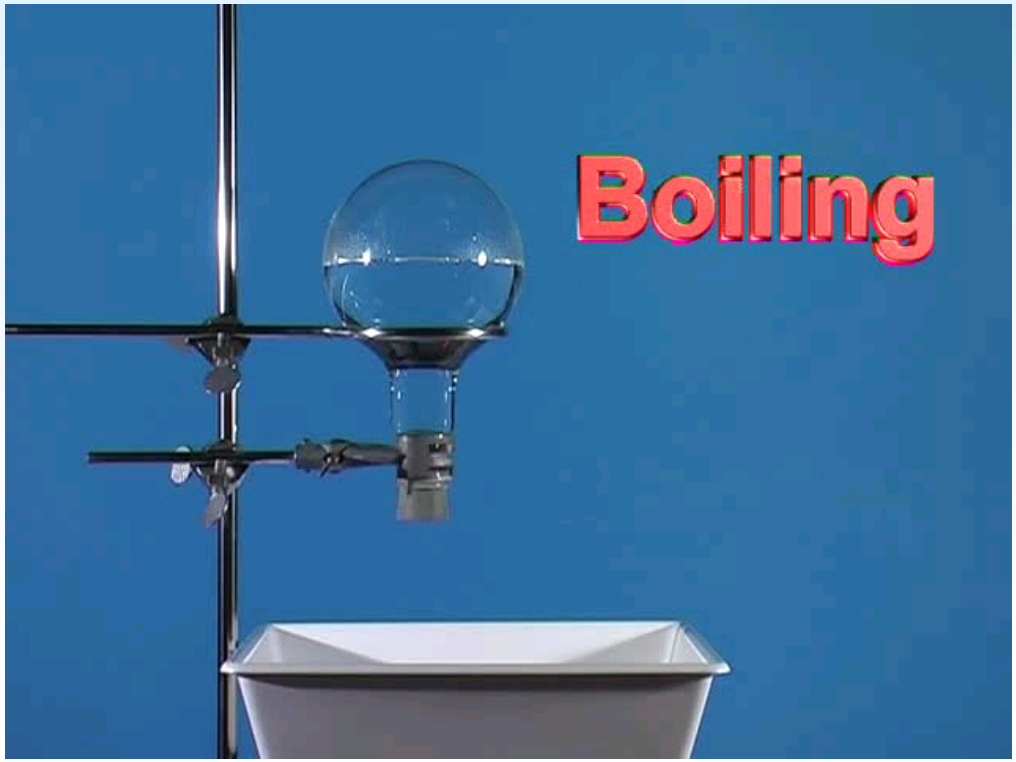


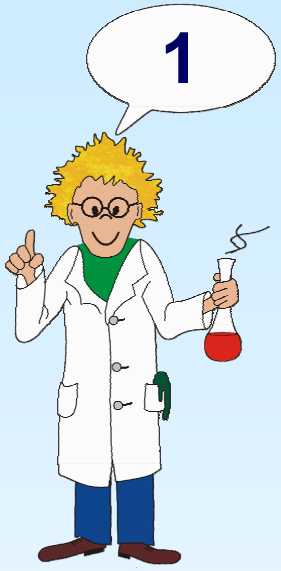
Boiling by Cooling

Procedure:

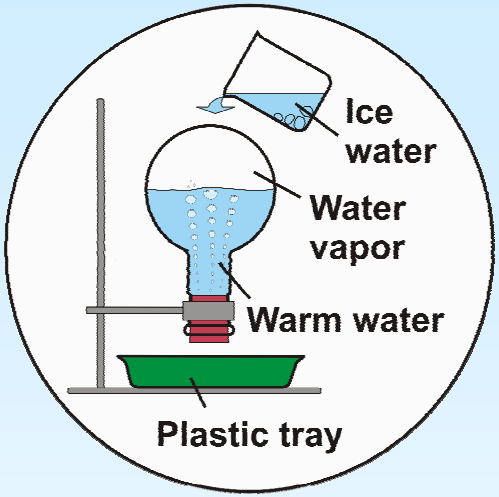
Ice water is poured over a flask filled with warm water and water vapor.







Boiling by Cooling



Procedure:

Ice water is poured over a flask filled with warm water and water vapor.

Observation:

The water begins to boil heavily.

Explanation:

The boiling process can be described by

$$H_2O|l \rightarrow H_2O|g$$

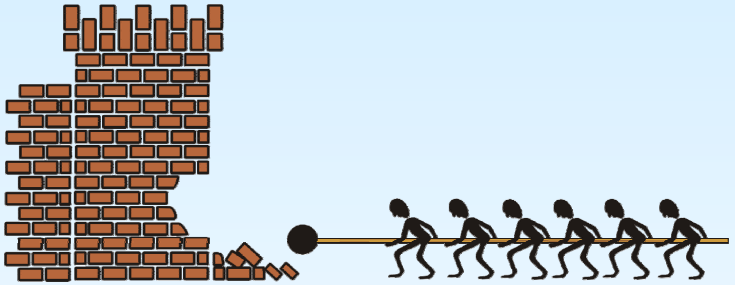
$\mu^{\ominus}$/kG	–237	<	–229
β/μG Pa^{-1}	18.1		$24.3 \cdot 10^3$

⇒ process not possible!

The chemical potential of water vapor, a gas, is strongly pressure dependent (β very large). At sufficiently low pressure (here caused by condensation of water vapor) we obtain already at temperatures much lower than 100 °C: $\mu(H_2O|l) > \mu(H_2O|g)$.

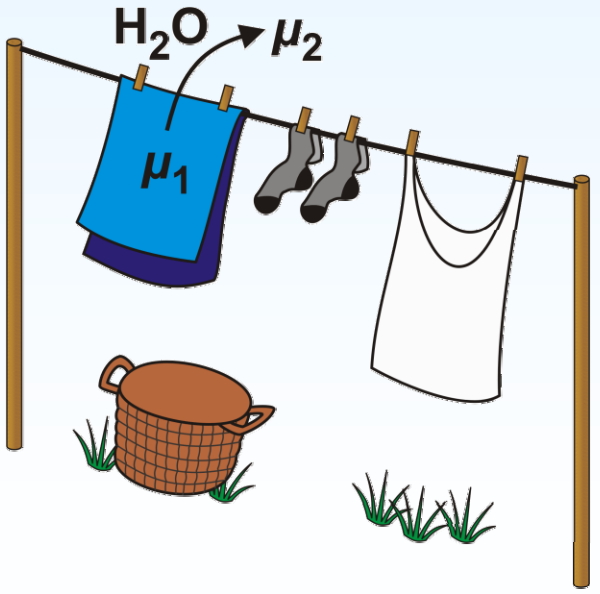
Mass Action

The tendency *μ* of substances to transform depends also on their *amounts n* or more precisely, their *concentrations c* (= *n*/*V*).



The more concentrated the application the more intense the effect.

Not the *mass* of a substance is decisive for mass action, but its "*massing*", its "density" in space, i.e. not the *amount*, but the *concentration*.



Example: *Evaporation* of water

$$H_2O|l \rightarrow H_2O|g$$

$\mu^{\ominus}$/kG –237 < –229 [G(ibbs) = J mol^{-1}]

However, if the water vapor is diluted by air, the value of its chemical potential decreases below that of liquid water.

Concentration Dependence I

If the concentration change $\Delta c = c - c_0$ is small, again a *linear* approach can be chosen:

$$\mu = \mu_0 + \gamma \cdot (c - c_0)$$

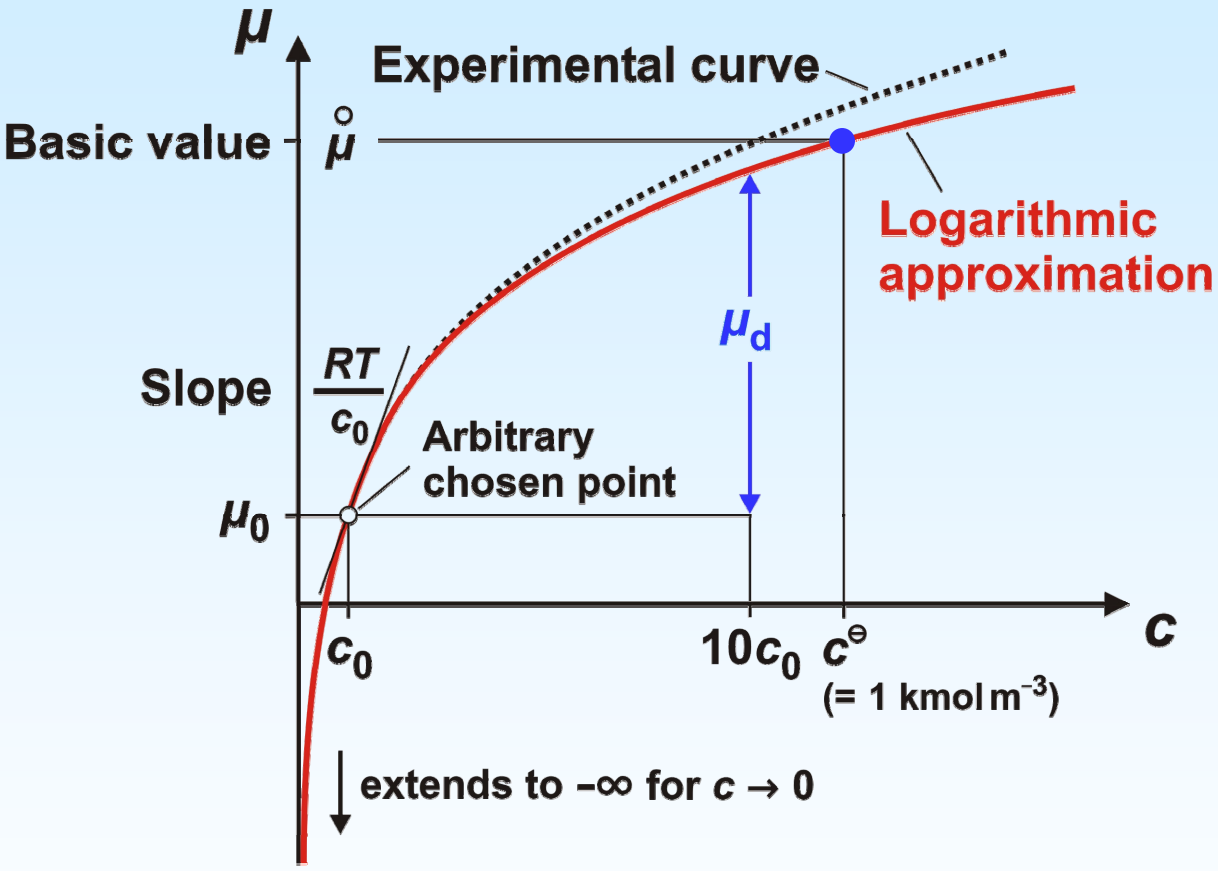
concentration coefficient γ: *universal quantity*, i.e. it is the same for all substances in every milieu (in contrast to α und β):

$$\gamma = \frac{RT}{c}$$ for small c at constant T

combination of these two relations:

$$\mu = \mu_0 + RT \ln(c/c_0) = \mu_0 + RT \ln c_r$$ *mass action equation*

Concentration Dependence II

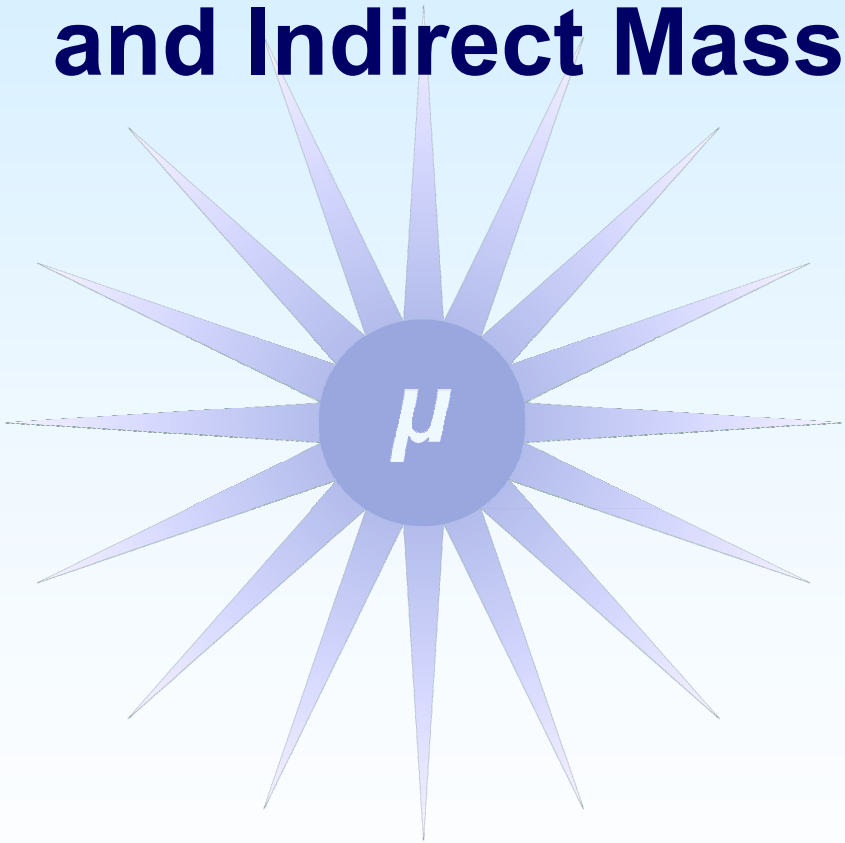


The *basic value* $\mathring{\mu}$ of the chemical potential of the dissolved substance (i.e. the value for the *standard concentration* $c^{\ominus}$ = 1 kmol m^{-3}) coincides with the logarithmic approximation and not with the measured function!

concentration *c* of a substance increases by a factor of ten

its chemical potential always increases by the same amount, the "*deca potential*" μ_d (5.71 kG ≈ 6 kG at 298 K)

3. Spreading of Substances and Indirect Mass Action



Spreading of Substances

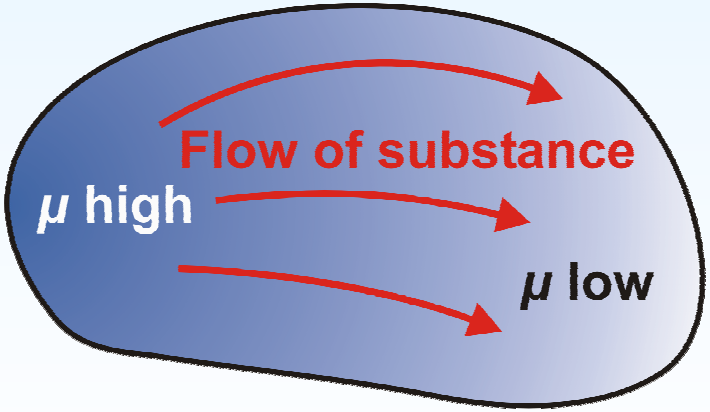
tendency to spread out in space easily noticeable in the case of strong smelling or colored substances e.g. scent of perfume or pungent odor of potent cheese

migration of a substance B considered as transformation:

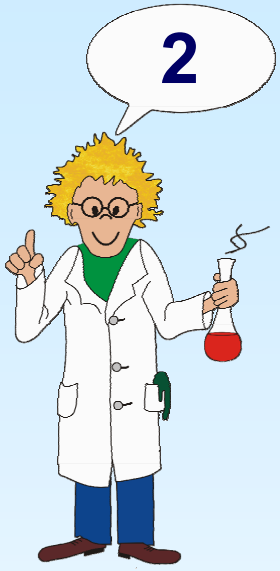
$$B|Origin \rightarrow B|Destination$$

$\Rightarrow$ transport of substances always in direction of a potential gradient, principally caused by the concentration dependence of μ:

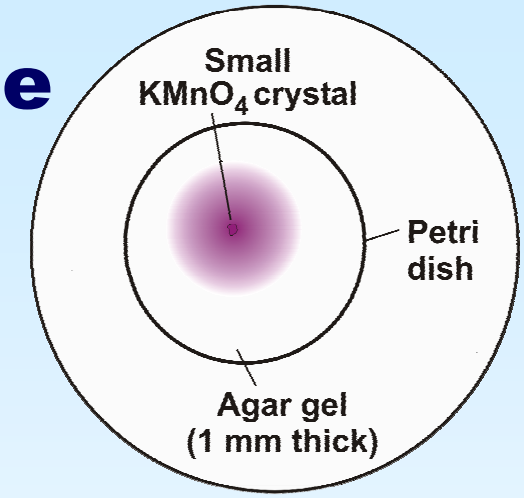
substance migrates from regions of higher concentration (μ high) into regions of lower concentration (μ low)



$\Rightarrow$ phenomenon of *diffusion*



Spreading of Potassium Permanganate



Procedure:

Small $KMnO_4$ crystals were placed on agar gel in a Petri dish.

Observation:

Immediately, a kind of red violet "halo" is formed around each crystal whose spreading can be observed easily.

Explanation:

The migration of potassium permanganate from one position to another,

$$KMnO_4|\text{Agar gel at position A} \rightarrow KMnO_4|\text{Agar gel at position B},$$

is determined by the potential gradient caused by the concentration difference.

Indirect Mass Action I

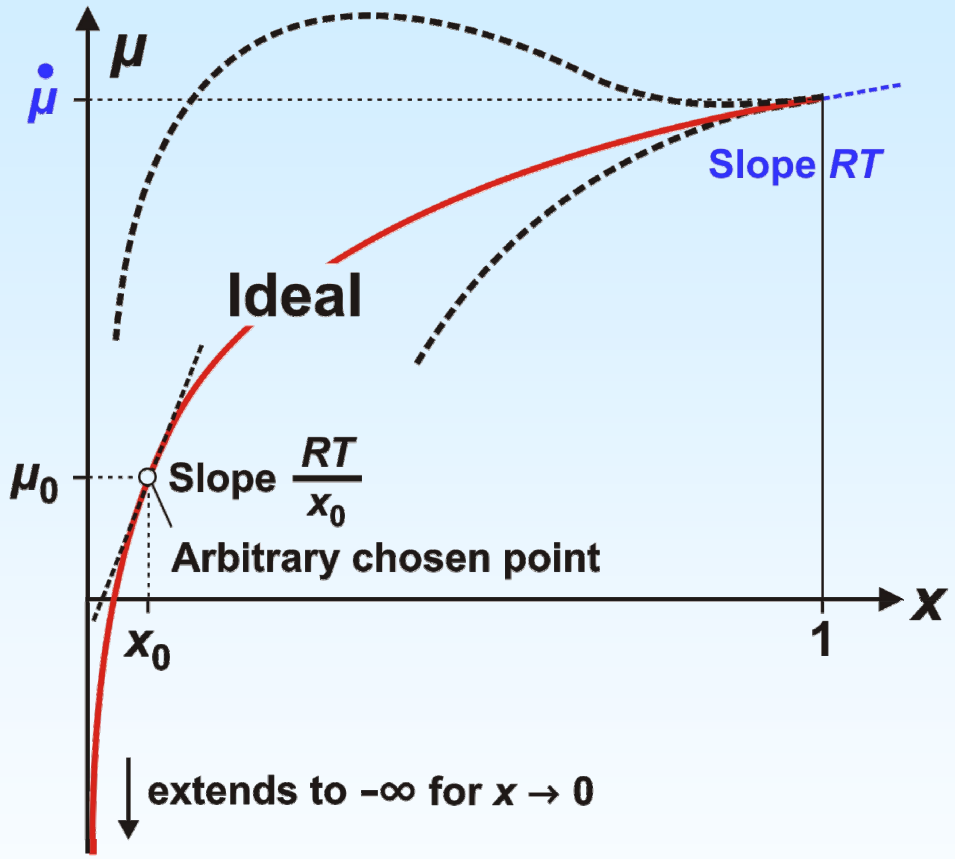
formulation of the mass action equation with the aid of *mole fraction x*:

$$\mu = \mu_0 + RT \ln(x/x_0) \qquad x, x_0 << 1$$

special case: $x_0 = 1 \Rightarrow$

$$\mu = \dot{\mu} + RT \ln x \qquad \text{for } x \to 1$$

with $\dot{\mu}$ as *basic value*, which corresponds in this case to the chemical potential of the *pure* substance



solid curve: ideal logarithmic relation

shape of curve near the point $x = 1$: all the $\mu(x)$ curves exhibit the *same slope RT*

Indirect Mass Action II

chemical potential of substance A (solvent) after addition of a small amount of foreign substance B:

$$\mu_A = \dot{\mu}_A + RT \ln x_A = \dot{\mu}_A + RT \ln(1 - x_B) \qquad \text{for } x_A \to 1$$

diluted solution: $\ln(1 - x_B) \approx -x_B$

$$\mu_A = \dot{\mu}_A - RT \cdot x_B$$

„colligative lowering of potential“

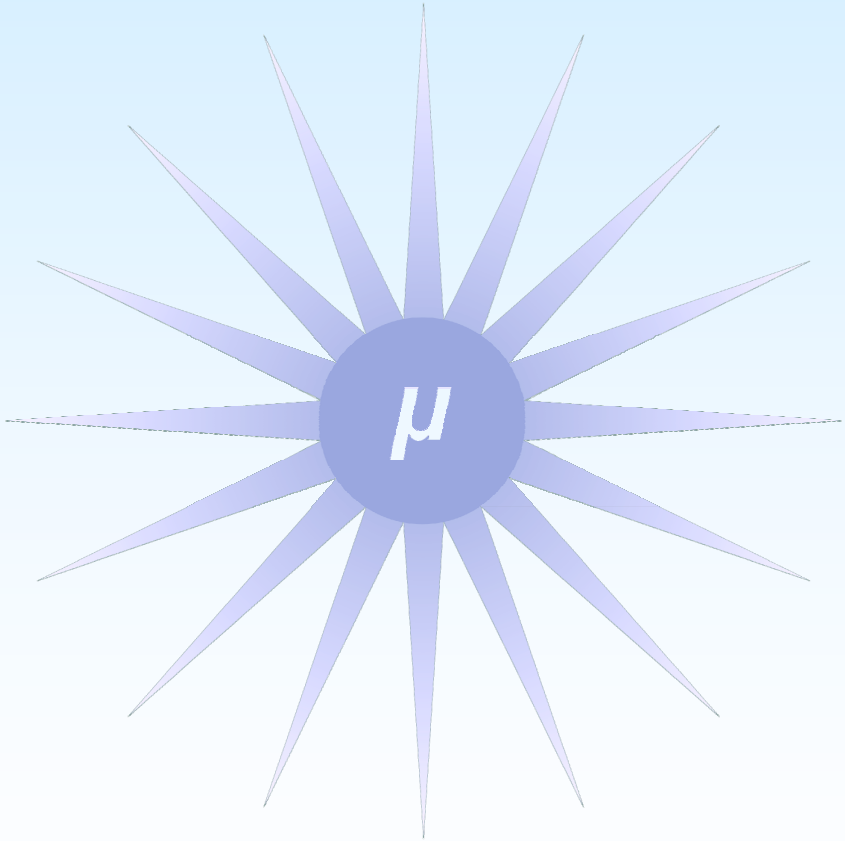
⇒ **universal law, independent of the type of substance in question**

Resulting experimentally observable effects like

- **development of osmotic pressure,**
- **freezing-point depression of the solution**

only depend from the mole fraction x_B and therefore the number of dissolved particles and not from their chemical nature (*colligative properties*).

4. Osmosis

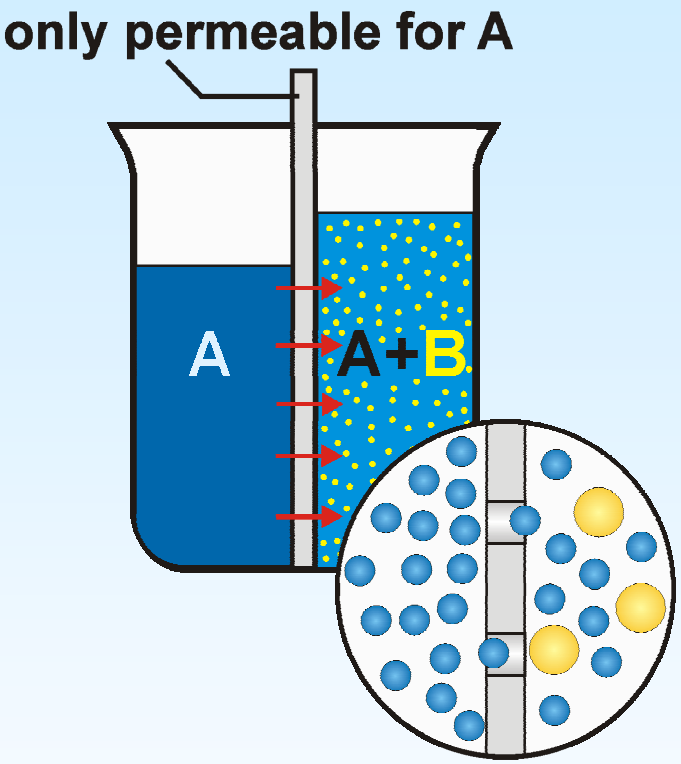


Osmosis

two solutions with different concentrations of a substance B are separated by a wall that only allows solvent A to pass through (so-called *semipermeable* membrane)

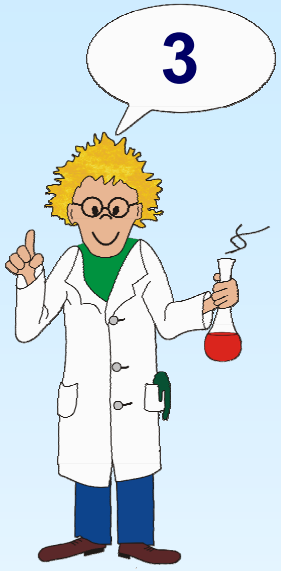
migration of solvent A according to the potential drop

A|pure → A|diluted with B

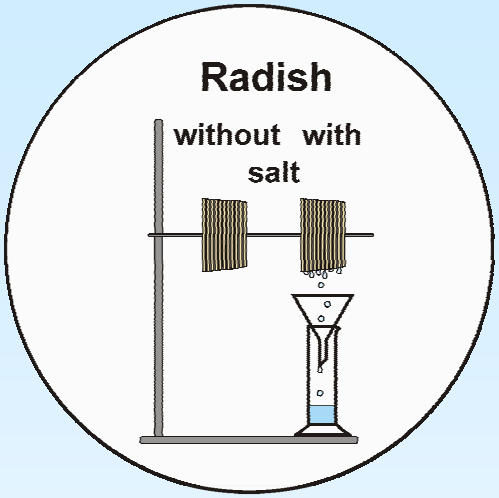


biological membranes surrounding living cells are also semipermeable

⇒ juice is “drawn out” from sugared fruit, cherries burst after a long rain



Juice “Extraction” from Slices of Salted Radish



Procedure:

Unsalted and salted slices of white radish are speared on a meat skewer.

Observation:

Immediately, juice begins to drip out of the stack with the salted slices.

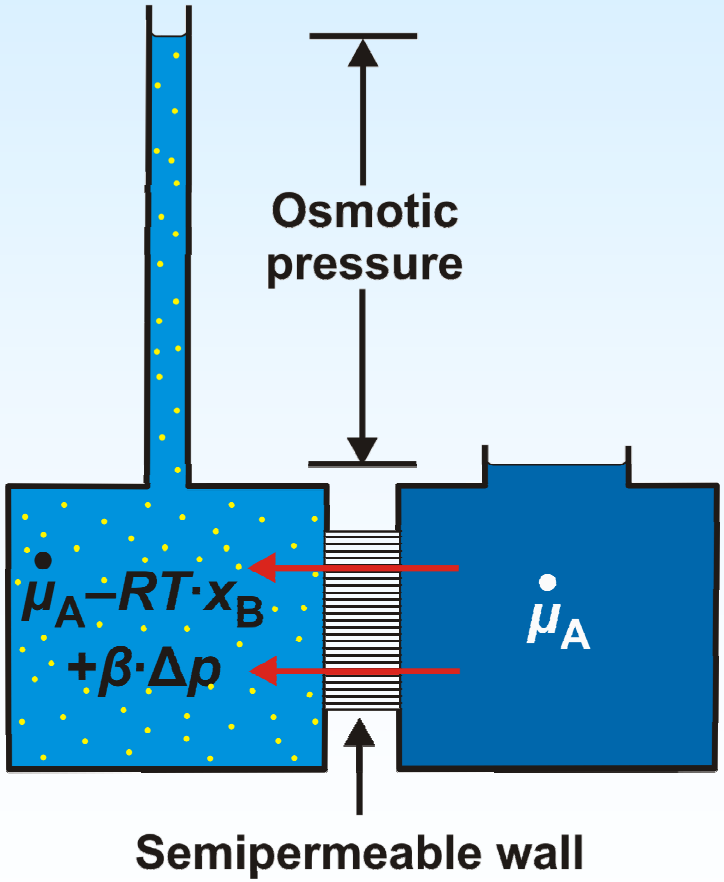
Explanation:

The solvent water migrates from the more diluted solution within the cells of the radish through the semipermeable cell membrane into the concentrated, therefore water-poor, salt solution on the outside.

Osmotic Cell

potential drop of solvent A:

$$\mu_A = \dot{\mu}_A - RT \cdot x_B \qquad \text{for } x_B << 1$$



suppression of inflow of solvent by increasing the pressure on the solution

$\Rightarrow$ *osmotic equilibrium*

$$\dot{\mu}_A - RT \cdot x_B + \beta \cdot \Delta p = \dot{\mu}_A$$

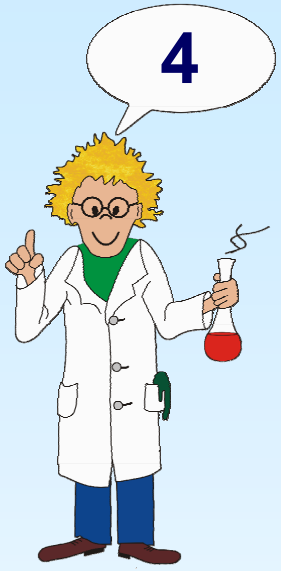
$$\Delta p = p_{osm} = \frac{RT}{\beta} x_B \qquad \textit{osmotic pressure}$$

$x_B = n_B/(n_A+n_B) \approx n_B/n_A$ (because $n_B << n_A$ in dil. sol.) and $\beta = V_{m,A} = V_A$ and $V \approx n_A \cdot V_A$

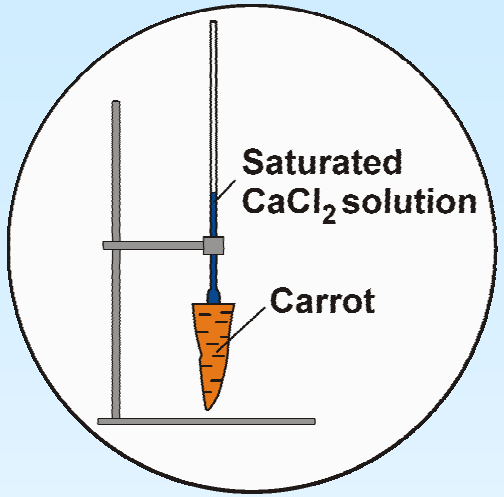
$$p_{osm} = \frac{RT}{V_A} \cdot \frac{n_F}{n_A}$$

$$p_{osm} = n_F \frac{RT}{V}$$

VAN´T HOFF



Osmotic Cell



Procedure:

A colored saturated $CaCl_2$ solution is filled into the hollowed carrot and a riser pipe is attached.

Observation:

After a short time, one observes a continuous rise of the solution in the riser pipe.

Explanation:

The solution in the cavity is more strongly concentrated and the solvent therefore more diluted than in the cells of the carrot. Because of the corresponding potential drop solvent flows through the semipermeable cell membrane into the salt solution. As result the liquid begins to rise in the riser pipe.

Osmosis and its Effects

$$p_{osm} = n_F \frac{RT}{V} = c_F RT$$ *VAN´T HOFF equation*

c_F: *osmotic concentration*: sum of concentrations of *all* types of particles

equation very similar to *general gas law*

Sample calculation:

solution of an arbitrary non-electrolyte with a concentration of 0.1 kmol m^{-3} at room temperature (T = 298 K)

$\Rightarrow$ osmotic pressure of 250 kPa (= 2.5 bar)

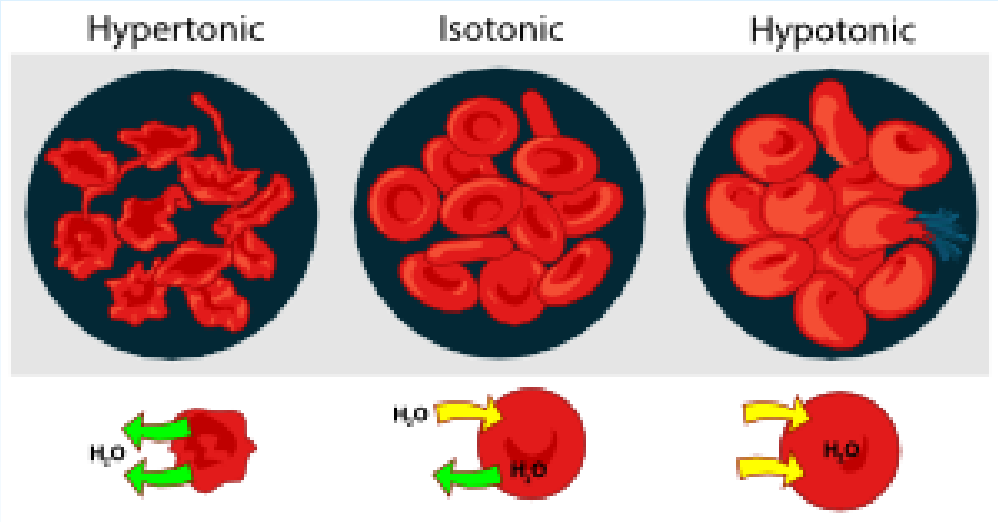
$\Rightarrow$ enough to raise the column of liquid more than 25 m

Osmotic phenomena play an essential role in biological processes. They have a great importance for the *balance of water in living organisms* and influence the form of their cells.

Red Blood Cells

osmotic concentration c_F of cell liquid in human red blood cells, for example, is approx. 300 mol m^{-3}

$\Rightarrow p_{osm} \approx 300\ \text{mol m}^{-3} \cdot 8.3\ \text{J mol}^{-1}\text{K}^{-1} \cdot 310\ \text{K} = 770\ \text{kPa}$ for body temp.



red blood cells in water:

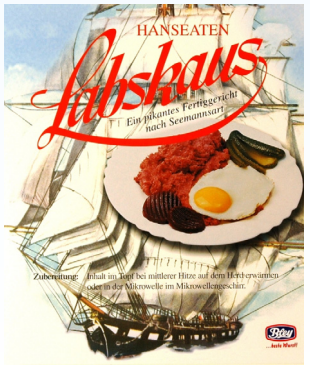
cells swell up and finally burst

same osmotic pressure inside the red blood cells and the surrounding solution (e.g. blood plasma):

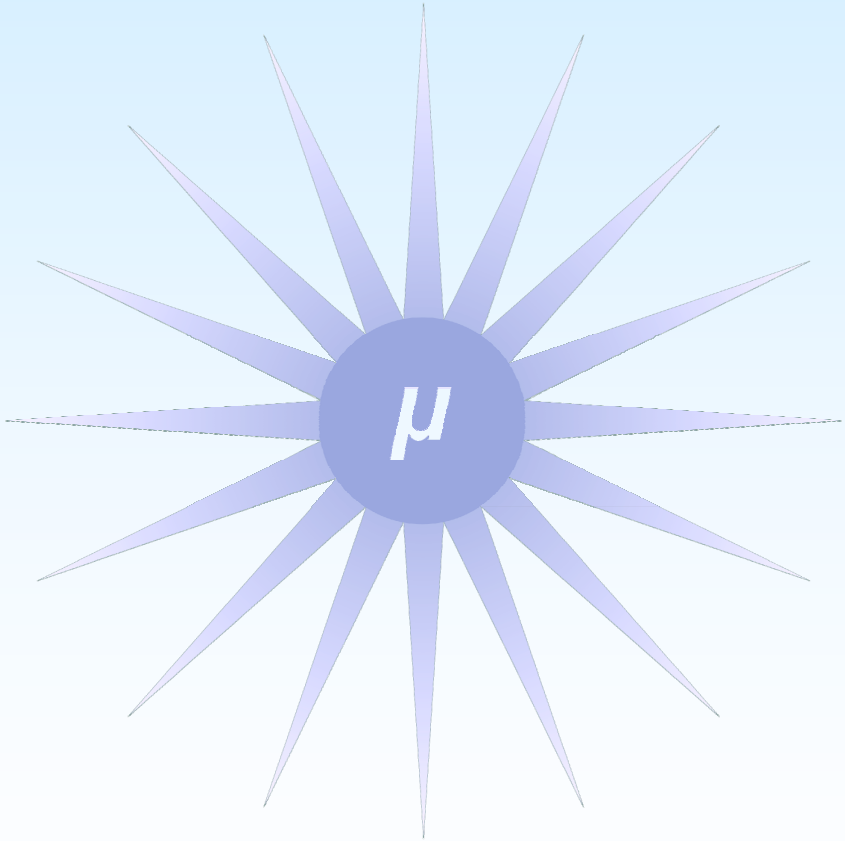
cells keep their shape

solutions where the water content of the cells remains constant (same $\mu(H_2O)$ inside and outside) called *isotonic*

cell damaging effect of conc. saline solutions used to preserve food (salting of meat)



5. And more ...

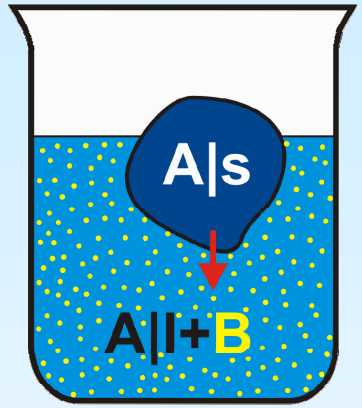


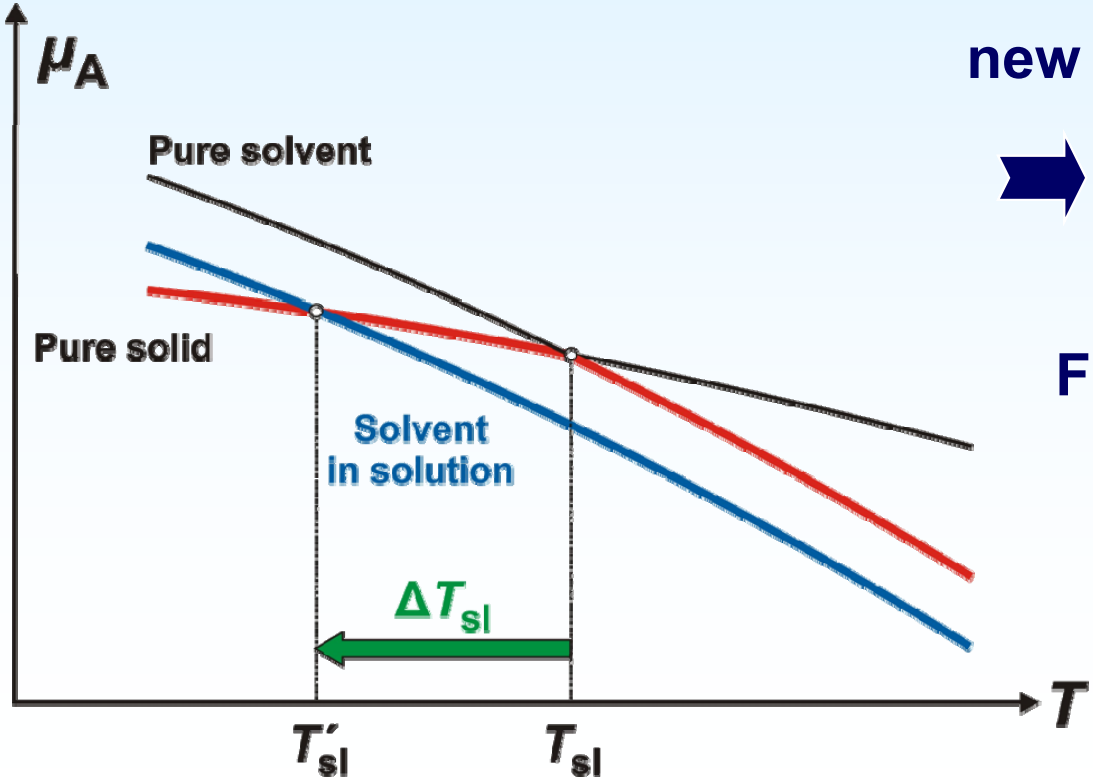
Freezing-Point Depression

at freezing point T_{sl} of pure liquid A, chemical potentials for liquid and solid state just equal ($\dot{\mu}_{A|l} = \dot{\mu}_{A|s}$)

dissolution of a foreign substance in the liquid phase reduces the chemical potential of the latter

$\Rightarrow$ solid phase begins to melt





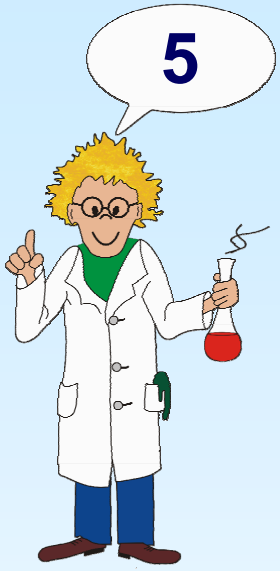
new equilibrium: $\mu_{A|l} = \mu_{A|s}$

$$\dot{\mu}_{A|l} - RT_{sl} \cdot x_B + \alpha_{A|l} \cdot \Delta T = \dot{\mu}_{A|s} + \alpha_{A|s} \cdot \Delta T$$

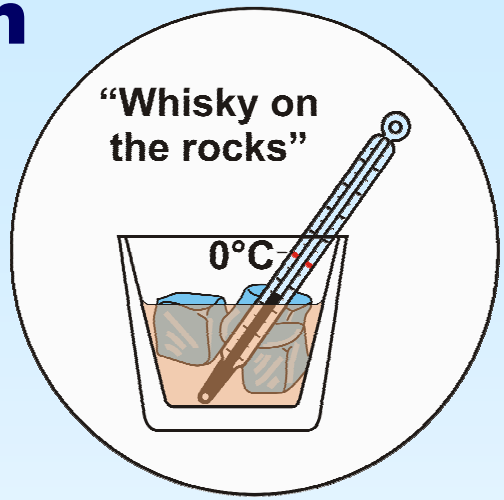
Freezing-point depression:

$$\Delta T_{sl} = \frac{RT_{sl} \cdot x_B}{\alpha_{A|s} - \alpha_{A|l}} \qquad \Delta T_{sl} < 0!$$

$\alpha = -S_m$: $\Delta T_{sl} = -\dfrac{RT_{sl} \cdot x_B}{\Delta_{sl} S_A}$



Freezing-Point Depression



Procedure:

Alcohol (ethanol) is poured over ice in a glass.

Observation:

After adding alcohol, the mixture becomes noticeably colder than 0 °C.

Explanation:

If a foreign substance (ethanol) is dissolved in a liquid phase (water), the chemical potential of this phase decreases so that it falls below that of the solid phase (ice) which then begins to melt. Therefore, the entire mixture cools down and the chemical potentials rise due to their negative temperature coefficients, but varyingly strong. This causes the potential gradient to dissappear again at a certain lower temperature and the melting process stops at this new freezing point.

Determining Molar Mass

effects related to the dissolution of a foreign substance B depend solely upon its mole fraction and therefore the number of dissolved particles, but not upon its chemical nature

➡ **determination of molar mass of substance B**

$$x_B \approx n_B/n_A = \frac{m_B}{M_B} \Big/ \frac{m_A}{M_A}$$

sensitivity of measuring methods:

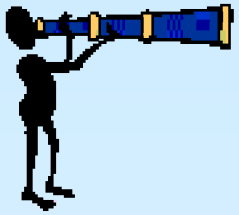
aqueous solution of cane sugar (0.01 mol kg^{-1})

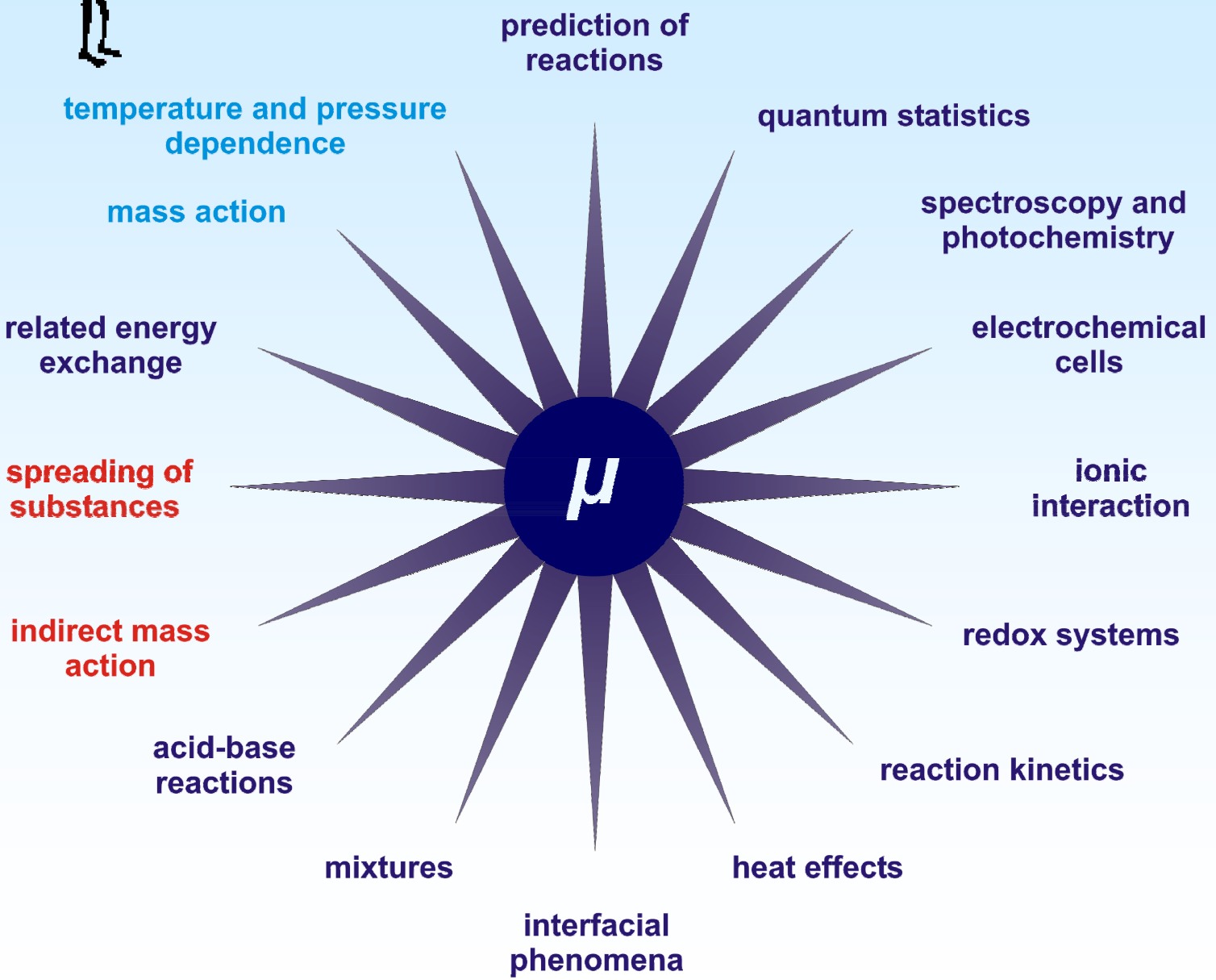
freezing-point depression: 0.02 K,

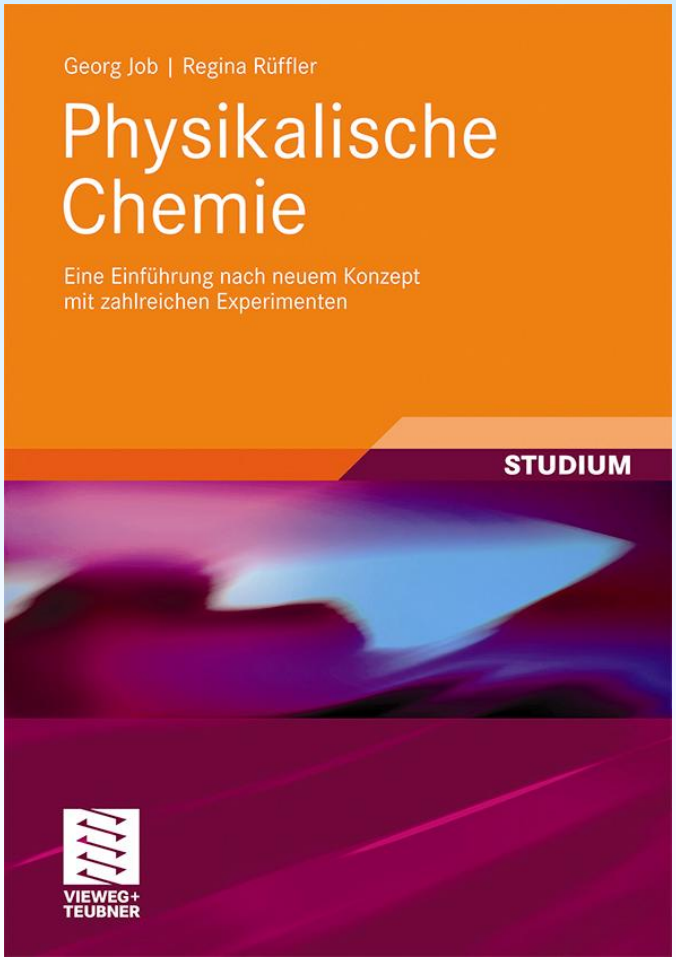
osmotic pressure: 25 kPa (0.25 bar)

use of osmometry for the investigation of macromolecular substances such as synthetic polymers, proteins or enzymes

Outlook




prediction of reactions
quantum statistics
spectroscopy and photochemistry
electrochemical cells
ionic interaction
redox systems
reaction kinetics
heat effects
interfacial phenomena
mixtures
acid-base reactions
indirect mass action
spreading of substances
related energy exchange
mass action
temperature and pressure dependence
μ



Georg Job, Regina Rüffler

Physical Chemistry From a Different Angle

An Introduction with New Concept and Numerous Experiments

published in English by Springer at the beginning of 2014

Thank you very much for your friendly attention.

Further information
(lecture notes, descriptions of experiments, videos etc.):

www.job-foundation.org