The "Secrets" of Mixtures

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Homogeneous and Heterogeneous Mixtures

Not only in chemistry but also in everyday life we are permanently confronted with mixtures be they homogeneous or heterogeneous.

hard liquor: basically *homogeneous* mixture of ethanol and water

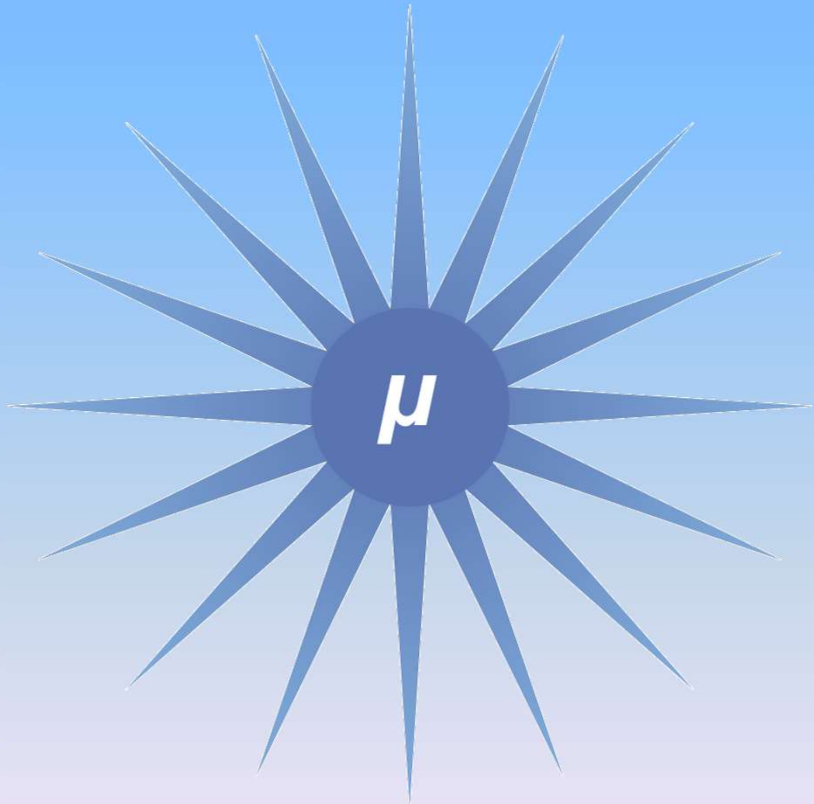
***demonstration experiment*: homemade “lava lamp”: *heterogeneous* mixture of (colored) water and vegetable oil, addition of pieces of fizzy tablets**

But why do certain mixtures split up when others do not 

Outline

1. Introduction—Chemical Potential
2. Influence of the Milieu
3. Chemical Potential **in** Mixtures
4. Chemical Potential **of** Mixtures
5. More “Secrets” of Mixtures
6. Outlook

1. Introduction—Chemical Potential



Introduction

The benefit of chemical thermodynamics is beyond question but the field is reputed to be difficult to learn. One of its most important fundamental quantities, the ***chemical potential μ***, commonly defined as the partial derivative

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{p,T}$$

of a quantity which involves energy and entropy, seems especially hard to grasp.

Chemical Potential as Basic Concept

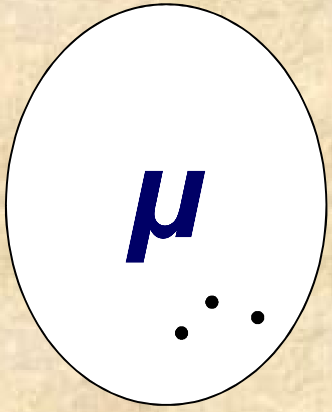
However, there is a simpler and faster way to an understanding of this quantity that does not make use of higher mathematics.

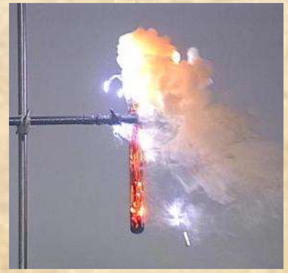
$$\cancel{\mu = \left(\frac{\partial G}{\partial n}\right)_{p,T}}$$

We propose to introduce μ as "*tendency to transform*" that is firstly characterized by its typical and easily observable properties, i.e. by designing a kind of "wanted poster" for this quantity.

The phenomenological definition is followed by a direct measuring procedure, a method that has long been used for various basic quantities such as mass.

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 <u>not</u> 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**

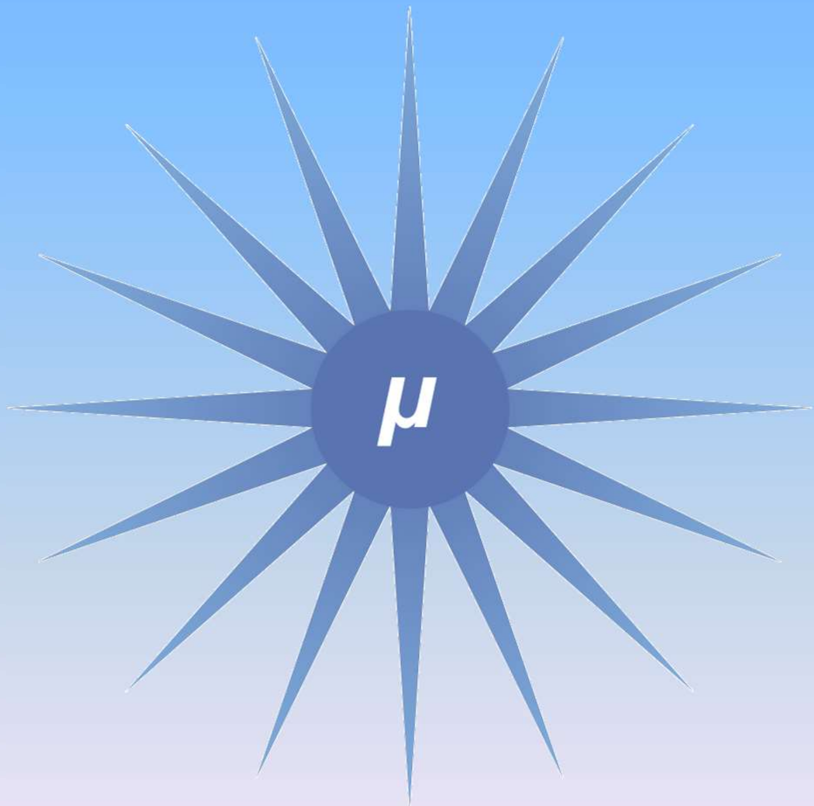
potential drop: $$\sum_{\text{initial}} \mu_i > \sum_{\text{final}} \mu_j \,.$$

Application

The proposed approach is elementary, does not require any special previous knowledge and immediately leads to results that can be utilized practically. This allows to start teaching the subject even at introductory high school level.

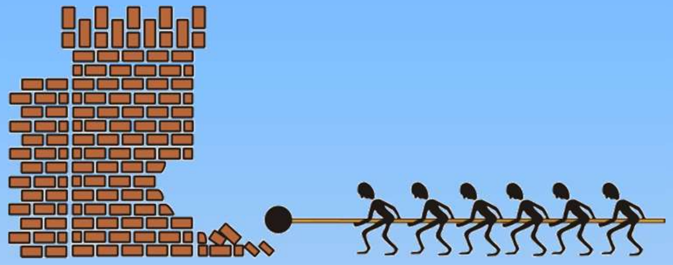
Numerous simple and safe demonstration experiments contribute essentially to deepen comprehension and forge links with everyday experiences.

2. Influence of the Milieu



Mass Action

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

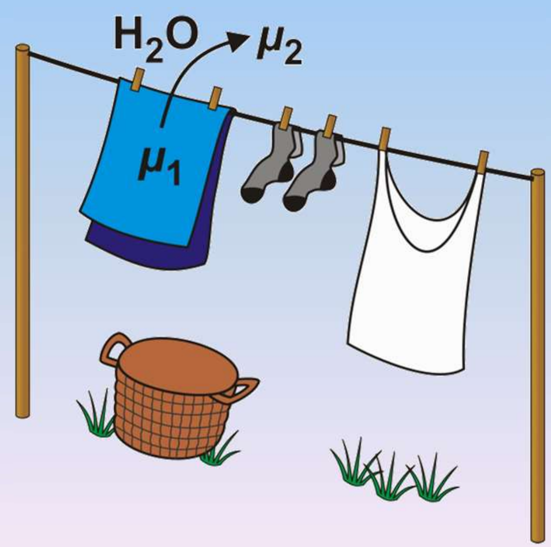


The more concentrated the action the more intense the effect.

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, a *linear* approach can be chosen:

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

μ_0: initial value of the chemical potential at the concentration c_0

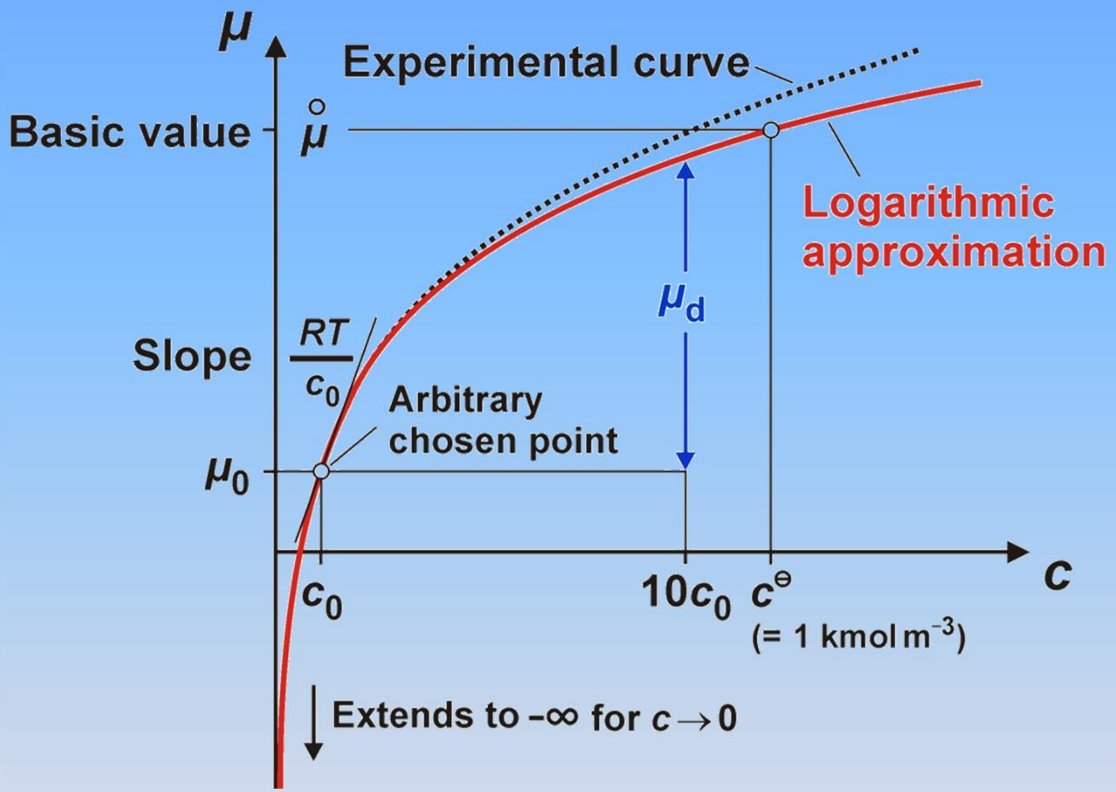
***concentration coefficient* γ: *universal quantity*, i.e. it is the same for all substances in every milieu:**

$$\gamma = \frac{RT}{c}$$ **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

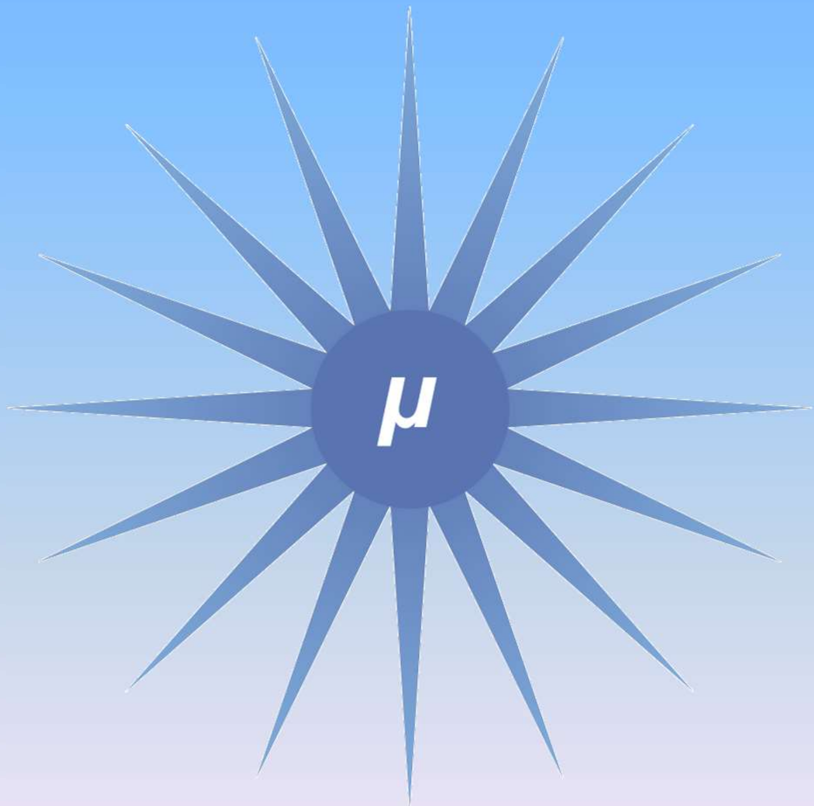


The *basic value* $\overset{\circ}{\mu}$ of the chemical potential of the dissolved substance (i.e. the value for the *standard concentration* $c^{\ominus}$ = 1 kmol m^{-3}) coincides with the logarithmic approximation and not with the measured function!

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

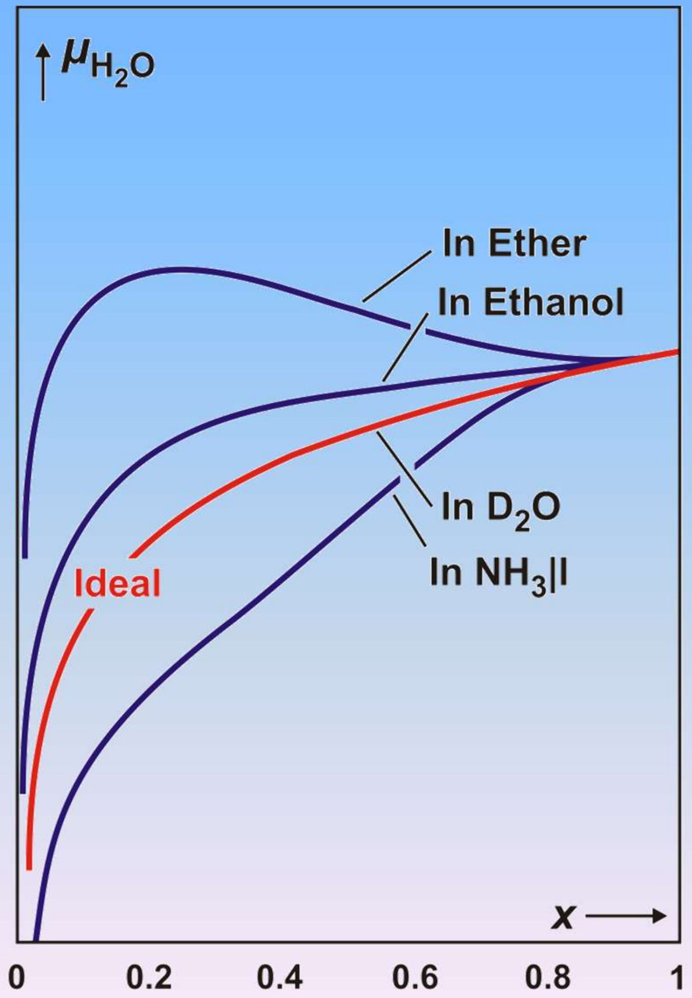
its chemical potential always increases by the same amount, the "*deca potential*" μ_d (5.71 kG ≈ 6 kG at 298 K)

3. Chemical Potential in Mixtures



Chemical Potential in Mixtures I

Chemical potential of water in various mixtures:



all $\mu(x)$ curves show the same slope *RT* in the vicinity of $x = 1$

formulation of the mass action equation by means of *mole fraction x*:

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

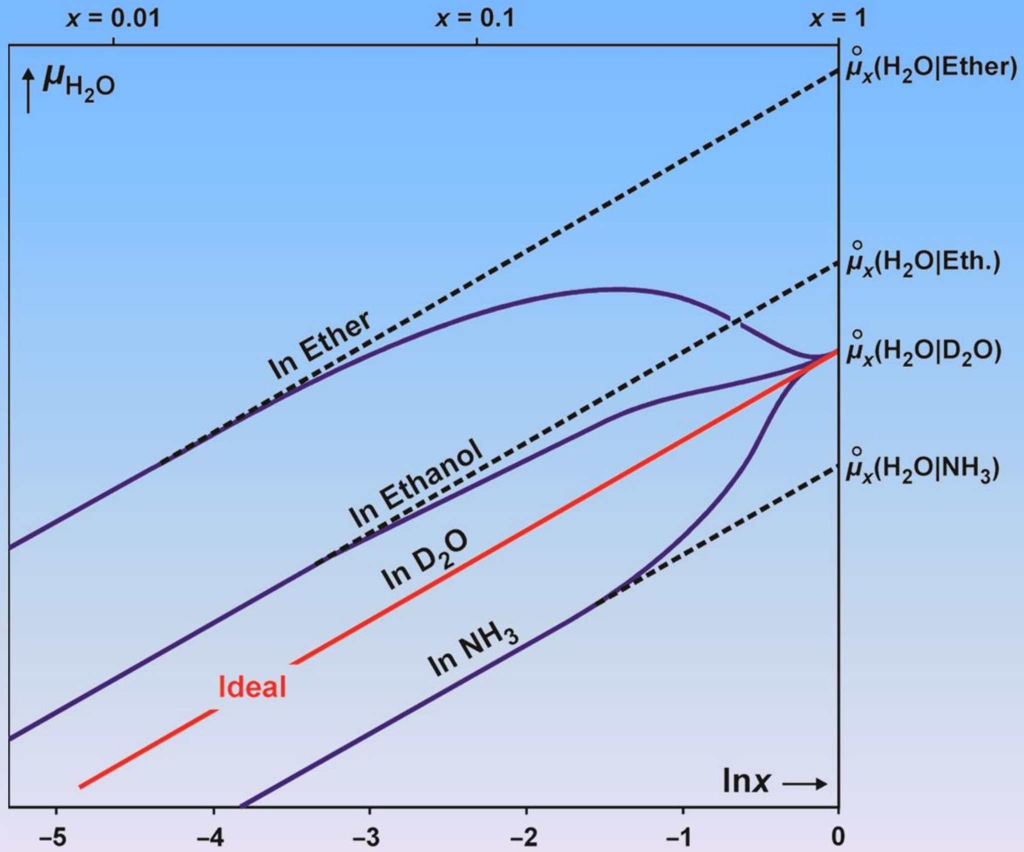
special case: $x_0 = 1 \Rightarrow$

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

$\mathring{\mu}$: *basic value*, here chemical potential of the *pure* substance (H_2O in the presented example)

Chemical Potential in Mixtures II

Chemical potential of water in various mixtures:



all $\mu(x)$ curves also show the *same slope RT* at low mole fractions, differing only in the intercepts on the *y*-axis

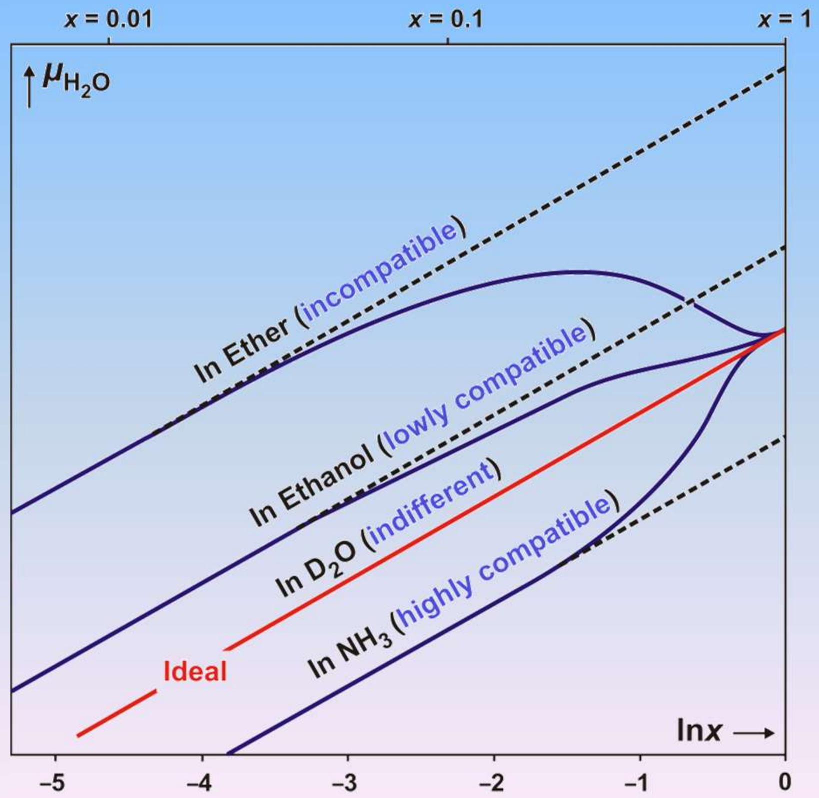
$$\mu = \overset{\circ}{\mu}_x + RT \ln x \quad \text{for small } x$$

$\overset{\circ}{\mu}_x$(B|A): *basic value*, here for a hypothetical state in which the interactions of the substance molecules (B; here H_2O) with the solvent molecules (A; here ether etc.) determine the outcome

Compatibility of Substances

between the limits near x = 1 as well as x = 0 the form of the functions varies noticeably

potential difference between $\overset{\circ}{\mu}_x(\mathrm{B|A})$ and $\overset{\bullet}{\mu}(\mathrm{B})$ measure for *compatibility* of B with A



the higher the value $\overset{\circ}{\mu}_x(\mathrm{B|A})$ lies *above* $\overset{\bullet}{\mu}(\mathrm{B})$ the stronger the tendency of B to separate from A

***lowly compatible*: they do not yet separate from each other**

***incompatible*: they do**

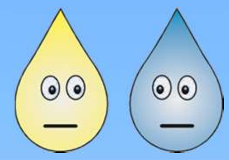
value of $\overset{\circ}{\mu}_x(\mathrm{B|A})$ *beneath* that of $\overset{\bullet}{\mu}(\mathrm{B})$: *highly compatible*

$\overset{\circ}{\mu}_x(\mathrm{B|A}) = \overset{\bullet}{\mu}(\mathrm{B})$: *indifferent*

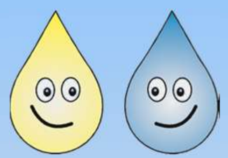
Chemical Background

varying behavior of mixtures due to different interactions of the components A and B at their molecular levels

attraction between particles of different types A and B equal to average attraction between particles of the same type (A and A or B and B) (e.g. H_2O/D_2O)



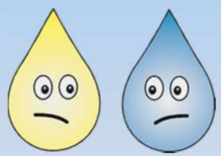
indifferent



highly compatible

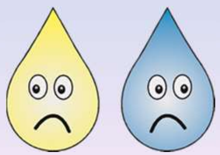
attraction between particles A and B stronger than that between the different types of particles themselves (e.g. H_2O/NH_3)

attraction between particles A and B weaker than that between the different types of particles themselves (e.g. H_2O/Ethanol)



lowly compatible

Special case: Demixing (e.g. H_2O/Ether)



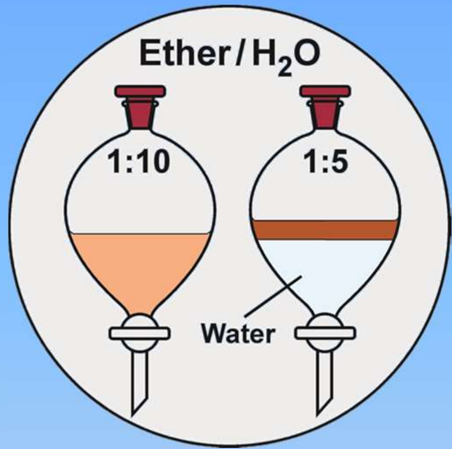
incompatible

Mixing of Ether with Water

Procedure and Observation:

A small amount of ether—colored brown with iodine—is added to water in a separatory funnel. Then, the funnel is shaken.

A homogeneous brownish colored solution results.



Subsequently, the same amount of ether is added once more and the funnel is shaken again.

A brown ether layer on top of the water layer is formed.

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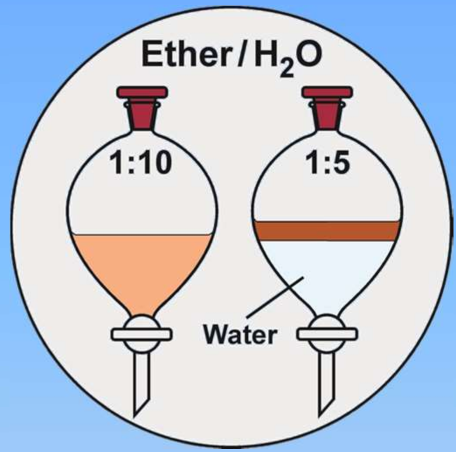


Subsequently, the same amount of ether is added once more and the funnel is shaken again.

A brown ether layer on top of the water layer is formed.

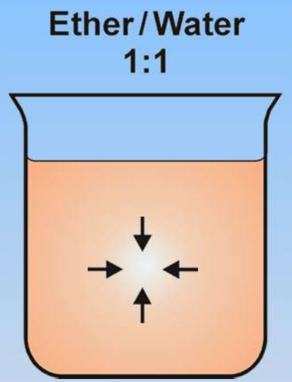
Explanation:

If only a small amount of ether is added to water, a homogeneous solution results. However, when the ratio of ether to water is 1:5, the ether separates as a brown layer on top of the water because water can only tolerate about 10 % of its own volume in ether.

Demixing of Ether-Water

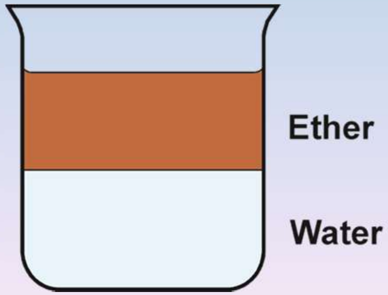
as long as one of the substances is added in very small amounts, it will always be tolerated; the situation can become critical when the amount is increased

Example: Demixing of a 1:1 mixture of ether and water



tiny arbitrary accumulation of H_2O molecules lowers the chemical potential μ of the water there

additional H_2O molecules migrate into this spot

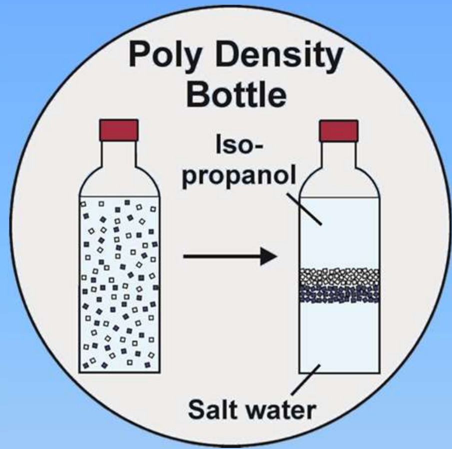


Final result:
water-poor lighter brown layer on top
water-rich heavier layer below

Poly Density Bottle

Procedure:

After shaking the bottle, the system is allowed to settle.



https://www.facebook.com/watch/?v=310817875948833

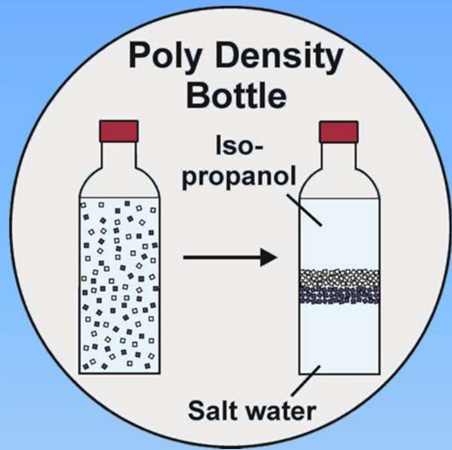
Poly Density Bottle

Procedure:

After shaking the bottle, the system is allowed to settle.

Observation:

First, the white beads rise to the top while the blue ones sink to the bottom. Then, they move slowly to the middle.



Explanation:

The alcohol and the salt water in the bottle are immiscible. When the bottle is shaken, the two liquids temporarily mix and form an emulsion.

Relative densities of all materials in the bottle:

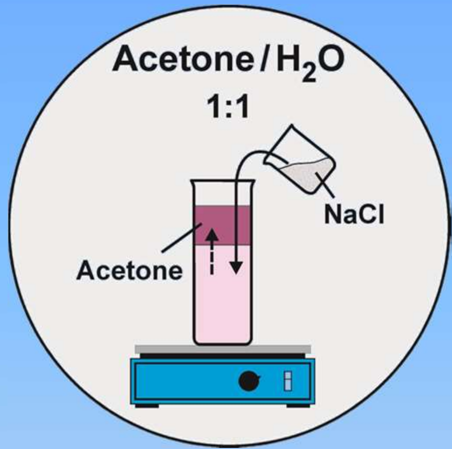
salt water > blue beads > emulsion > white beads > isopropanol

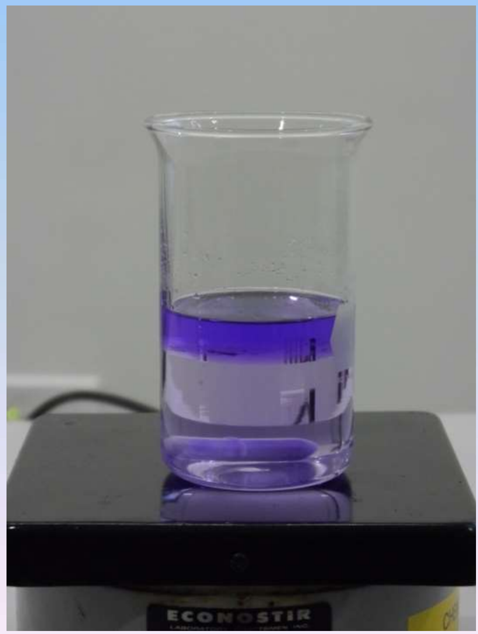
Thus, the white beads float on top and the blue ones sink to bottom. As the separation of the emulsion progresses, the layers of beads move with the liquid-liquid interfaces from both sides to the middle.

Demixing of Acetone-Salt Water

Procedure:

Sodium chloride is added to a homogeneous mixture of acetone and water colored pale purple by some methyl violet.





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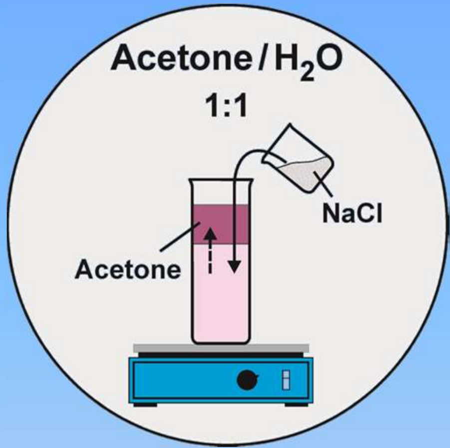


Observation:

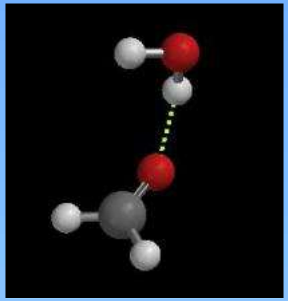
A deep purple acetone layer on top of a pale purple water layer is formed.

Explanation:

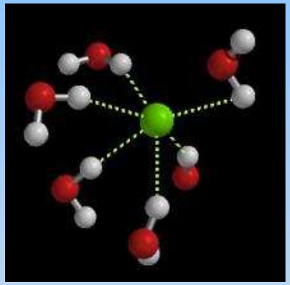
The compatibility and hence the miscibility of the components acetone and water is obviously influenced by the addition of the salt. This "salting out" technique can be used, for example, to remove organic molecules from an aqueous solution.

Demixing of Acetone-Salt Water

Acetone and pure water are completely miscible due to the formation of hydrogen bonding interactions between the oxygen atom of acetone molecules and the O-H bond of water molecules.



from Tom Kuntzleman



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When the salt is added to the mixture, the resulting Na^+ and Cl^- ions interact very strongly with the water molecules through ion-dipole forces.

These ion-dipole interactions are much stronger than the acetone-water hydrogen bonds.

As a result, the acetone molecules are forced out of the aqueous phase and two layers are formed: a less dense acetone layer on top and a salt water layer at the bottom.

Extra Potential

ideal case for the potential μ of a substance in a homogeneous mixture:

$$\mu = \overset{\bullet}{\mu} + RT\ln x \qquad \text{for } 0 \le x \le 1$$

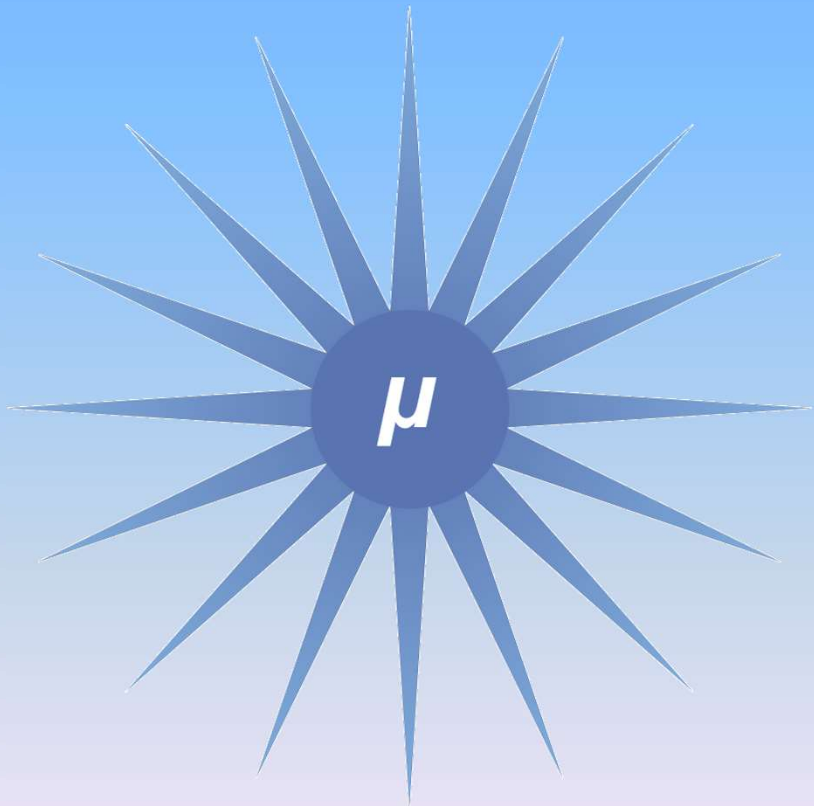
deviations from this simple mass action equation corrected by addition of an *extra potential* $\overset{+}{\mu}$:

$$\mu = \overset{\bullet}{\mu} + RT\ln x + \overset{+}{\mu}(x)$$

for strongly diluted substances:

$$\mu = \underbrace{\overset{\bullet}{\mu} + \overset{+}{\mu}_0}_{\overset{\circ}{\mu}_x} + RT\ln x \qquad \text{for small } x$$

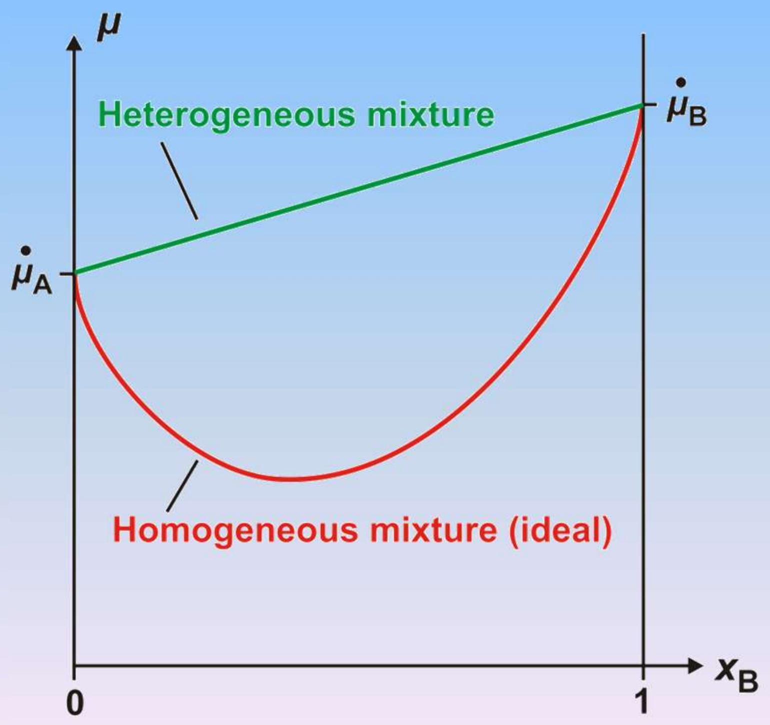
4. Chemical Potential of Mixtures



Chemical Potential of Mixtures

Just as in the case of pure substances, an (average) chemical potential μ_{ave} can be assigned to a mixture of two components A and B with the mole fractions x_A and x_B:

$$\mu_{ave} = x_A \mu_A + x_B \mu_B$$



Homogeneous mixture M (ideal):

$$\mu_M = x_A \overset{\bullet}{\mu}_A + x_B \overset{\bullet}{\mu}_B + RT(x_A \ln x_A + x_B \ln x_B)$$

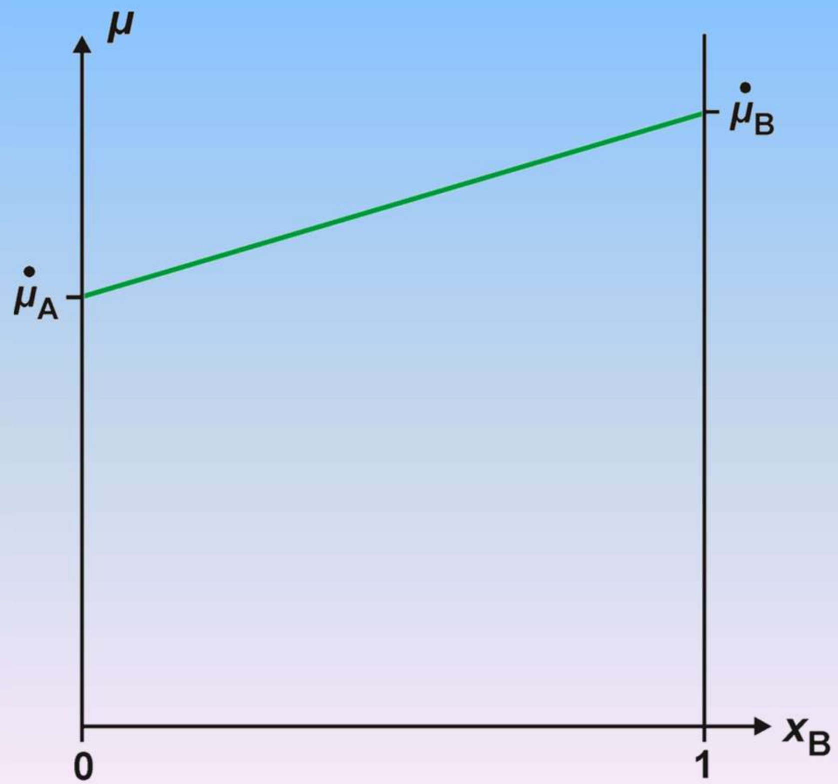
Heterogeneous mixture $\mathcal{M}$:

$$\mu_{\mathcal{M}} = x_A \overset{\bullet}{\mu}_A + x_B \overset{\bullet}{\mu}_B$$

Chemical Potential of Real Mixtures

In real mixtures the extra potential must be taken into account:

$$\mu_M = \underbrace{x_A \overset{\bullet}{\mu}_A + x_B \overset{\bullet}{\mu}_B}_{\boxed{\overset{\circ}{\mu}_M}} + \underbrace{RT(x_A \ln x_A + x_B \ln x_B)}_{\overset{\times}{\mu}_M} + \underbrace{x_A \overset{+}{\mu}_A + x_B \overset{+}{\mu}_B}_{\overset{+}{\mu}_M(x)}$$



"basic term" $\overset{\circ}{\mu}_M$: straight line

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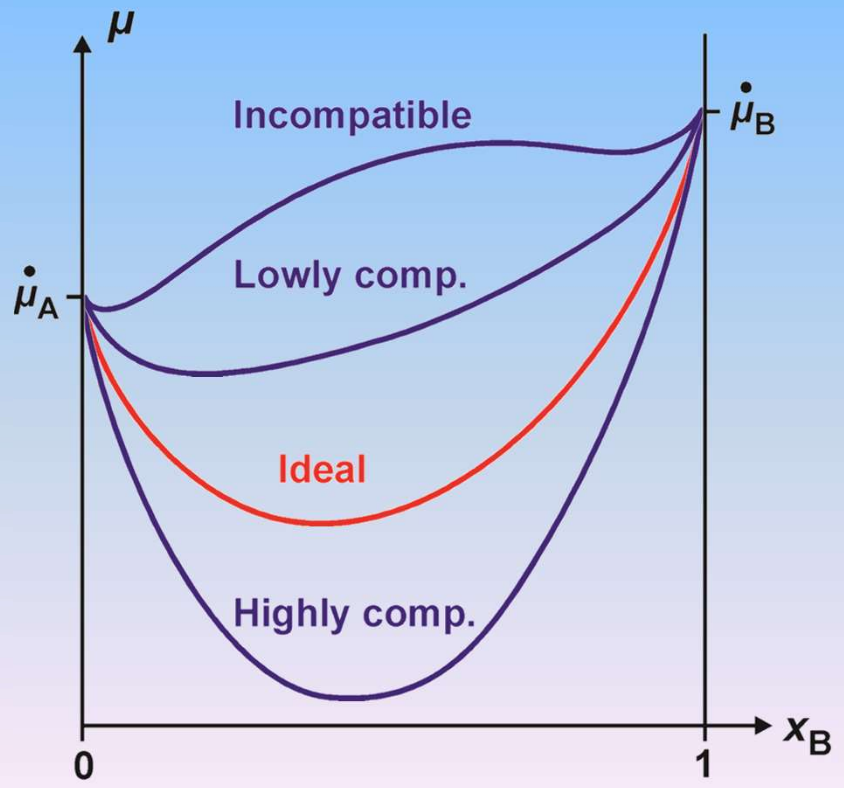
$$\mu_M = \underbrace{x_A \dot{\mu}_A + x_B \dot{\mu}_B}_{\mathring{\mu}_M} + \underbrace{RT(x_A \ln x_A + x_B \ln x_B)}_{\boxed{\overset{\times}{\mu}_M}} + \underbrace{x_A \overset{+}{\mu}_A + x_B \overset{+}{\mu}_B}_{\boxed{\overset{+}{\mu}_M(x)}}$$



"basic term" $\mathring{\mu}_M$: straight line

"mass action term" $\overset{\times}{\mu}_M$: "drooping belly" (ideal)

"extra term" $\overset{+}{\mu}_M$: deformation of the "belly"

$\overset{+}{\mu}_M < 0$: highly compatible

$\overset{+}{\mu}_M > 0$: lowly comp. or incomp.

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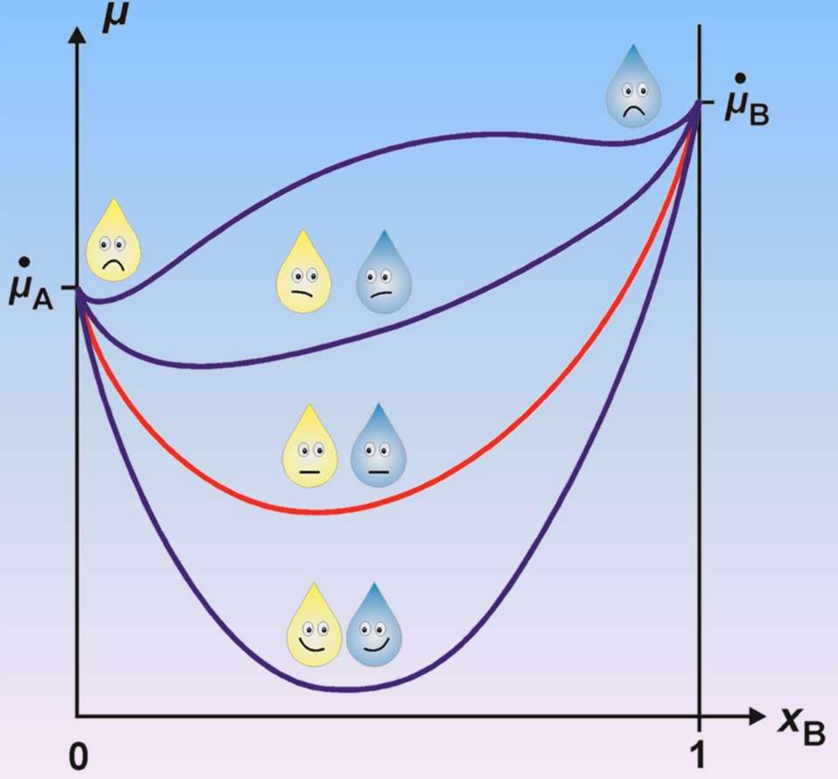

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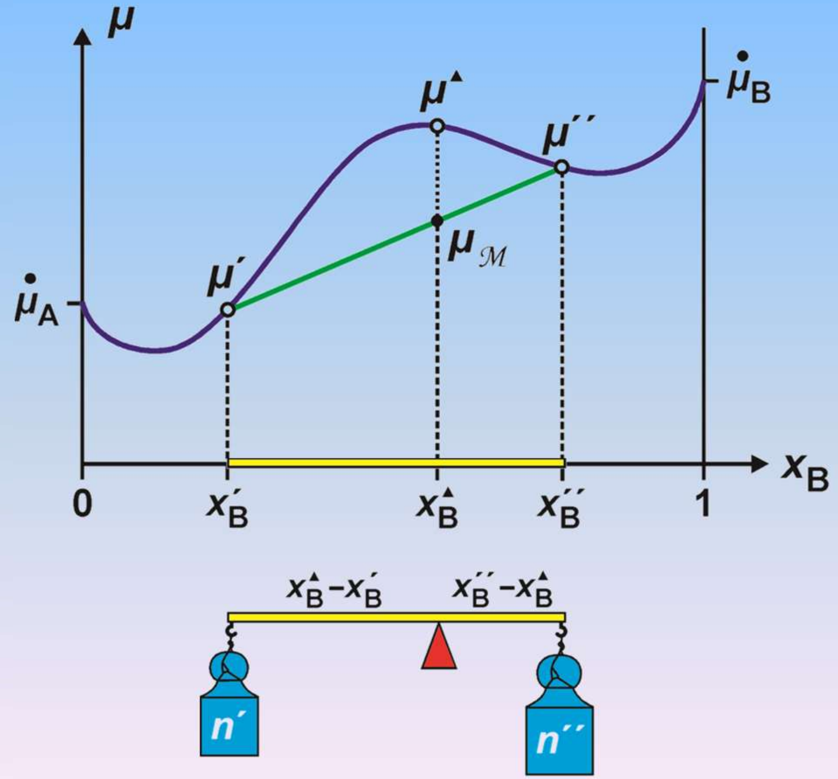
Demixing and Lever Rule

A mixture M$^\blacktriangle$ separates into two homogeneous mixtures M´ and M´´ if its chemical potential $\mu^\blacktriangle$ has a higher value than the chemical potential $\mu_{\mathcal{M}}$ of the heterogeneous mixture, which is made up of M´ with the fraction *n´* and M´´ with the fraction *n´´*.



"*Lever Rule*" (name borrowed from mechanics):

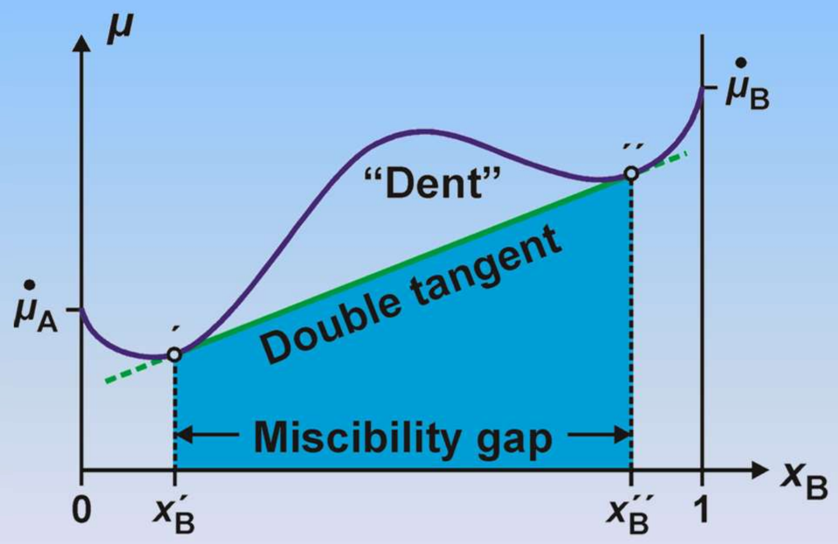
$$n' \times (x_B^\blacktriangle - x_B') = n'' \times (x_B'' - x_B^\blacktriangle)$$

"load × load arm = force × force arm"

Miscibility Gap

The lowest possible $\mu_{\mathcal{M}}$ value can be found by connecting the points of contact of the common tangents on the "dented" curve, creating a *double tangent*.

These two points limit the so-called *miscibility gap*.



Compositions which lie in the range of the gap:

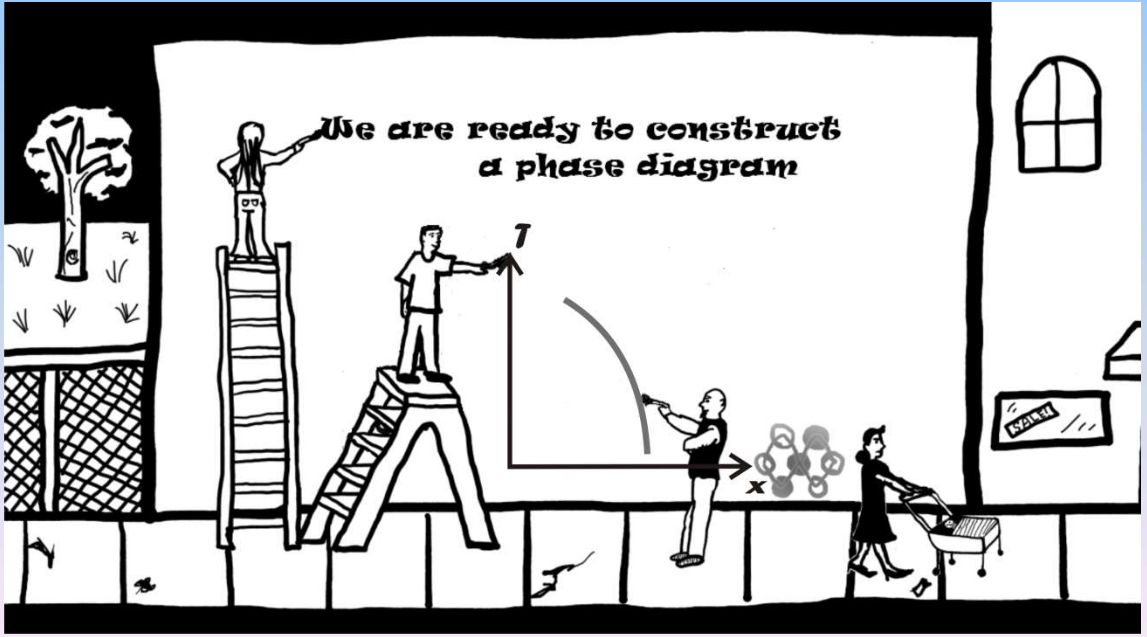
no homogeneous mixture

heterogeneous mixture $\mathcal{M}$ of the two homogeneous mixtures M´ and M´´

Construction of Phase Diagrams

The average chemical potential depends not only on the composition but also on the temperature.

Together with the fact that the phase with the lowest chemical potential at a given temperature will be stable these dependencies can be used to construct the phase diagrams of mixtures.



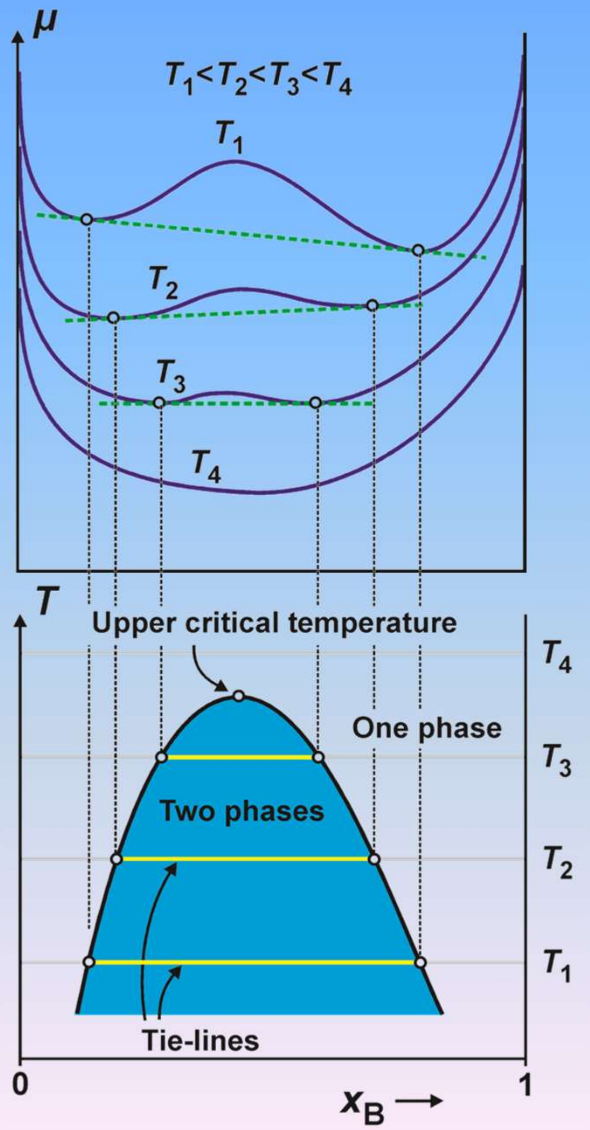
Miscibility Diagram

mixture of two liquid components A and B:

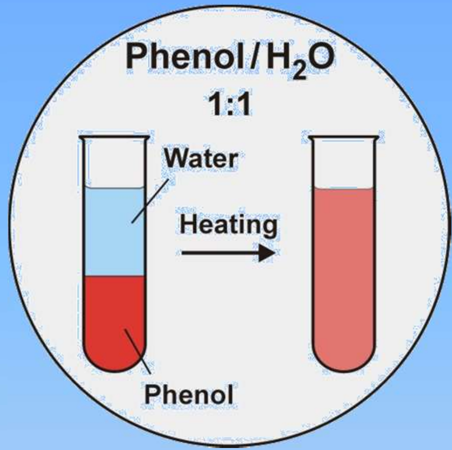
high temperature (*T_4*): single minimum
$\Rightarrow$ homogeneous mixture

low temperatures (*T_3 – T_1*): one maximum and two minima:
$\Rightarrow$ in the composition range between the two minima a heterogeneous mixture of two phases is more stable than a single-phase solution

construction of the corresponding *T*(*x*) diagram (*miscibility diagram*) with an *upper critical solution point*



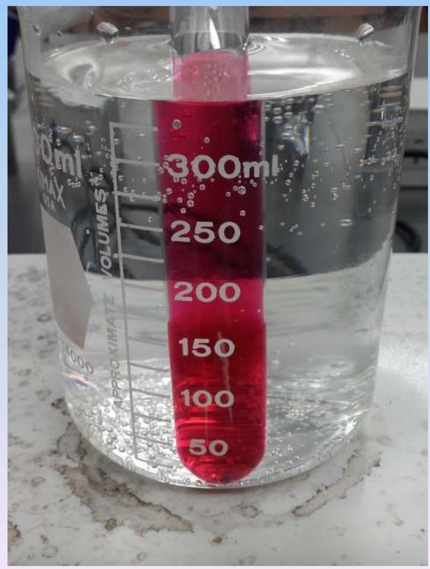
Mixing and Demixing in the System Phenol / Water



Procedure:

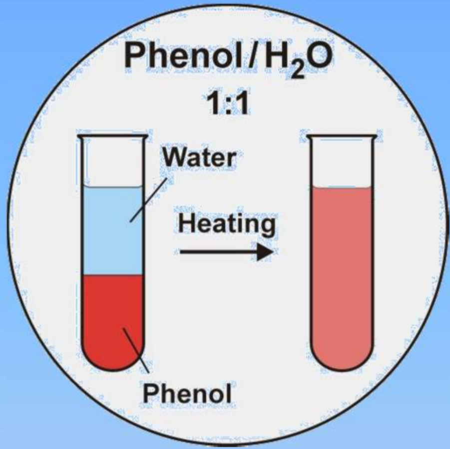
A heterogeneous mixture of equal amounts of phenol—colored by methyl red—and water is heated in a water bath to more than 66 °C.

cold



hot

Mixing and Demixing in the System Phenol / Water



Procedure:

A heterogeneous mixture of equal amounts of phenol—colored by methyl red—and water is heated in a water bath to more than 66 °C.

Observation:

After a while, the two liquids merge.

Explanation:

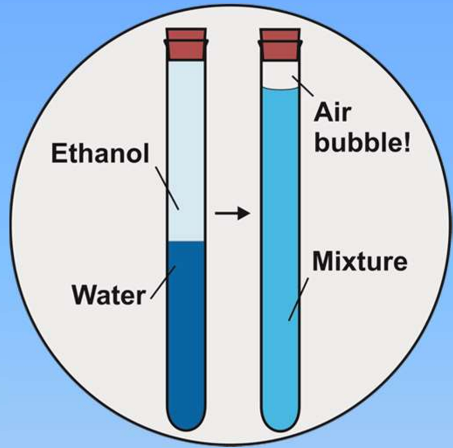
At intermediate compositions and below the upper critical solution temperature of about 66 °C mixtures of phenol and water separate into two liquid phases. When such a sample is heated above the upper critical solution temperature, phenol and water are completely miscible.

5. More “Secrets” of Mixtures

Mixing of Water and Ethanol

Procedure:

The test tube is half-filled with water, then filled to the top with ethanol and closed with a rubber stopper. Finally, the test tube is inverted repeatedly.



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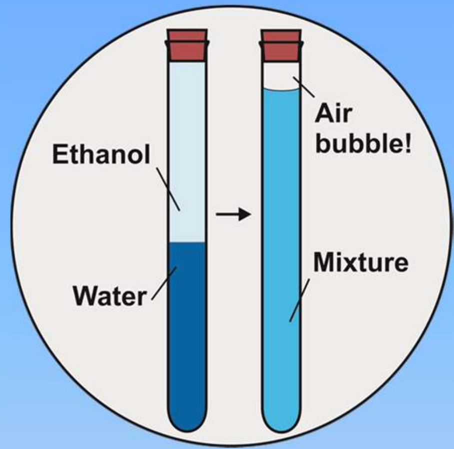
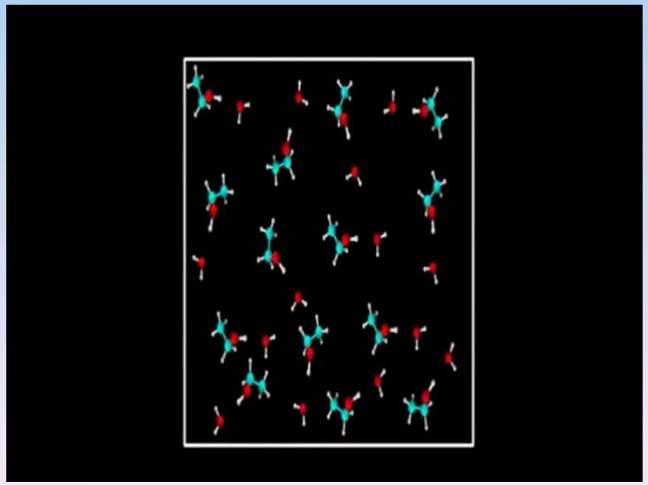


Observation:

A decrease in volume of about 4 % can be noticed.

Explanation:

The volume contraction, which can be observed when ethanol is dissolved in water, is due to hydrogen bonds between the water and ethanol molecules. This bonding draws the different molecules closer together.



Extra Molar Volume

volume V_M of a homogeneous mixture M in the *ideal* case:

$$V_M(\text{ideal}) = x_A \overset{\bullet}{V}_A + x_B \overset{\bullet}{V}_B$$

$\overset{\bullet}{V}_A$, $\overset{\bullet}{V}_B$: molar volumes of the pure components A and B

deviations from ideal behavior can be taken into account by introduction of an *extra molar volume* $\overset{+}{V}_m(x)$ for each component:

$$V_M(\text{real}) = x_A \overset{\bullet}{V}_A + x_B \overset{\bullet}{V}_B + x_A \overset{+}{V}_A + x_B \overset{+}{V}_B$$

Molar Volume of Mixing

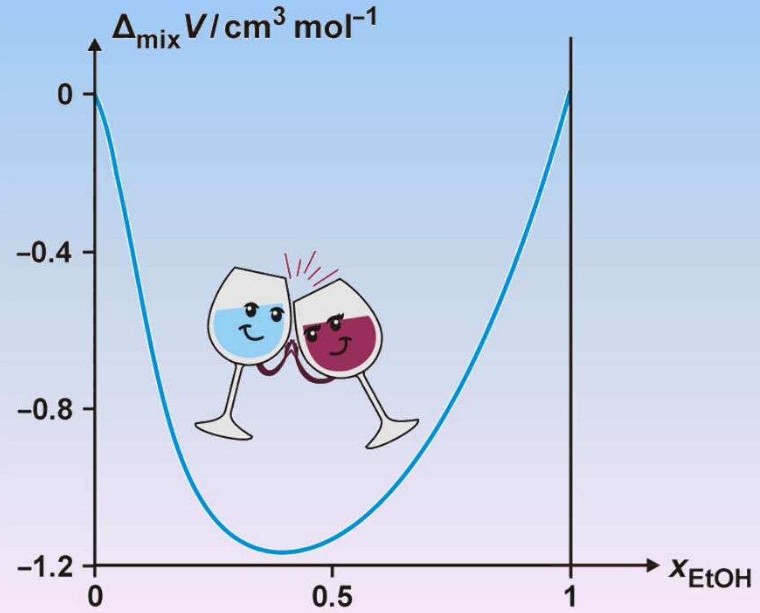
molar volume of mixing $\Delta_{mix}V$ defined as the difference between the volume of a real mixture and the volume that would occur in an ideal solution under the same conditions:

$$\Delta_{mix}V = V_M(\text{real}) - V_M(\text{ideal})$$

$$\Delta_{mix}V = (x_A \overset{\bullet}{V}_A + x_B \overset{\bullet}{V}_B + x_A \overset{+}{V}_A + x_B \overset{+}{V}_B) - (x_A \overset{\bullet}{V}_A + x_B \overset{\bullet}{V}_B)$$

$$\Delta_{mix}V = x_A \overset{+}{V}_A + x_B \overset{+}{V}_B$$

Example: Molar volume of mixing as function of the composition for the system ethanol-water (at 298 K)

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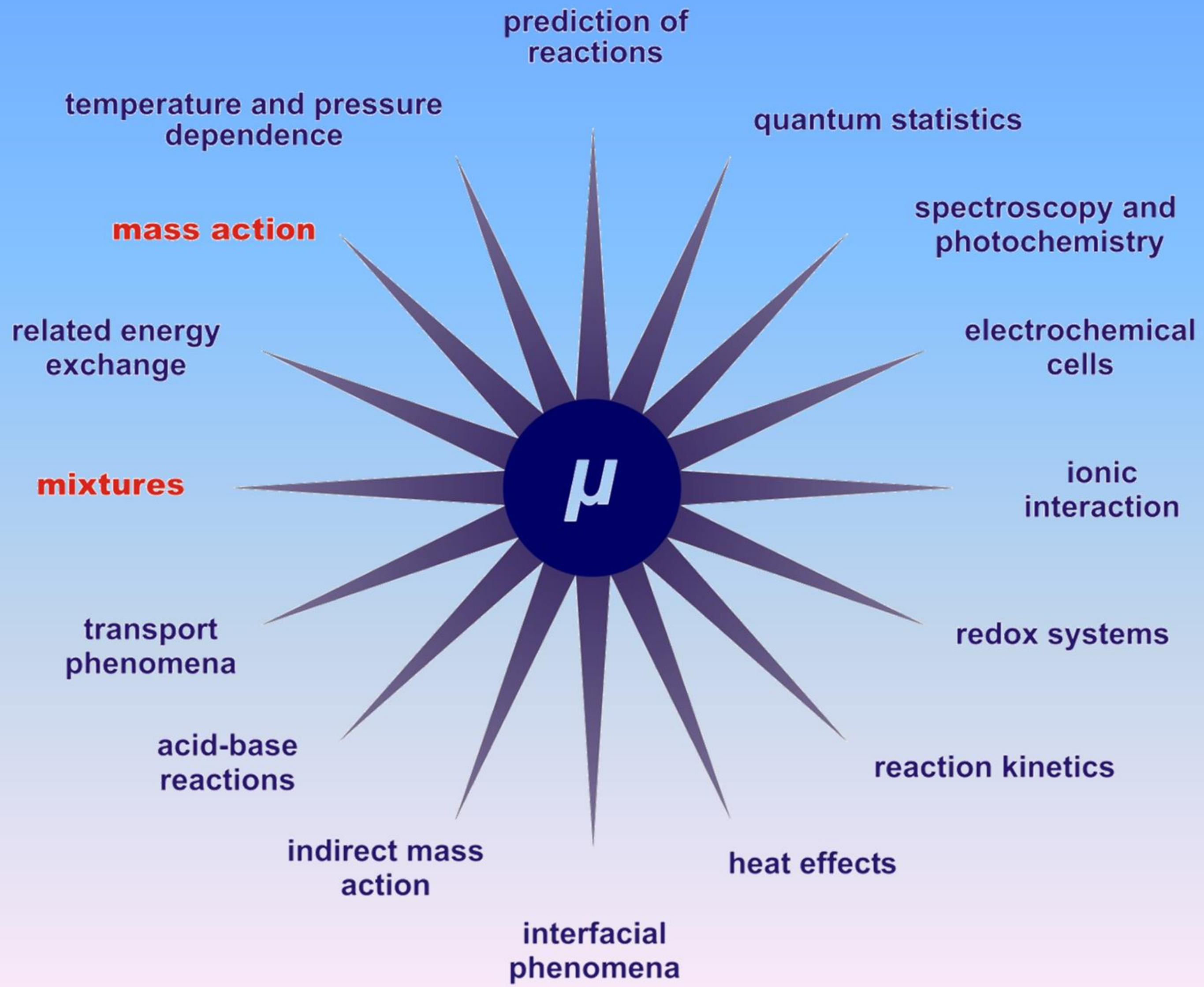
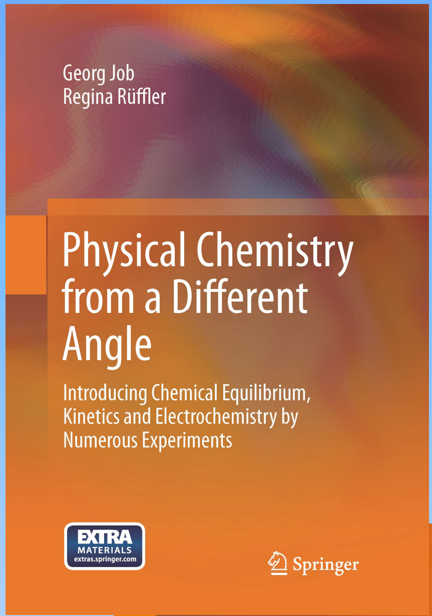
6. Outlook

Key Role of the Chemical Potential



6. Outlook



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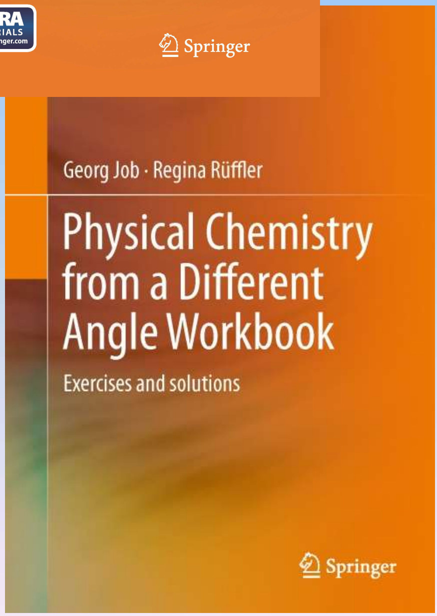

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