Chemical Potential from the Beginning

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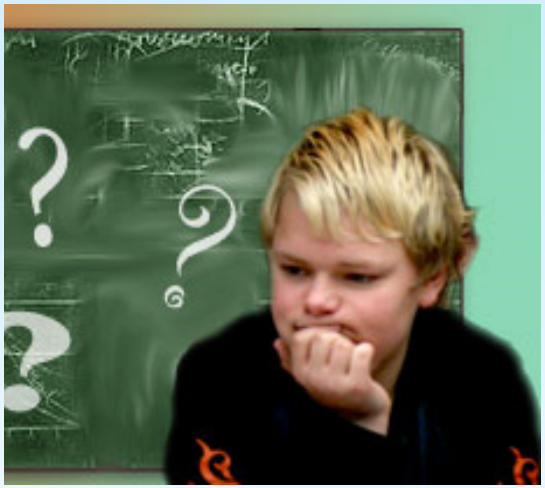
Introduction

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.

Introduction

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

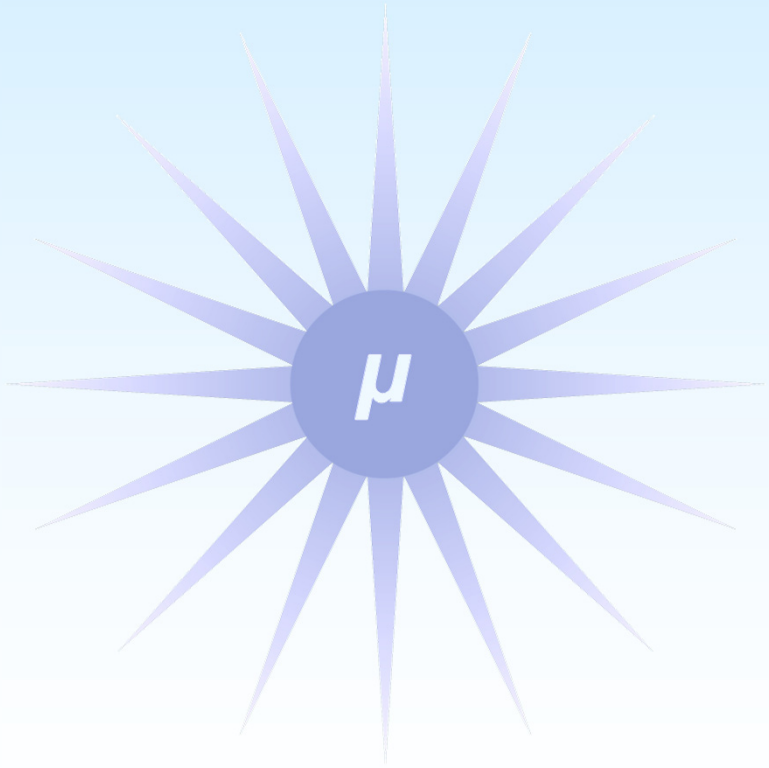
$$\mu = \left(\frac{\partial G}{\partial n}\right)_{p,T}$$

We propose to introduce μ as a basic concept in analogy to quantities such as length, mass etc. This approach allows to teach the subject even at introductory high school level. Selected simple and safe demonstration experiments help to strengthen the understanding.

Outline

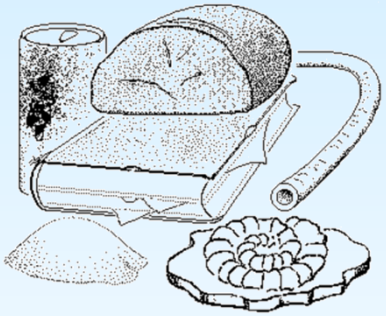
1. Chemical Potential as Basic Concept
2. Main Characteristics of the Chemical Potential
3. Quantifying the Chemical Potential
4. First Applications
5. Influence of the Milieu
6. Mass Action – A Question of the Milieu
7. Outlook

1. Chemical Potential as Basic Concept



Understanding the Chemical Potential

Starting point: Everyday experience that things around us change their shape and composition more or less rapidly (HERACLITUS: "Everything flows – Nothing stands still"), e.g.



- **Bread dries out,**
- **Iron rusts,**
- **Rocks weather etc.**

but also change

- **Tinned food in an unopened can or chemicals in a sealed bottle**

⇒ Substances tend to transform by themselves, i.e. we can ascribe to each and every substance an inherent "tendency to transform"

The chemical potential μ can be interpreted as

measure for the general tendency of matter to transform

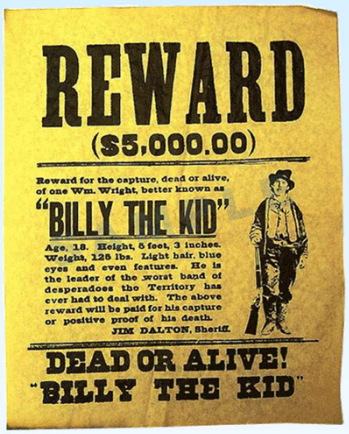
Basis of *phenomenological characterization*

Phenomenological Characterization

Definition: An object or living being is characterized by its *external properties* (and <u>not</u> by its *internal structure*).

For identifying for example a person often a few characteristic traits are sufficient:

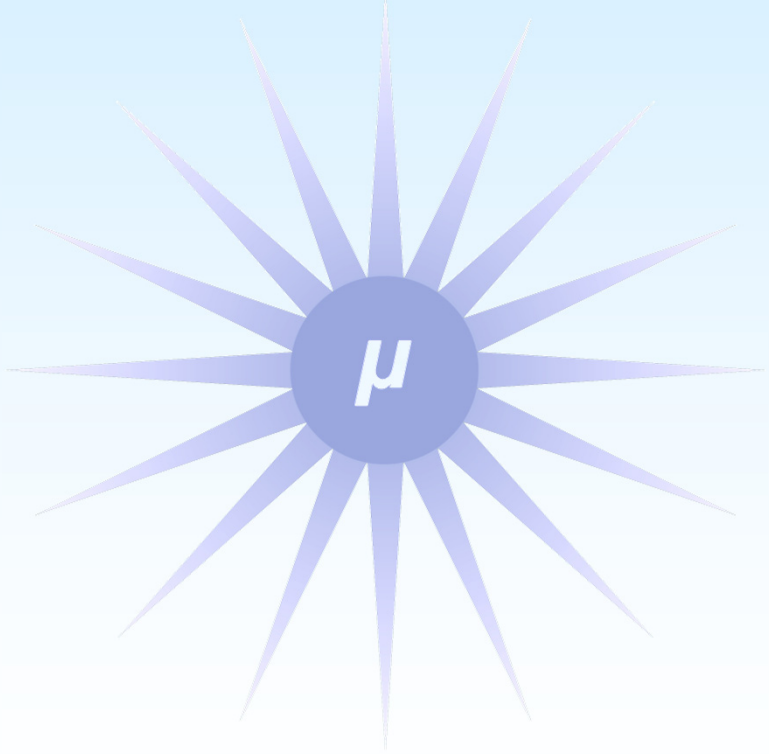
- **height: 5 feet 3 inches**
- **weight: 129 lbs**
- **light hair**
- **blue eyes**
- **18 years old**
- **dangerous desperado**



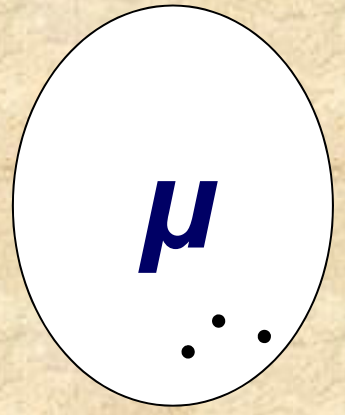
The "bundle" of these characteristics is basically what makes up a person; his or her name is just an identification code for this list.

Our intent is to design a kind of "wanted poster" for the chemical potential μ that allows it to be defined as measurable physical quantity.

2. Main Characteristics of the Chemical Potential

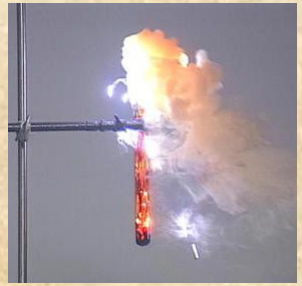


Wanted



- 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.



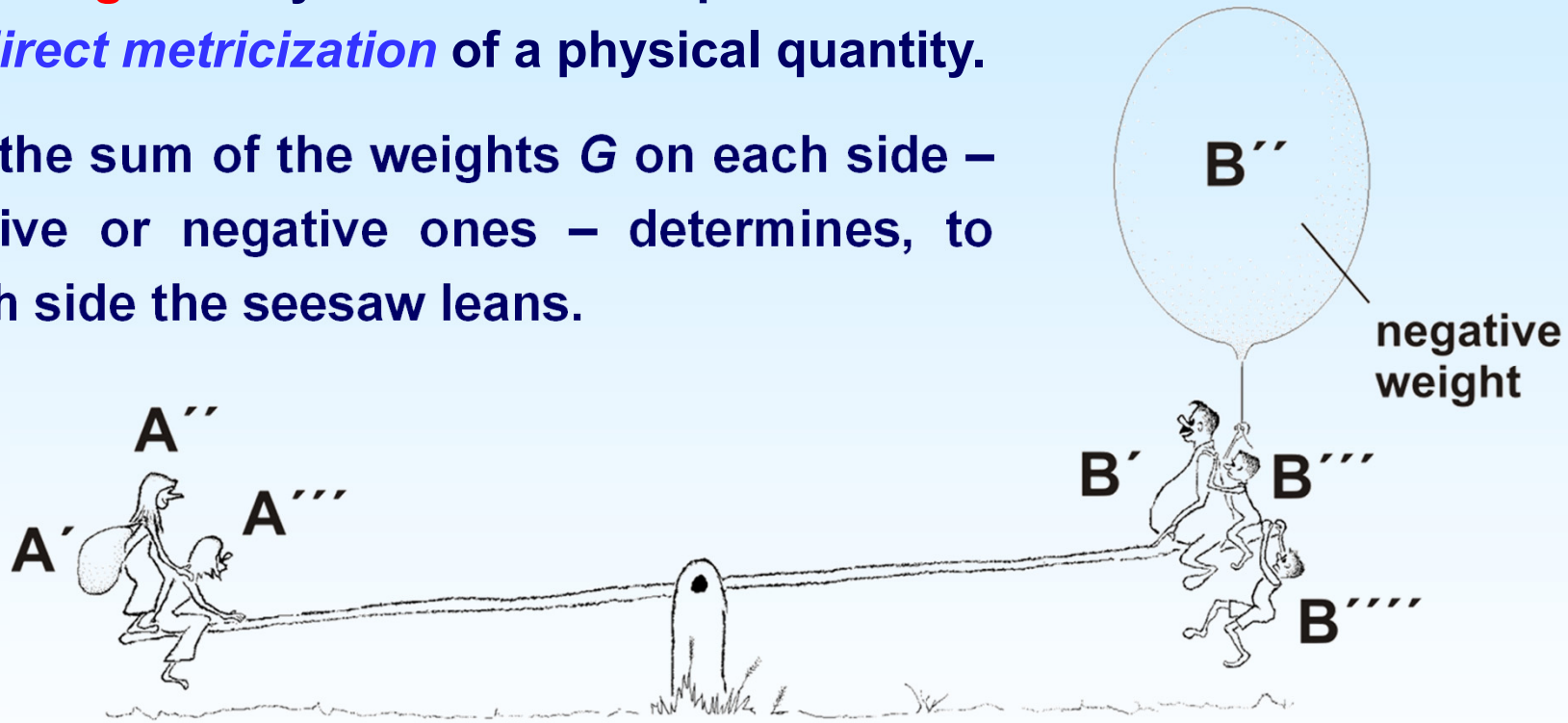
- The magnitude of this tendency, meaning the numerical value of μ
  - is determined by the *nature* of the substance, as well as
  - by its *milieu* (temperature, pressure, concentration, ...),
  - but <u>not</u> by the nature of reaction partners or the products.
- A *reaction*, *transition*, *redistribution* 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: $\sum_{\text{initial}} \mu_i > \sum_{\text{final}} \mu_j$.

Weight as Model

The "weight" may serve as a simple model for the *direct metricization* of a physical quantity.

Just the sum of the weights *G* on each side – positive or negative ones – determines, to which side the seesaw leans.



Generally:

The left side wins if $G(A') + G(A'') + \ldots > G(B') + G(B'') + \ldots$

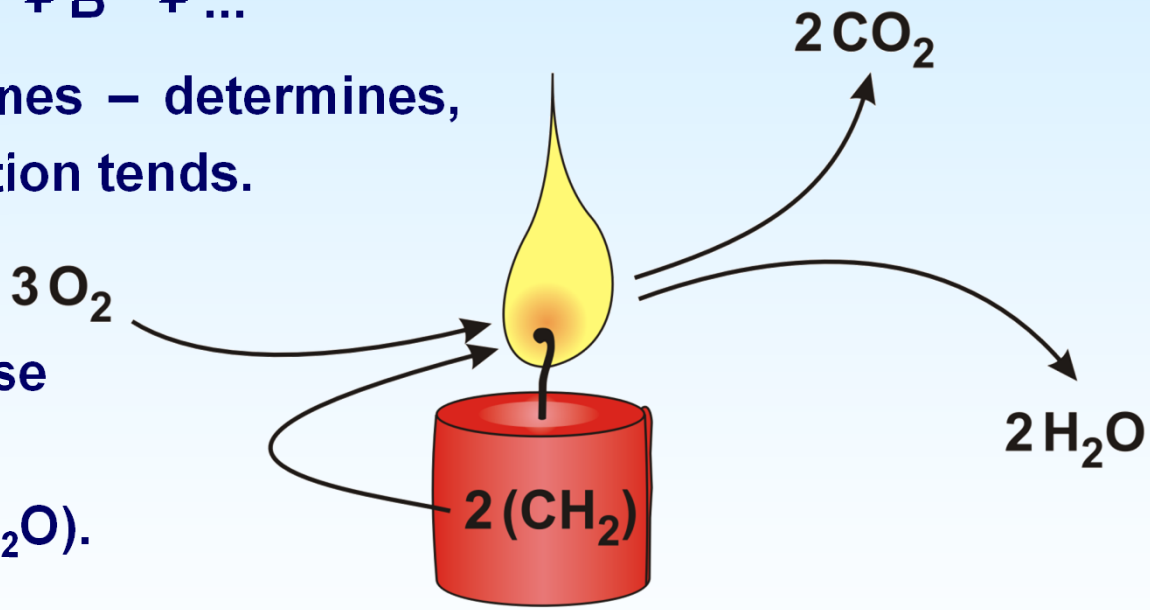
Equilibrium is reached when $G(A') + G(A'') + \ldots = G(B') + G(B'') + \ldots$

Competition between Substances

The sum of the chemical potentials μ on each side of the reaction equation

$$A' + A'' + \ldots \rightarrow B' + B'' + \ldots$$

– positive or negative ones – determines, in which direction a reaction tends.



The candle burns, because

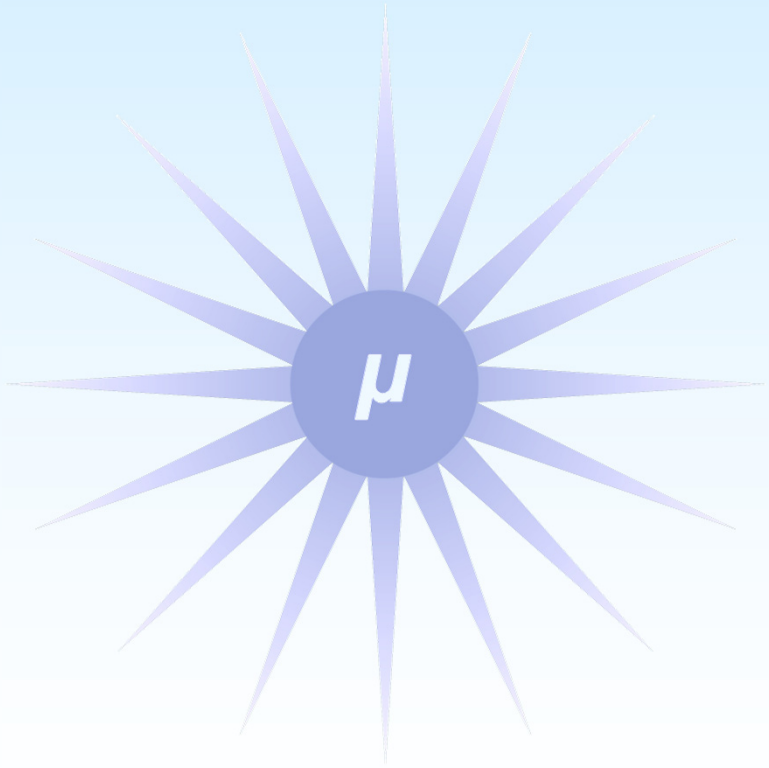
$3\,\mu(O_2) + 2\,\mu((CH_2)) > 2\,\mu(CO_2) + 2\,\mu(H_2O)$.

Generally:

The left side "wins" if $\mu(A') + \mu(A'') + \ldots > \mu(B') + \mu(B'') + \ldots$

Equilibrium is reached when $\mu(A') + \mu(A'') + \ldots = \mu(B') + \mu(B'') + \ldots$

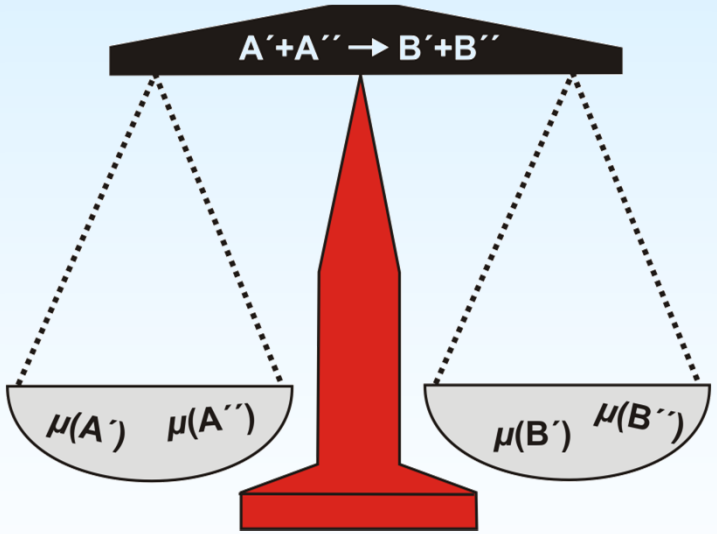
3. Quantifying the Chemical Potential



Metricization of the Chemical Potential

Each substance shows a *tendency to transform* (to *react*, to undergo a phase *transition*, to *redistribute*). A measure *μ* of this tendency can be defined in a way analogously to that for the weight.

Each realizable reaction is comparable to a kind of scale which allows the comparison of chemical potentials or their sums, respectively.



But the measurement is often impossible due to inhibitions. In that case, we have to use indirect methods.

Because we are interested in a first basic knowledge of the chemical potential, we consider the values at the moment as given.

Reference Level of Chemical Potentials

The heights of mountains are not referred to the geocentre but to the sea level,

temperatures in everyday life are not referred to absolute zero but to the freezing point of water.

It is similarly practical to choose for the values of the chemical potential a convenient *reference level*, for example the *pure elements in their most stable modification under standard conditions* (298 K and 100 kPa). Their chemical potential $\mu^{\ominus}$ is zero per definition.

For *dissolved substances* the concentration *c* in addition to *p* and *T* has to be specified (usual reference value: 1 kmol/m^3 = 1 mol/L).

***Ions* can be assigned a chemical potential as well. The most commonly appearing type of ion, H^+, receives the $\mu^{\ominus}$ value of zero.**

Examples for Values of Chemical Potentials

***Pure* and *dissolved substances* at standard conditions (298 K, 100 kPa)**

Substance	Formula	$\mu^{\ominus}$ / kG
Iron	Fe|s	0
Water	H_2O|l	–237
Marble	$CaCO_3$|s	–1129
Cane sugar	$C_{12}H_{22}O_{11}$|s	–1558
Paraffin wax	≈(CH_2)|s	+4
Benzene	C_6H_6|l	+125
Ethyne	C_2H_2|g	+210
Cane sugar	$C_{12}H_{22}O_{11}$|w	–1565
Ammonia	NH_3|w	–27
Calcium(II)	Ca^{2+}|w	–554

Unit: Gibbs, short G (= J/mol)

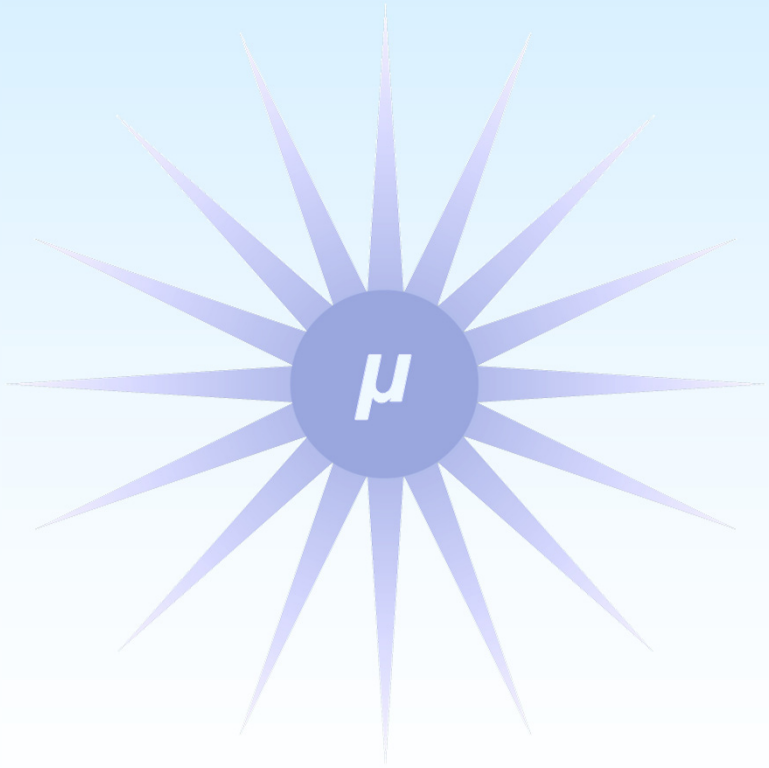
$\mu = 0$ valid for elements

$\mu < 0$ means that the substance can be produced spontaneously from the elements.

$\mu > 0$ means that the substance tends to decompose into the elements.

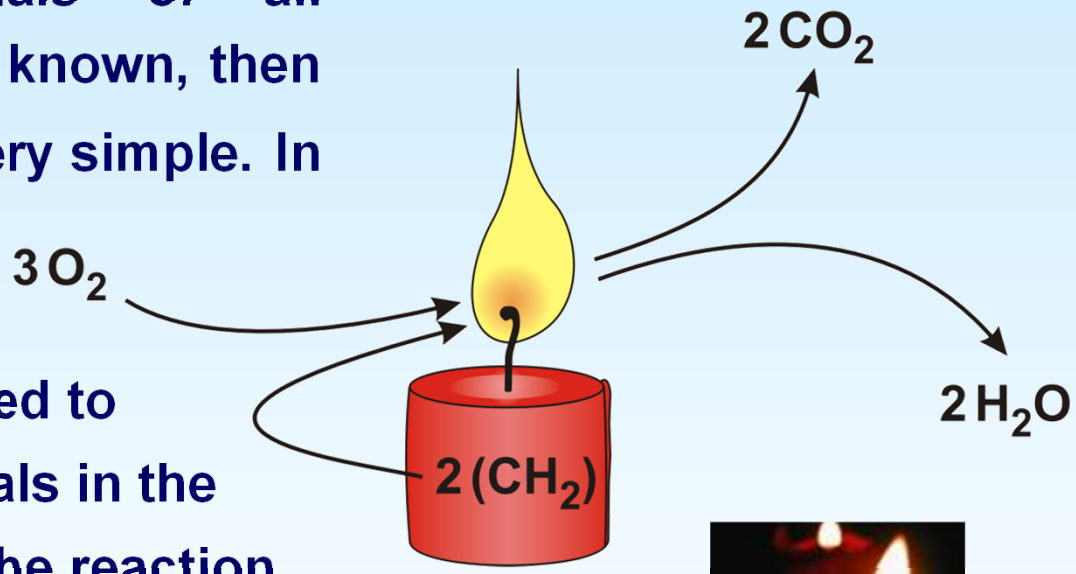
additionally specified standard concentration of c = 1 kmol/m^3

4. First Applications



Prediction of Possible Reactions

If the chemical potentials of all substances in question are known, then their useful application is very simple. In order to predict whether a process can happen spontaneously or not we only need to compare the sum of potentials in the initial and the final state of the reaction.



$$3\,O_2|g + 2\,(CH_2)|s \rightarrow 2\,CO_2|g + 2\,H_2O|g$$

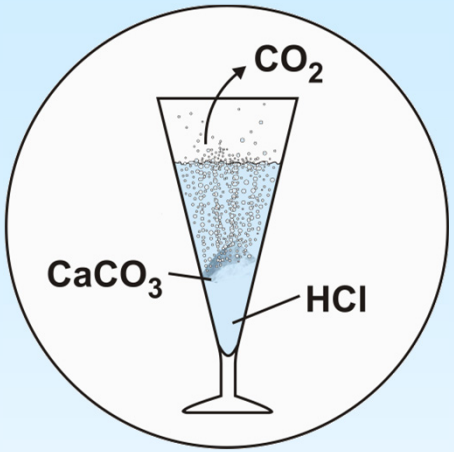
$\mu^{\ominus}$/kG $\quad \underbrace{3\cdot 0 \quad + 2\cdot(+4)}_{+8} \quad > \quad \underbrace{2\cdot(-394) + 2\cdot(-229)}_{-1246}$

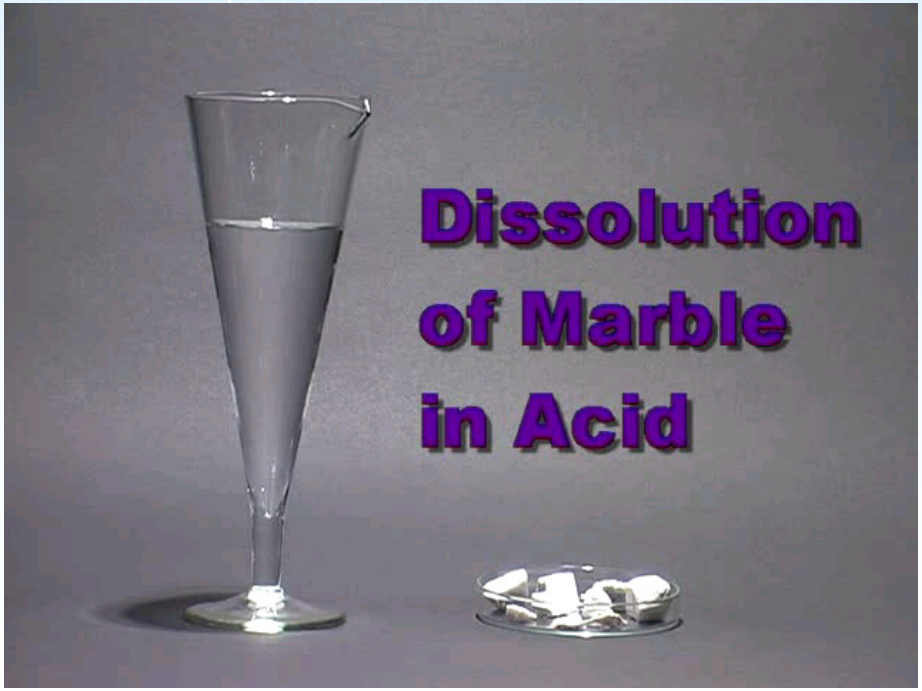
➡ process possible!

Dissolution of Marble

Procedure:

Pieces of marble are thrown into hydrochloric acid.





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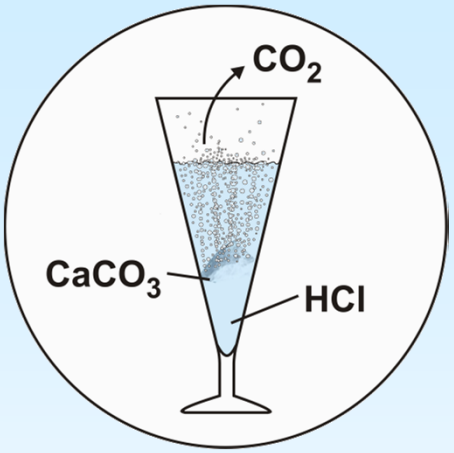


Observation:

A strong effervescence can be observed.

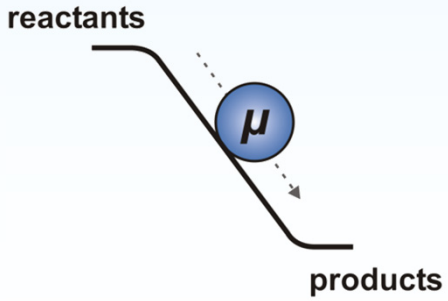
Explanation:

Calcium carbonate is dissolved by hydrochloric acid, thereby forming gaseous carbon dioxide:

$$CaCO_3|s + 2\ H^+|w \rightarrow Ca^{2+}|w + H_2O|l + CO_2|g$$

$\mu^{\ominus}$/kG $\quad (-1129) + 2 \cdot 0 > (-554) + (-237) + (-394)$

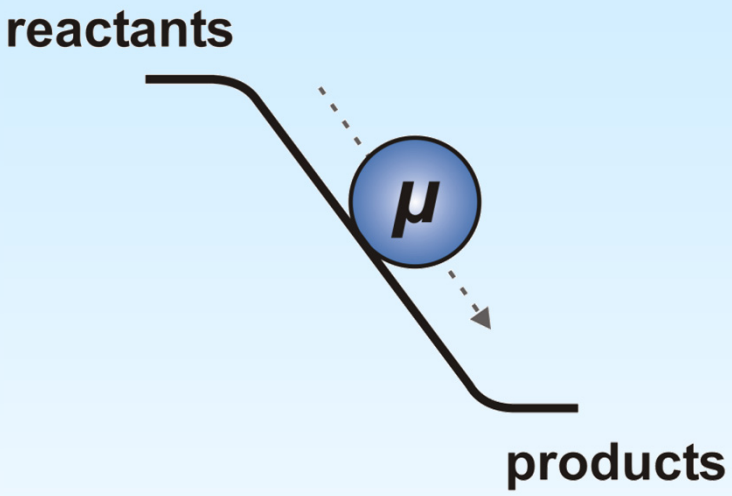
$\quad -1129 > -1185$



reaction possible!

Preparation of Substances with Positive μ

As discussed a reaction always runs in the direction of a potential drop. This might give students or pupils the impression that substances with a positive potential cannot ever be prepared by normal reactions of stable substances (with negative μ).

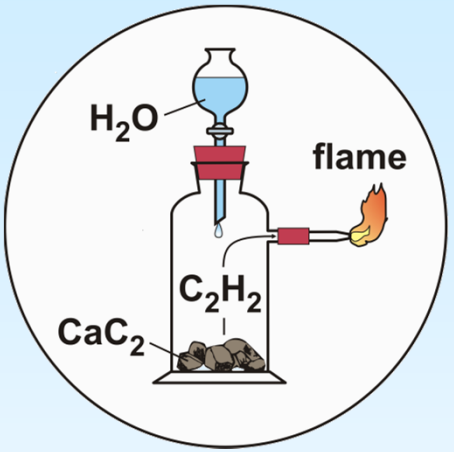


The preparation of ethyne (acetylene) with a high positive chemical potential from calcium carbide and water shows that this is not the case.

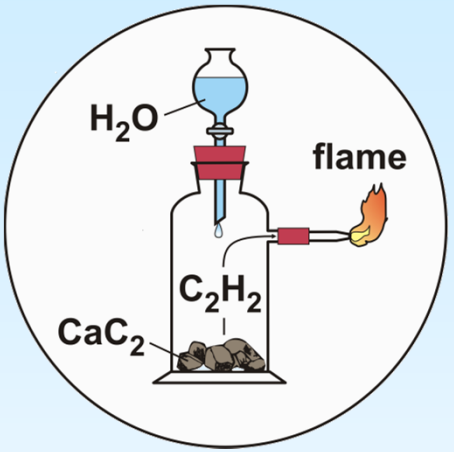
Carbide Lamp

Procedure:

Water is dripped cautiously onto some grayish brown lumps of calcium carbide.



Carbide Lamp



Procedure:

Water is dripped cautiously onto some lumps of calcium carbide.

Observation:

The produced gaseous ethyne burns with a bright and sooty flame.

Explanation:

Calcium carbide reacts with water under formation of ethyne (acetylene) according to

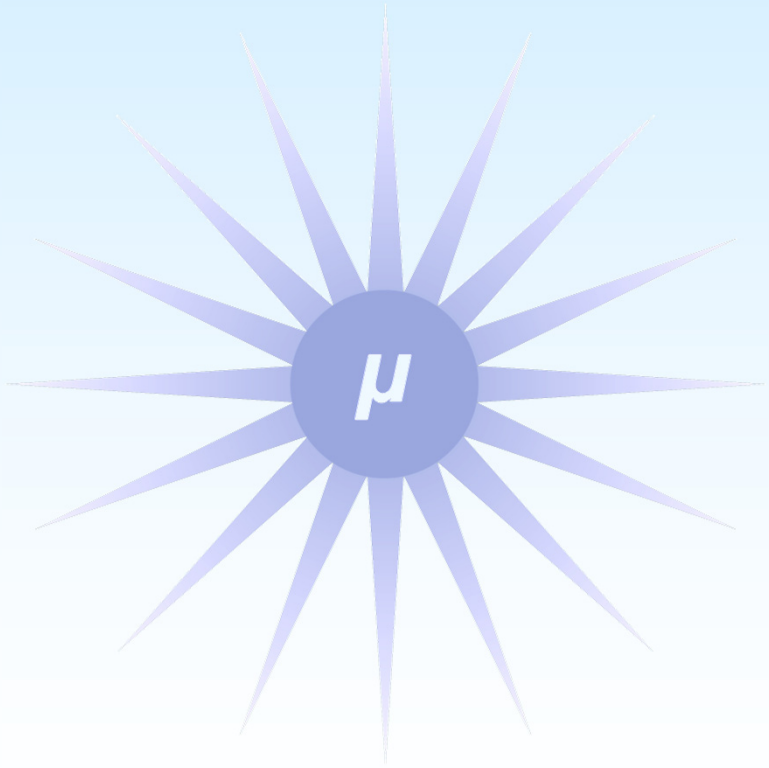
$$CaC_2|s + 2\ H_2O|l \rightarrow Ca(OH)_2|s + C_2H_2|g$$

$$\mu^{\ominus}/kG \quad (-65) + 2\cdot(-237) > (-898) + (+210)$$

$$-539 > -688$$

also substances with positive μ can be produced

5. Influence of the Milieu



Temperature and Pressure Dependence

Only in a zero approximation μ can be considered to be constant.

A more detailed approach considers the temperature and pressure 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 of the chemical potential

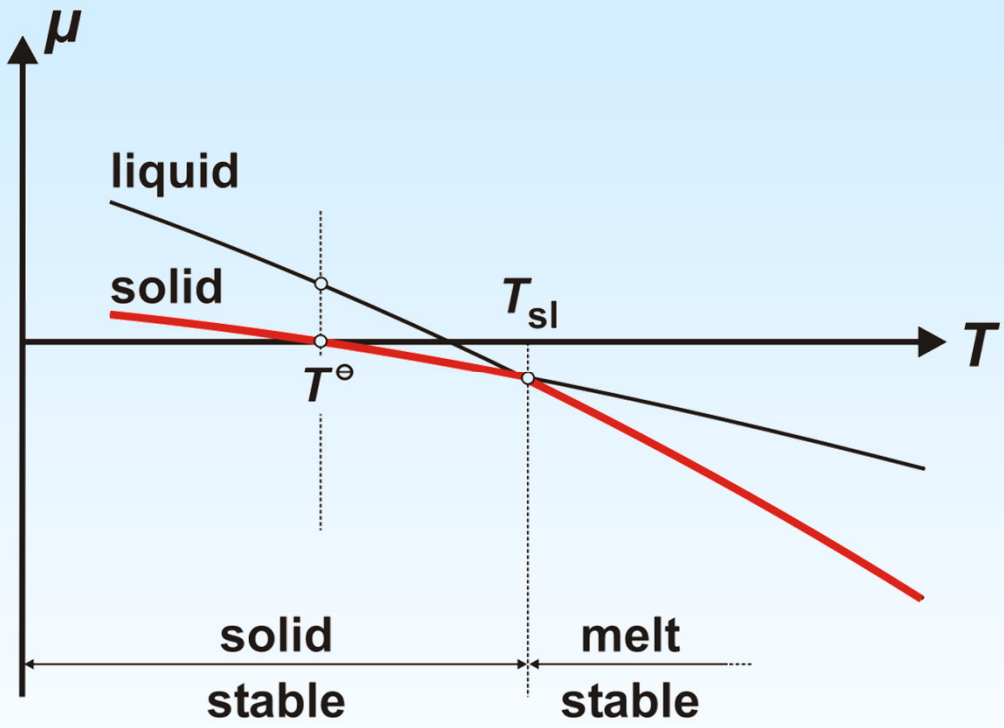
For the *temperature coefficients* α and *pressure coefficients* β of the chemical potential of a substance B the following rules are valid:

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

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

Already these qualitative rules allow many useful conclusions.

Melting Point



Determination of T_{sl}:

Condition for equlibrium:

$$\mu_s = \mu_l$$

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)

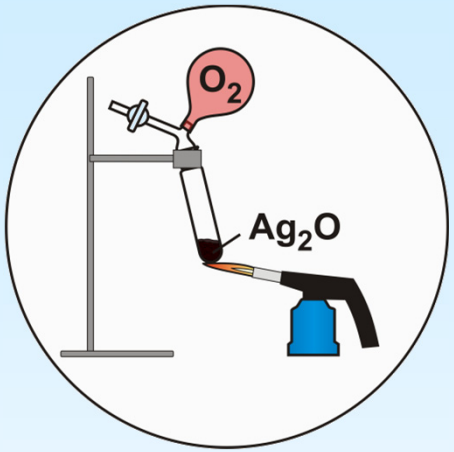
The chemical potentials decrease with warming and this happens more quickly in the liquid state than in the solid (α(B|l) < α(B|s) < 0).

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

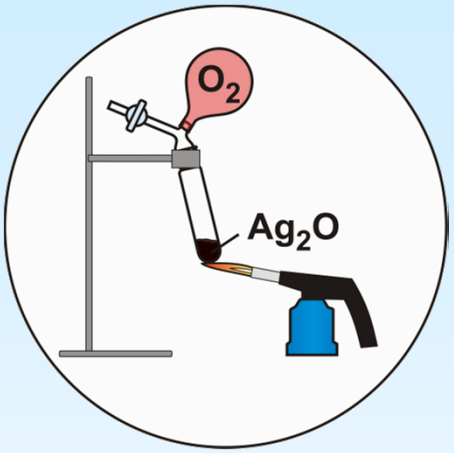
Annealing of Silver Oxide

Procedure:

Blackish brown silver oxide is heated by a burner.



Annealing of Silver Oxide



Procedure:

Blackish brown silver oxide is heated by a burner.

Observation:

The presence of oxygen can be demonstrated with a glowing splint. White shiny silver metal remains in the test tube.

Explanation:

The thermal decomposition of silver oxide can be described by:

$$2\,Ag_2O|s \rightarrow 4\,Ag|s + O_2|g$$

$\mu^{\ominus}$/kG	2·(–11)	<	4·0	+ 0	➡	reaction not possible!
α/G K^{-1}	2·(–121)		4·(–43)	–205		

➡ decomposition temperature $T_D \approx 465$ K (calculable similarly to T_{sl})

Influence of Pressure

Because of

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

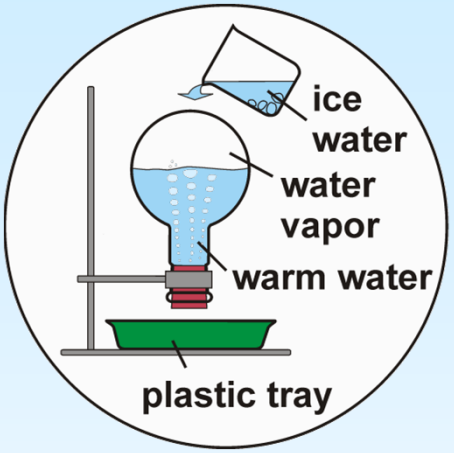
an increase in pressure results in an increasing chemical potential, but the increase is different for the different states of aggregation with the smallest change in the solid state. Therefore, at high pressures the solid state is normally preferred compared to the others.

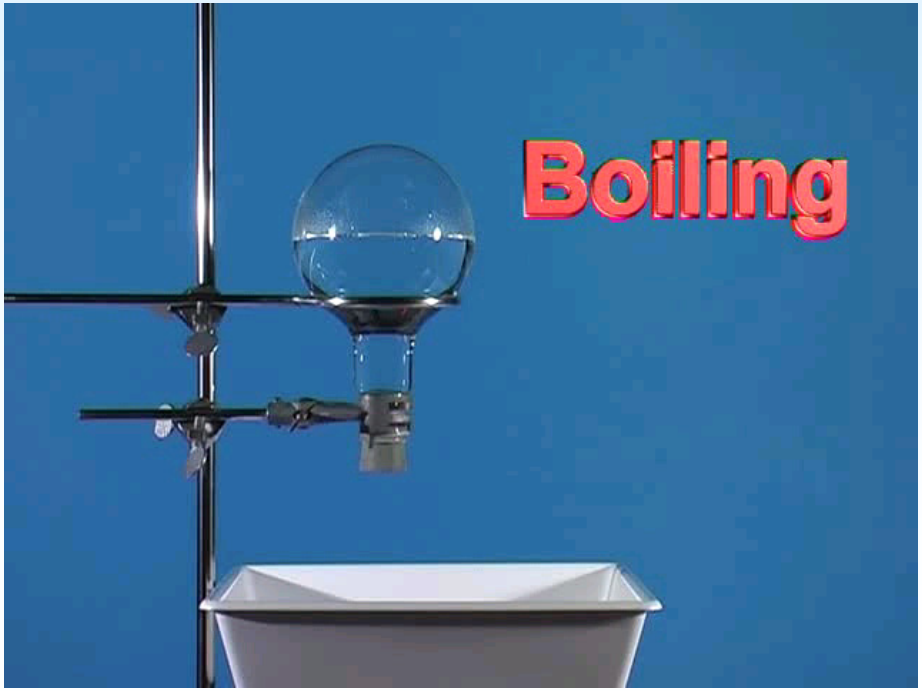
Conversely, a pressure reduction results in the preference of the gaseous state.

Boiling by Cooling

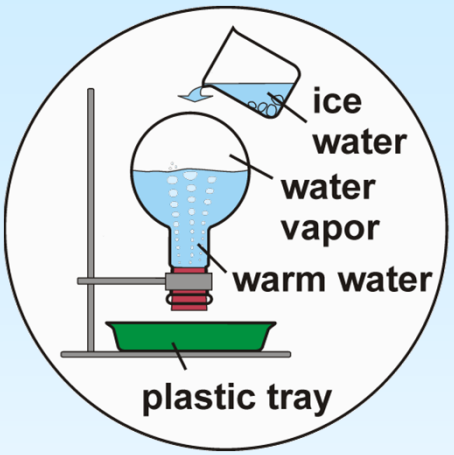
Procedure:

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	➡ process not possible!
β/μG Pa^{-1}	18.1		$24.3 \cdot 10^3$	

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: $\mu(H_2O|l) > \mu(H_2O|g)$.

Phase Diagram

A simultaneous temperature and pressure dependence can be described by

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

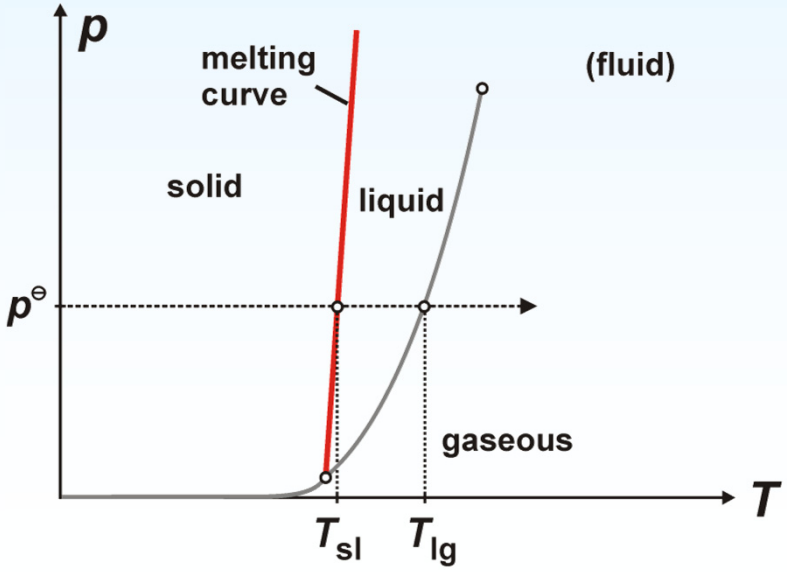
By use of this equation the *phase diagram* of a substance can be calculated if the phase transition is formulated as reaction and the equilibrium condition is considered, for example the melting process:

$$B|s \rightarrow B|l \qquad \mu_s = \mu_l$$

Calculation of the melting curve:

$$\mu_{s,0} + \alpha_s \cdot (T - T_0) + \beta_s \cdot (p - p_0) = \mu_{l,0} + \alpha_l \cdot (T - T_0) + \beta_l \cdot (p - p_0)$$

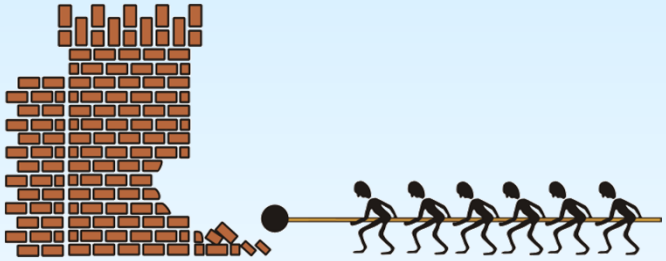
$$p = p_0 - \frac{\mu_{s,0} - \mu_{l,0}}{\beta_s - \beta_l} - \frac{\alpha_s - \alpha_l}{\beta_s - \beta_l}(T - T_0)$$



6. Mass Action –
A Question of the Milieu

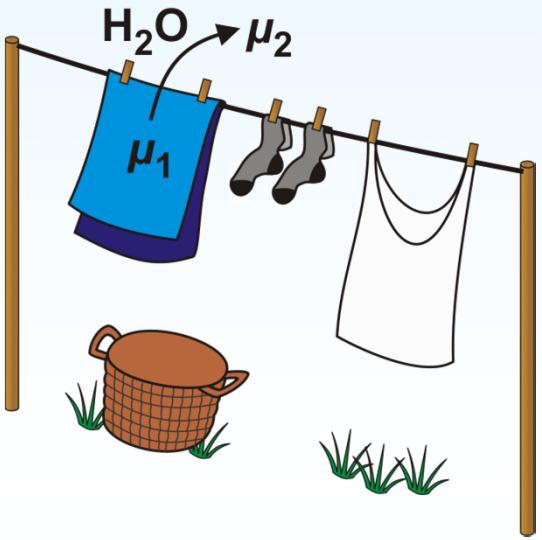
Mass Action

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 action the more punching the effect.

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



Example: *Evaporation* of water

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

$\mu^{\ominus}$/kG $\quad -237 < -229$

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:

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

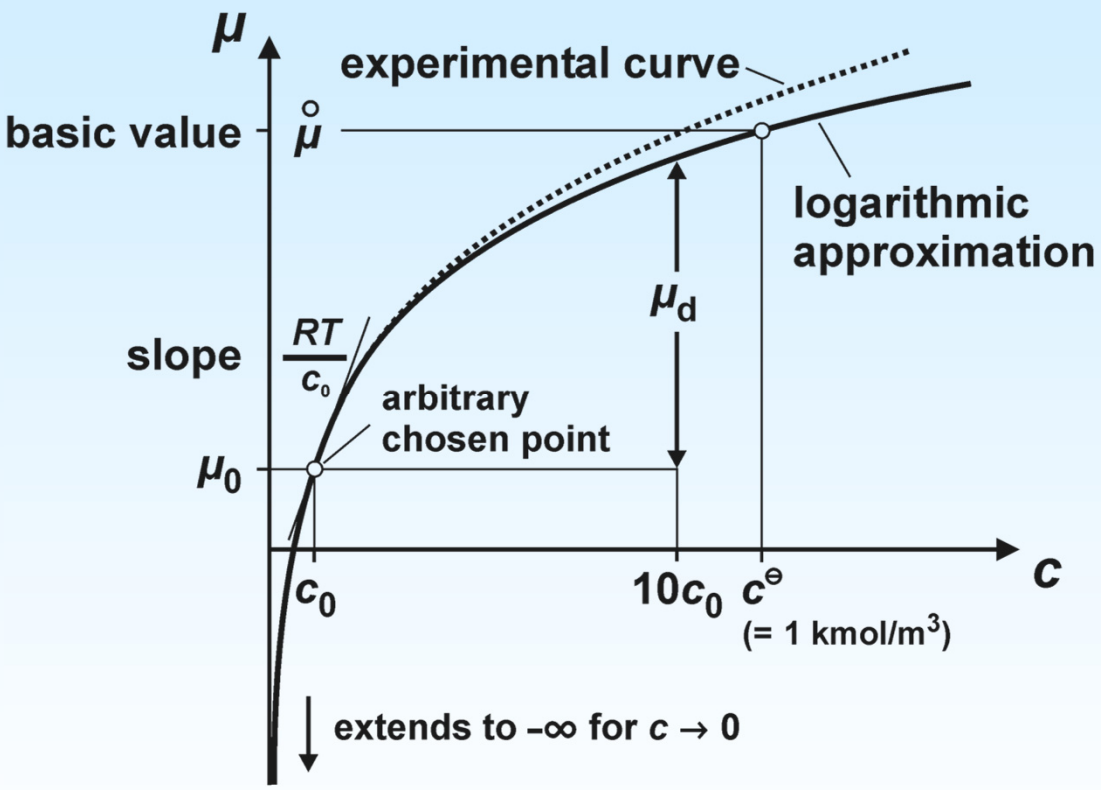
While α and β (except for gases) still depend from the type and the milieu of the given substance the *concentration coefficient* γ is a *universal quantity*, that means it is the same for all substances in every milieu:

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

The combination of these two relations results in the so-called "*mass action equation*:"

$$\mu = \mu_0 + RT \ln(c/c_0) = \mu_0 + RT \ln c_r \qquad \textit{mass action equation}$$

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!

If the concentration c increases one decade (a factor of ten), the chemical potential always increases by the same amount, the "deca potential" μ_d (5.71 kG $\approx$ 6 kG at 298 K).

Mass Action Law

A very important application is the derivation of the "*mass action law*."

Considering a general reaction

$$B + C + \ldots \rightarrow D + E + \ldots$$

equilibrium is established when the potential gradient disappears, i.e.

$$\mu_B + \mu_C + \ldots = \mu_D + \mu_E + \ldots$$

Application of the mass action equation (valid for small *c*):

$$\mathring{\mu}_B + RT \ln c_r(B) + \mathring{\mu}_C + RT \ln c_r(C) + \ldots = \mathring{\mu}_D + RT \ln c_r(D) + \mathring{\mu}_E + RT \ln c_r(E) + \ldots$$

From this follows:

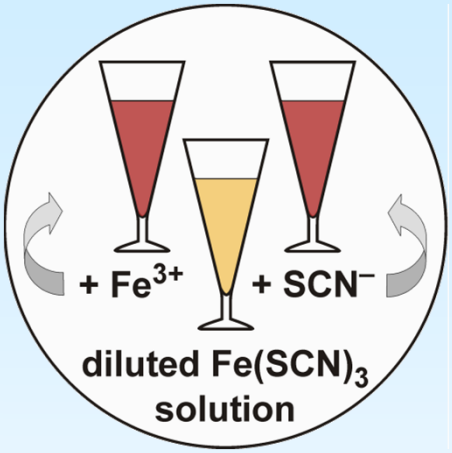
$$\frac{c_r(D) \cdot c_r(E) \cdot \ldots}{c_r(B) \cdot c_r(C) \cdot \ldots} = \exp\left(\frac{\mathring{\mu}_B + \mathring{\mu}_C + \ldots - \mathring{\mu}_D - \mathring{\mu}_E - \ldots}{RT} \right) = \mathring{K}_c$$

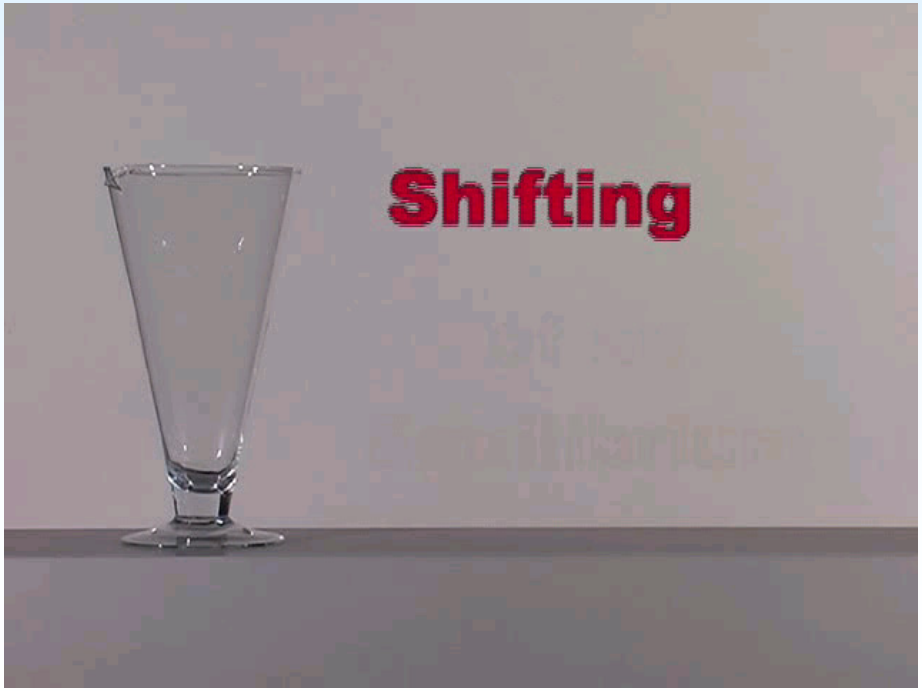
equilibrium constant

Iron(III) Thiocyanate Equilibrium

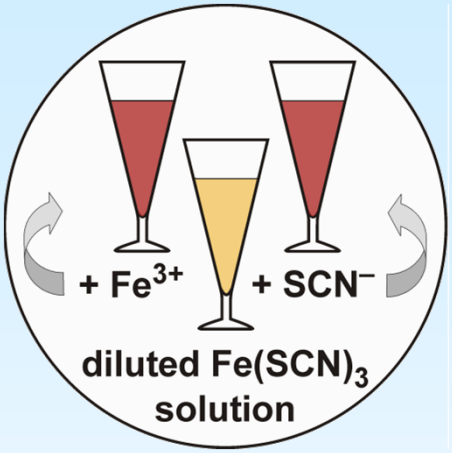
Procedure:

A pale orange diluted iron thiocyanate solution is treated alternatively with excess iron(III) or excess thiocyanate.





Iron(III) Thiocyanate Equilibrium



Procedure:

A pale orange diluted iron thiocyanate solution is treated alternatively with excess iron(III) or excess thiocyanate.

Observation:

The color gets deep red in both cases.

Explanation:

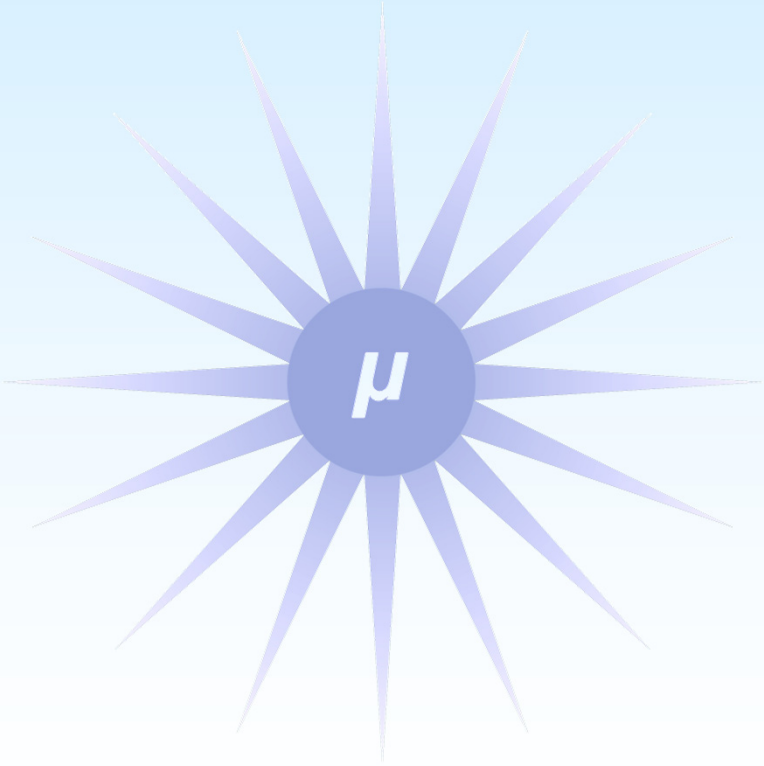
The equilibrium can be described simplifying according to

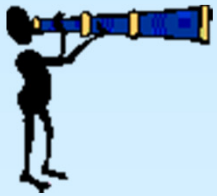
$$[Fe(H_2O)_6]^{3+} + 3\ SCN^- \leftrightarrows [Fe(H_2O)_3(SCN)_3] + 3\ H_2O,$$

the corresponding mass action law is: $\overset{\circ}{K}_C = \dfrac{c([Fe(H_2O)_3(SCN)_3])}{c([Fe(H_2O)_6]^{3+}) \cdot c(SCN^-)^3}$

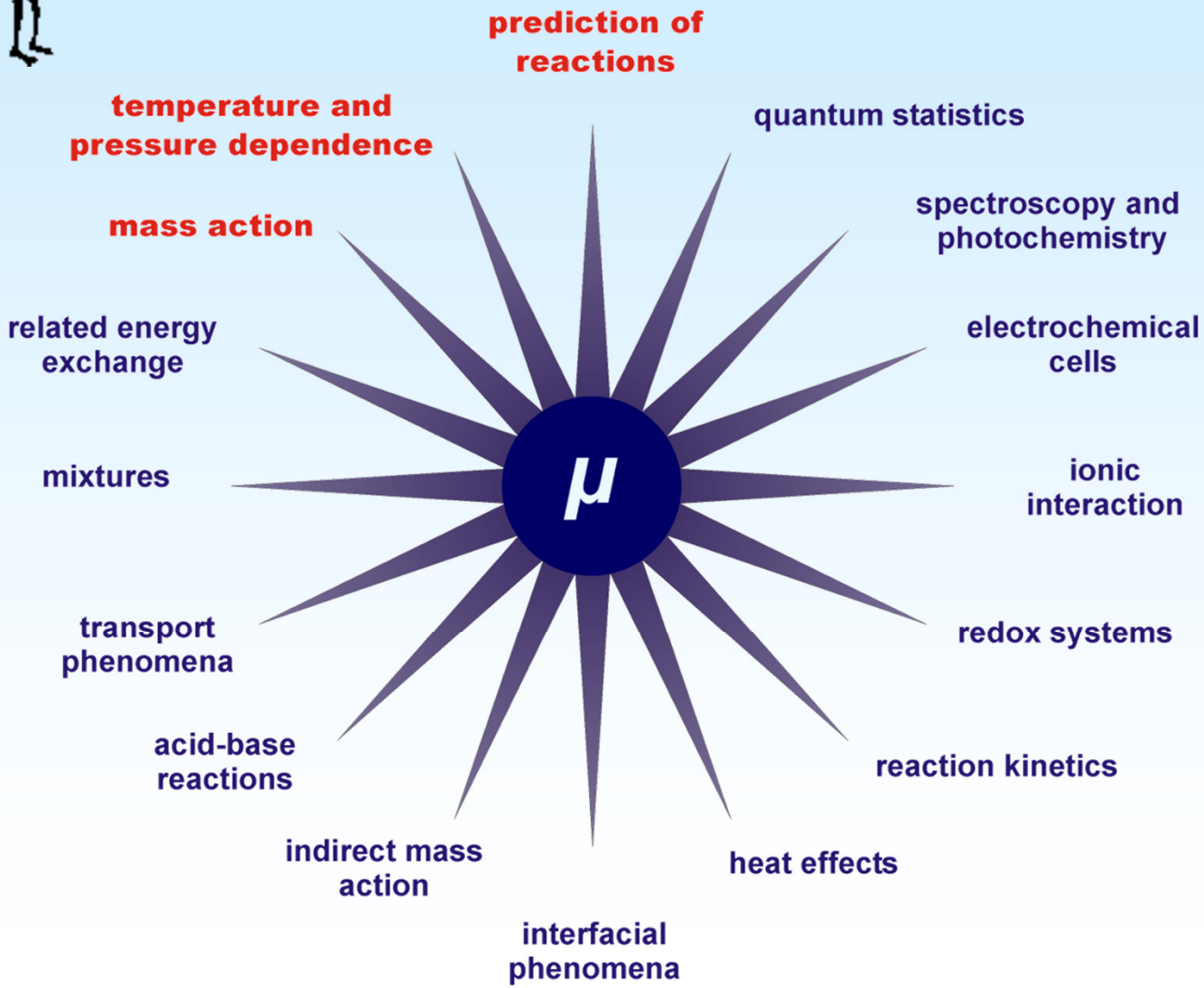
The addition of water shifts the equilibrium in direction of the reactants, that of iron(III) or thiocyanate again in direction of the products.

7. Outlook





Outlook


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

Thank you very much for your friendly attention.

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

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