

# **Teaching Thermodynamics: Chemical Potential from the Beginning**

Lecture in Taormina on 20<sup>th</sup> February 1991

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## Contents

1.	Introduction .....	1
2.	First Basic Assumption .....	4
3.	Descriptive Interpretation of the Basic Assumption .....	5
4.	Linear Equation .....	6
5.	Application in Zeroth Approximation .....	8
6.	Applications in First Approximation .....	9
7.	Second Basic Assumption, Mass Action .....	11
8.	Application of the Mass Action Formula .....	12

# Teaching Thermodynamics: Chemical Potential from the Beginning

Georg Job

Lecture in Taormina on 20th February 1991

**Summary:** Since 1973 a new concept of chemical thermodynamics has been used in the beginner's course of chemistry at the University of Hamburg, in which the chemical potential is introduced in the first lesson.

The course has the following characteristics:

- (1) The affinity of a reaction is introduced by using a direct measuring method (like length, time or mass) using neither energy nor entropy. The chemical potential of a substance is defined as the affinity of the decomposition reaction of this substance into the elements in their standard states.
- (2) The pressure, temperature, concentration dependence of the chemical potential is discussed using only linear functions in the first stage. Logarithmic equations are used in the next stage to describe the mass action of a solute or gaseous substance.
- (3) Various applications are discussed qualitatively and quantitatively: stability of compounds, phase transitions, calculation of melting and boiling points and their dependence on pressure, vapour pressure curve, solubilities and equilibrium constants including their temperature and pressure dependence ... up to MAXWELL'S distribution law of molecular velocities (further colligative properties, diffusion and migration, chemical kinetics, multi-phase systems, elektromotive forces etc. not described here).
- (4) Entropy is introduced only for the description of the thermochemical phenomena (not described here).

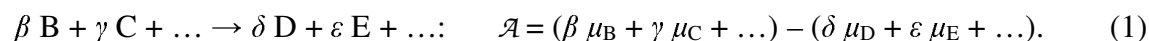
## 1. Introduction

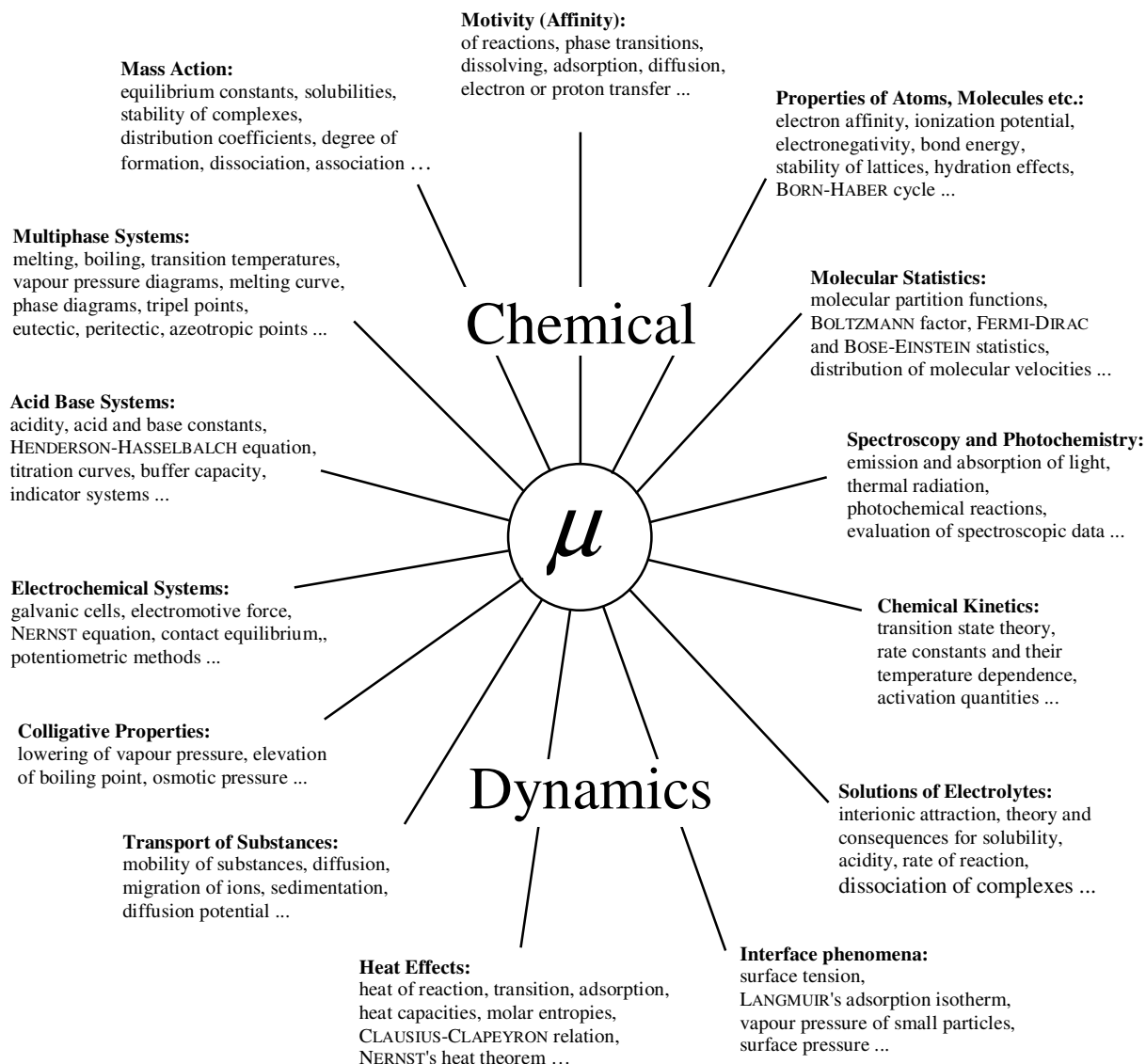
Just like a description of Mesopotamia can begin with Adam and Eve in the Garden of Eden, or *in medias res* with the current events in Iraq, the calculation of chemical reactions can begin with an introduction to the quantum theory and quantum statistics, or *in medias res* with a definition of the chemical potential  $\mu$ .

The most simple way to do so is by using a direct measuring procedure as it is usual for various quantities such as length, time and mass. This method is elementary, does not require any special previous knowledge and immediately leads to results which can be utilized most practically. Even more, it has become evident that by using this method 95 ... 98% of all problems for which a chemist employs thermodynamics or statistics can be accomplished.

In diagram 1 this coherence is represented graphically. Different areas of chemistry are presented in key words which more or less comprise what is understood by the heading "chemical dynamics". The chemical potential  $\mu$  forms the central turntable through which the individual areas can be reached and through which data from all directions can be distributed in all directions. Only the field of "heat effects" belongs to the sphere of thermodynamics in the original sense, constituting only a small fraction of the entire area.

Historically seen, chemical dynamics have been developed from several sides. The oldest approaches had pursued the quantification of the so-called *affinities*  $\mathcal{A}$ . (see diagram 1, upper part) which means from the modern point of view the determination of the potential differences between the reactants and products of a reaction





**Diagram 1:** Areas of chemistry which can be categorized by the heading “Chemical Dynamics”. The chemical potential has a central position in this entire area. Only the field of “heat effects” belongs to thermodynamics in the actual sense (see to the left at the bottom of the diagram).

The first table of affinity values was published in 1786<sup>1</sup>. As only the potential differences are of importance to chemical reactions, only these are chemically measurable. This restriction permits, in the reverse case, to specify the potential values of the elements to a large extent arbitrarily. This can be used to simplify the potential tables<sup>2</sup>.

<sup>1</sup> By GUYTON DE MORVEAU, according to H. KOPP in “Geschichte der Chemie”, Braunschweig (1844), vol. 2, p. 303. Instead of using the notation “affinity”, the more neutral word “motivity” is recommendable. The notation “affinity” for the quantity  $\mathcal{A}$  collides with the normal usage of the word in chemistry. Strictly speaking, it is only useable for reactions of the type  $B + C + D \dots \rightarrow BCD\dots$  and is meaningless for processes such as dissociations, phase transitions and diffusion.

<sup>2</sup> In chemistry only the  $\mathcal{A}$ -values of reactions are used for which 1) the quantities of substance of the elements are preserved (in free or combined states) and 2) the temperatures of the reactants and resultants are the same and 3) the isotopic composition of the elements is not altered.  $\mathcal{A}$ -values of this type are invariant towards the potential transformations  $\mu \rightarrow \mu^\#$ :

$$\mu^\#(A_a B_b C_c \dots, T, \dots) = \mu(A_a B_b C_c \dots, T, \dots) + a \eta(A, T) + b \eta(B, T) + c \eta(C, T) + \dots,$$

whereas  $A_a B_b C_c \dots$  is a compound of the elements A, B, C, ... and  $\eta(E, T)$  is an arbitrary function of the species of the element E, the temperature  $T$  and the isotopic composition of E. If we choose, for example,  $\eta(E, T) = \mu(E, T, p_0)$ , then  $\mu^\#(E, T, p_0) \equiv 0$ . The symbol  $\mu(E, T, p_0)$  represents the potential value in its standard state. Reversely, the  $\mathcal{A}$ -values determined from the  $\mu$ -values are only then uniquely defined if the function  $\eta(E, T)$  has been stipulated in any manner.

In Hamburg we go back to the old approach during the beginners' courses for chemists, by no means for nostalgic reasons, but for pragmatical purposes. Under the given circumstances it is the fastest and the easiest way. In about one lesson, it is possible to reach the chemical potentials and then easily go over to many other areas. How efficiently the process can be organized can be shown in the schedule in diagram 2.

1st lesson:	<b>Motivity (Motive Power) of Chemical Reactions:</b> Definition of quantity $\mathcal{A}$ , preliminary unit, measuring of $\mathcal{A}$ by linkage of reactions, types of reaction linkages (chemical, electrical or mechanical), extent $\zeta$ and turnover $\Delta\zeta$ of a reaction, work of reaction $W = -\mathcal{A} \cdot \Delta\zeta$ , SI unit of $\mathcal{A}$ .
2nd lesson:	<b>Chemical Potential:</b> Descriptive meaning and main attributes, reference states for the elements, values of the chemical potentials, usage of tables, application to reactions and phase transitions.
3rd lesson:	<b>Influence of Pressure and Temperature on Material Conversions:</b> The temperature coefficient of $\mu$ , calculation of melting-, boiling-, transition-, decomposition- and reaction-temperatures; pressure coefficient of $\mu$ , transition under pressure, behaviour of gases under pressure, calculation of vapour pressure curves.
4th lesson:	<b>Mass Action:</b> History and meaning of the term, concentration coefficient of the chemical potential, mass action formula, $\mu(c)$ -curves, standard values of potentials, quantity pH, law of mass action, temperature and pressure dependence of the equilibrium constants.
5th lesson:	<b>Velocity of Chemical Reactions:</b> Rate of reaction for homogeneous and heterogeneous reactions, elementary reactions, transition state, activation, chemical potential of the activated complex, temperature dependence on the rate of reaction.
6th lesson:	<b>Solutions of Electrolytes:</b> Chemical potential of soluted ions, cause for electrolytic dissociation, electrical potential, forces in chemical and electrical potential gradients, mobility of a substance, derivation of the law of diffusion, migration of ions, conductivity.
7th lesson:	<b>Electrochemical Cells:</b> Chemical potential of electrons, reductant oxidant systems, electrical potential difference between different metals and between metals and solutions, electromotive force of galvanic cells, diffusion potential.
8th lesson:	<b>Entropy and Temperature:</b> ..... .....

**Diagram 2:** Example for a schedule used for introductory lectures in “chemical dynamics” for freshmen. This schedule has been used in the University of Hamburg since 1973 in a more or less similar form. Only the first 7...8 lessons (1 lesson  $\hat{=}$  45 minutes) are shown.

To avoid thermodynamics consequently would mean that not only entropy but also the concept of temperature would be omitted. Such a puristic procedure is feasible, but more complicated. The difficulties involved are the same as with mechanics if one tries to determine lengths by means of a measuring rule without presupposing the concept of temperature. Due to the fact that temperature is an unproblematic quantity frequently used in everyday life, we tolerate this quantity from the beginning as a provisional empirical parameter which is later defined within the scope of thermodynamics.

## 2. First Basic Assumption

I would like to present a procedure which immediately leads to the chemical potential. We proceed on the following assumption:

To each substance B, a quantity  $\mu_B$  can be associated which is denoted as the chemical potential of B, with the following attributes:

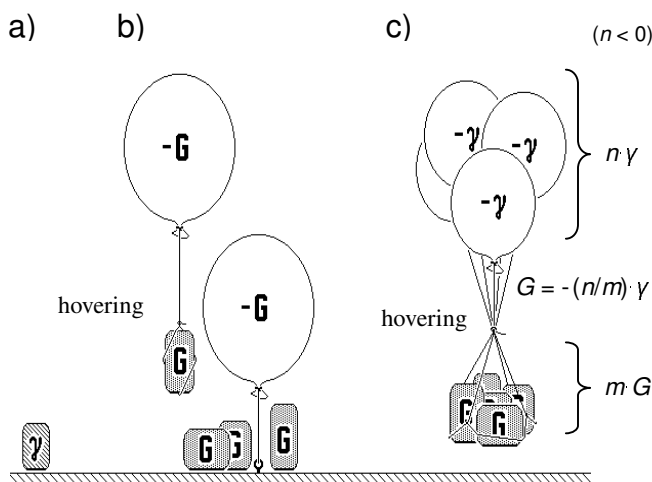
- $\mu_B$  is a scalar quantity which is dependent only on the species and milieu of B.
- If a reaction  $0 = \sum_B \nu_B B$  is in equilibrium, then  $0 = \sum_B \nu_B \mu_B$  is valid.

Some comments on the contents of the sentence:

- The *milieu* of the substance is to be understood as the totality of the parameters which characterize the material surroundings in which the substance is situated: state of aggregation, solvent A, temperature  $T$ , pressure  $p$ , mole fractions  $x_B, x_C \dots$
- The term *reaction* also includes, in a wider sense, phase transition and exchange of substances between adjacent regions.
- We say that a conversion is *equilibrated* when it remains at rest after eliminating possible inhibitions and after excluding possible linkages with other self-proceeding processes (i.e. other reactions, charge displacement in the electrical field, mass shift in the gravitational field etc.).

We know from chemical thermodynamics that the above assumption is correct. The remarkable point in above statement is that the potential differences  $\mathcal{A} = - \sum_B \nu_B \mu_B$ , which are important in chemistry, thus are all determined only requiring a free scale factor. One only needs to stipulate one single  $\mathcal{A}$ -value of a well defined and well reproducible self-proceeding reaction to fix all other  $\mathcal{A}$ -values. The remaining arbitrariness in the  $\mu$ -values can be eliminated by stipulating the  $\mu$ -values for certain reference states. The chemical potentials are thus defined by the above statement, except for some scale transformations which are without significance for the application. Neither entropy nor energy are mentioned here at all!

To prove this, a measuring procedure can be constructed on the lines of the assumed attributes. The procedure (Figures 1 and 2) is conceptually not more difficult than the measurement of weights<sup>3</sup>. The explanation however does take some time so that I better miss it out for the moment since later out of the equations, which one can derive with the help of the chemical potentials, several procedures can be provided to determine the values of the potentials.

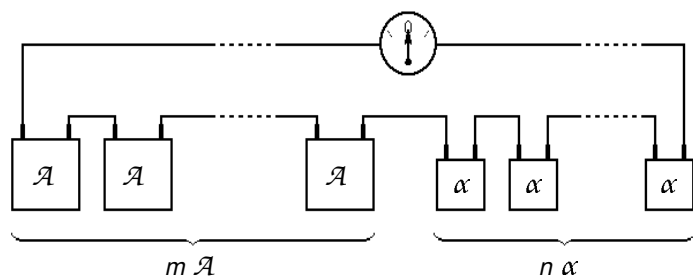


**Figure 1:** Elementary Procedure for the Measuring of Weight

- A body is chosen which is to represent in certain surroundings (for example in air under room conditions) the weight unit  $\mu$
- For the body to be measured with the weight  $G$  further bodies are sought, first, bodies with the weight  $-G$  and then, in addition to these, others with the weight  $+G$  Criterion: two bodies with the oppositely same weight hover when they are linked.  $G_{\text{total}} = G + (-G) = 0$ . The weight unit is duplicated accordingly.
- The body to be measured is linked to so many bodies of the same weight and so many specimens of the positive or negative unit weights until the total weight „zero“ is reached. In this case we find:  

$$G_{\text{total}} = mG + n\gamma = 0 \quad \text{or} \quad G = -(n/m) \cdot \gamma.$$

<sup>3</sup> G. JOB: "Chemische Dynamik I", chimica didact. 8 (1982) 229



**Figure 2:** Measurement of Motivity (Affinity) by Electrical Linkage of Reactions – The cells on the left side represent the value  $\mathcal{A}$  to be measured, the cells on the right side represent the unit  $\alpha$ . If the latter are poled in reverse, their motivities enter into the motivity of the total process with a negative sign. Their number is denoted in this case by a negative  $n$ . Equilibrium is achieved if the circle becomes currentless with a fitting number  $m$  and  $n$  of cells. In this case we find  $\mathcal{A}_{\text{ges.}} = m \cdot \mathcal{A} + n \cdot \alpha = 0$  oder  $\mathcal{A} = -(n/m) \cdot \alpha$ . The measurement can be performed in a similar manner by chemical (by enzymes for example) or mechanical linkage of the reactions.

If required, one can take in consideration the accompanying energy balance and show that the *reaction work*  $W$  for small changes  $\Delta\zeta$  of the extend of reaktion must be proportional to the product  $\mathcal{A}\Delta\zeta$ :  $W \sim \mathcal{A}\Delta\zeta$ . The free scale factor for the  $\mathcal{A}$ -values already mentioned can be chosen in a way that the factor of proportionality becomes + 1 or, so that the energy delivered obtains a negative sign, - 1:

$$W = - \mathcal{A} \Delta\zeta. \quad (2)$$

As the  $\mathcal{A}$ -values and  $\mu$ -values are often used, it is recommendable to use an individual unit for them. We utilize the unit “Gibbs”<sup>4</sup>, abbreviated to “G”:

$$1 \text{ G} = 1 \text{ J mol}^{-1}$$

### 3. Descriptive Interpretation of the Basic Assumption

The above sentence can be used in its abstract form. It is also possible, however, to integrate a descriptive concept. To interpret the quantity  $\mu$  as introduced above, one can assume that every substance has the tendency to vanish by annihilation, by transformation into another form of substance or by spreading in space. In this sense, the quantity  $\mu$  is the quantitative measure for this vanishing, transforming and spreading tendency of a substance.

It is not very difficult to make such facts clear during the first lessons in chemistry<sup>5</sup>. The assumption that all substances have a transformation tendency is not more pretentious than the assumption that all bodies attract each other by gravity. The conclusion that a substance B transforms into a substance C spontaneously,  $B \rightarrow C$ , if B has a greater transformation tendency,  $\mu_B > \mu_C$ , seems obvious. Even the generalization that a reaction  $B + C + \dots \rightarrow D + E + \dots$  proceeds spontaneously if  $\mu_B + \mu_C + \dots > \mu_D + \mu_E + \dots$  is valid, seems almost self-evident<sup>6</sup>.

By means of this description, we can support our first basic assumption by giving it a descriptive form:

<sup>4</sup> At the suggestion of E. WIBERG: “Die chemische Affinität”, 2nd edition., de Gryter, Berlin, New York (1972)

<sup>5</sup> Compare G. JOB: “Das chemische Potential im Physik- und Chemie-Elementarunterricht” in “Konzepte eines zeitgemäßen Physikunterrichts”, vol. 2, Schroedel, Hannover (1978), page 67

<sup>6</sup> The name “chemical potential” is not very descriptive. A notation such as “drive” might be closer to the meaning of “transformation drive” or “spreading drive” of a substance.

a) The tendency of a substance B to react with any other substance, or to transform itself into any other state, or to spread to another place, can be expressed quantitatively by means of only one quantity which we name  $\mu_B$ .

b) The strength of this tendency, that is the value of  $\mu_B$ , is defined by the species of the substance and also by the milieu that is the condition of the material area in which the substance is located.

c) A reaction, transformation or spreading of the substance B proceeds spontaneously after elimination of possible inhibitions, if the tendency to do so is more strongly pronounced in the initial state than in the final state. This means that:

- in case of a reaction, if the total sum of the  $\mu$ -values of all reactants is larger than the total sum of the resultants.
- in case of a transformation, if  $\mu_B$  in the reactant form of B is larger than that of the resultant form.
- in case of a substance transfer, if  $\mu_B$  is larger at the starting point than at the end point.

#### 4. Linear Equation

Because of the assumption b), we can regard  $\mu_B$  as a function of temperature  $T$  and pressure  $p$  and, in the case of soluted substances, also with the composition  $x_B, x_C, \dots$  of the solution:  $\mu_B(T, p, x_B, x_C \dots)$ . As we see chemical potentials as being measurable quantities, these functions for all substances B can be considered as being given. This can be done as an example most simply by giving the Taylor coefficient for a certain choice of reference states  $(T_0, p_0, x_{0,B}, x_{0,C} \dots)$ , especially for the *norm state*<sup>8</sup> usually employed in praxis. If the series is broken off after the linear terms, this leads to the following equation, for example in the case of a soluted substance:

$$\mu_B(T, p, x_B, x_C \dots) = \mu_{0,B} + \alpha_B \Delta T + \beta_B \Delta p + \gamma_B \Delta x_B + \delta_B \Delta x_C + \dots \quad (3)$$

$\mu_0$  means the potential value, further  $\alpha$  the temperature coefficient,  $\beta$  the pressure coefficient,  $\gamma, \delta \dots$  the mole fraction coefficients of the chemical potential, all values in the reference state:

$$\begin{aligned} \mu_{0,B} &= \mu_B(T_0, p_0, x_{0,B}, x_{0,C} \dots), \\ \alpha_B &= \frac{\partial \mu_B}{\partial T}(T_0, p_0, x_{0,B}, x_{0,C} \dots), \quad \beta_B = \frac{\partial \mu_B}{\partial p}(T_0, p_0, x_{0,B}, x_{0,C} \dots) \quad \text{etc..} \end{aligned}$$

For moderate requirements regarding precision, the range of application is roughly:

$$\begin{aligned} |\Delta T| &\ll 10^3 \text{ K}, \\ |\Delta p| &\ll 10^9 \text{ Pa} \quad \text{for condensed substances}, \quad |\Delta p| \ll p_0 \quad \text{for gases.} \\ |\Delta x| &\ll x_0. \end{aligned} \quad (4)$$

Table 1 shows examples for the values of the coefficients. The following rules are of use for qualitative considerations<sup>7</sup>:

$$\begin{aligned} 0 > \alpha_{B|c} > \alpha_{B|l} \approx \alpha_{B|A} \gg \alpha_{B|g}, & \quad 0 < \gamma_{B|c} < \gamma_{B|l} = \gamma_{B|g} \ll \gamma_{B|A}, \\ 0 < \beta_{B|c} < \beta_{B|l} \approx \beta_{B|A} \ll \beta_{B|g}, & \quad 0 \approx \delta_{B|A}. \end{aligned} \quad (5)$$

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<sup>7</sup> Index lc read "in crystalline state" or abbr. "solid" symbol << read "distinctly smaller than"  
 lg read "in gaseous state" or abbr. "gaseous" <<< read "much smaller than"  
 ll read "in liquid state" or abbr. "liquid" >> read "distinctly larger than"  
 lA lies "solved in A" or abbr. "in A", ≈ read "of same magnitude as"



Table 1: Chemical Potentials in the Norm State<sup>8</sup>

$\alpha$  temperature coefficient,  $\beta$  pressure coefficient,  $\gamma$  mole fraction coefficient; 1 G = 1J mol<sup>-1</sup>. For the zero level of the potential scale in all temperature ranges the pure elements were chosen in their natural isotopic compositions and their stable modifications under normal pressure.

Substance	State	Formula	$\frac{\mu}{\text{kG}}$	$\frac{\alpha}{\text{GK}^{-1}}$	$\frac{\beta}{10^{-6}\text{GPa}^{-1}}$	$\frac{\gamma}{\text{kG}}$
<i>Solids</i>						
Graphite	solid	C	0	0	5,4	2,48
Diamond	solid	C	2,9	3,3	3,4	2,48
Quicklime	solid	CaO	-604,2	104,3	16,5	2,48
Table salt	solid	NaCl	-384,0	67,9	27,0	2,48
Ice	solid	H <sub>2</sub> O	-236,6	188,3	19,7	2,48
Silver oxide	solid	Ag <sub>2</sub> O	-11,2	66,3	32,4	2,48
Limestone	solid	CaCO <sub>3</sub>	-1128,8	261,9	36,9	2,48
Cane sugar	solid	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	-1543,5	2272,3	217,0	2,48
Spruce	solid	C <sub>0,32</sub> H <sub>0,47</sub> O <sub>0,21</sub>	≈ -10		≈ 10	2,48
<i>Liquids</i>						
Mercury	liquid	Hg	0	0	14,8	2,48
Water	liquid	H <sub>2</sub> O	-237,2	163,2	18,1	2,48
Ethanol	liquid	C <sub>2</sub> H <sub>6</sub> O	-174,7	344,9	58,8	2,48
<i>Gases</i>						
Oxygen	gaseous	O <sub>2</sub>	0	0	24465	2,48
Carbon dioxide	gaseous	CO <sub>2</sub>	-394,4	-3,0	24465	2,48
Ammonia	gaseous	NH <sub>3</sub>	-16,4	99,0	24465	2,48
Stream	gaseous	H <sub>2</sub> O	-228,6	44,4	24465	2,48
Ethin	gaseous	C <sub>2</sub> H <sub>2</sub>	+209,2	-58,9	24465	2,48
Ethanol	gaseous	C <sub>2</sub> H <sub>6</sub> O	-168,6	223,6	24465	2,48
Air	gaseous	N <sub>1,56</sub> O <sub>0,42</sub> Ar <sub>0,01</sub>	-1,4	-4,7	24465	2,48
<i>Solutes</i>						
Oxygen	in water	O <sub>2</sub>	+16,4	95,6	≈ 10 <sup>1</sup>	137,59
Ammonia	in water	NH <sub>3</sub>	-26,6	180,3	24,1	137,59
Carbon dioxide	in water	CO <sub>2</sub>	-386,0	91,1	≈ 10 <sup>1</sup>	137,59
Cane sugar	in water	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	-1552		219,9	137,59
Oxygen	in ethanol	O <sub>2</sub>	+12,6		≈ 10 <sup>1</sup>	53,81
<i>Aqueous ions</i>						
Hydrogen(I)	in water	H <sup>+</sup>	0	0	0,2	137,59
Sodium(I)	in water	Na <sup>+</sup>	-261,9	-72,8	-1,6	137,59
Calcium(II)	in water	Ca <sup>2+</sup>	-553,0	-33,8	-17,7	137,59
Chloride	in water	Cl <sup>-</sup>	-131,3	120,3	18,0	137,59
Carbonate	in water	CO <sub>3</sub> <sup>2-</sup>	-527,9	500,7	-3,5	137,59

<sup>8</sup> Norm state means: temperature  $T^\ominus = 298.15$  K, pressure  $p^\ominus = 101325$  Pa, and

a) mole fraction  $x^\ominus = 1$  for substances regarded as pure or mixed (i.e. understood as equal partners in a mixture) or as solvents

b) molality  $b^\ominus = 1$  mol/kg for solutes, which corresponds to a reference value  $x^\ominus_A = b^\ominus M_A$  dependent on the solvent. As an example: for water as a solvent the reference value is  $x^\ominus(\text{H}_2\text{O}) = 0.01802$ .

The fact that  $\alpha$  and  $\beta$  are related to the molar entropy and the molar volume of a substance<sup>9</sup> is without importance for numerical calculations, so that there is no reason to discuss this subject at this point.

## 5. Application in Zeroth Approximation

It is sufficient to regard the chemical potentials as constant if we limit the conditions not to deviate too far from the norm state. This are reactions taking place at room temperature and under normal pressure between substances which are more or less pure or in solutions of usual concentration (magnitude  $1 \text{ kmol m}^{-3}$ ). Already in this zeroth approximation many useful deductions are possible.

(1) **Stability of Compounds:** As we have equated arbitrarily the potentials of the elements in their stable modifications to zero, the potential  $\mu(A_a B_b C_c \dots)$  of a compound  $A_a B_b C_c \dots$  of the elements A, B, C ... describes the strength of the decomposing tendency – the “decomposing drive” – of the compound into the elements (in their stable modifications):

$$A_a B_b C_c \dots \rightarrow a A + b B + c C + \dots, \quad \mathcal{A} = \mu(A_a B_b C_c \dots) - \underbrace{a \mu_A - b \mu_B - c \mu_C - \dots}_{0}$$

Substances with a negative potential, that means with a negative decomposing tendency are thus stable against a decomposition into elements. On the contrary they are formed spontaneously out of the elements.

(2) **Stability of Phases:** The state of aggregation or modification with the lowest chemical potential is the most stable one. Under room conditions carbon is stable as graphite, water and ethanol are stable as liquids:

$$\mu/\text{kG}: \quad \begin{array}{ccc} \text{Diamant} \rightarrow \text{Graphit} & \text{H}_2\text{Olc} \rightarrow \text{H}_2\text{Oll} \leftarrow \text{H}_2\text{Olg} & \text{C}_2\text{H}_6\text{Oll} \leftarrow \text{C}_2\text{H}_6\text{Olg} \\ 2,9 > 0 & -236,9 > -237,2 < -228,6 & -174,7 < -168,6 \end{array}$$

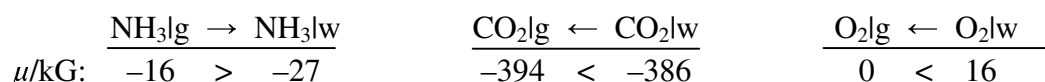
(3) **Prediction of Reactions:** To be able to decide whether a chemical reaction can proceed spontaneously or not, it is sufficient to compare the sums of the potentials in the initial and final state. Two examples may illustrate the procedure, e.g. the absorption of carbon dioxide by quicklime and the combustion of ethanol:

$$\mu/\text{kG}: \quad \begin{array}{ccc} \text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3 & \text{C}_2\text{H}_6\text{Oll} + 3 \text{O}_2 \rightarrow 2 \text{CO}_2 + 3 \text{H}_2\text{Oll} \\ \underbrace{-604 \quad -394}_{-998} > \underbrace{-1129} & \underbrace{-175 \quad 3 \cdot 0}_{-175} > \underbrace{2 \cdot (-394) \quad 3 \cdot (-237)}_{-1499} \\ \mathcal{A} = 131 \text{ kG}, & \mathcal{A} = 1324 \text{ kG}. \end{array}$$

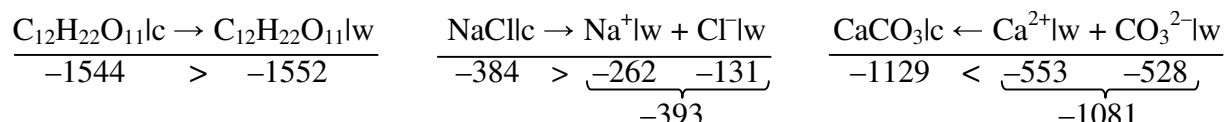
Both processes thus have a strong motivity  $\mathcal{A}$ . If the gases are mixed with other gases (such as oxygen in the air) or with each other (in comparable quantities), then their potentials are slightly lower (by some kG). Due to the high  $\mathcal{A}$ -values ( $\mathcal{A} \gg 10 \text{ kG}$ ), such small deviations are not of importance. Equally, the motivity does not change significantly if the corresponding vapours are utilized instead of the liquid ethanol or liquid water:  $\mathcal{A} = 1308 \text{ kG}$ .

<sup>9</sup> For the values in the table:  $-\alpha = \Delta_B S_B$  (molare entropie of formation of B),  $\beta = V_B$  (molare volumen of B).

(4) **Dissolving Processes:** Comparison of the potential values in the pure and the solute state directly shows that ammonia easily dissolves in water, whereas carbon dioxide and oxygen on the other hand have the tendency to volatilize out of aqueous solutions<sup>10</sup>:



Likewise, it can be recognized that sugar and common salt are soluble in water, whereas lime is not. Reversely, lime precipitates when calcium ions and carbonate ions meet:



## 6. Applications in First Approximation

Of course, if we for more accuracy consider the dependence of the potentials on temperature, pressure and mole fraction, this allows further conclusions. If we limit ourselves to linear equations, the numerical results are not particularly exact, but in many cases still quite useable. We look at the four above-mentioned areas once again.

(1) **Stability of Compounds:** A compound which is stable at room temperature need not to be so under other conditions. Silver oxide has a small negative potential  $\mu$ , whereas the temperature coefficient  $\alpha$  is strongly positive. If the oxide is heated up, consequently the sign of the potential is reversed and the compound becomes instable. The decomposition temperature  $T_Z$ , at which the potential just disappears, is easily calculated:

$$\mu = \mu_0 + \alpha \cdot \Delta T = 0 \quad \text{or} \quad T_Z = T_0 - \frac{\mu_0}{\alpha} \quad (6)$$

With real values substituted into this equation, the result is  $T_Z = 298 \text{ K} - (-11,2 \text{ kG}/66,3 \text{ GK}^{-1}) = 467 \text{ K}$  (measured 455 K). The same calculation, applied to ammonia or water vapour, results in decomposition temperatures of 467 and 5450 K (actually 456 and 4310 K). The result for water is found to be far outside the extent of the validity of the linear equation ( $\Delta T \ll 10^3 \text{ K}$ ), nevertheless it is fairly correct.

(2) **Stability of Phases:** Similar to the decomposition temperatures, the phase transition temperatures can be calculated approximately. To determine the boiling temperature  $T_V$  of ethanol, we proceed on the condition that the potential of liquid and vapour are equal,  $\mu_{\text{ll}} = \mu_{\text{lg}}$  or

$$\mu_{0\text{ll}} + \alpha_{\text{ll}} \cdot \Delta T = \mu_{0\text{lg}} + \alpha_{\text{lg}} \cdot \Delta T \quad \text{or} \quad T_V = T_0 - \frac{\Delta \mu_0}{\Delta \alpha} \quad (7)$$

With the values substituted, the result is  $T_V = [298 - \frac{(-168600) - (-174700)}{223,6 - 344,9}] \text{ K} = 348 \text{ K}$  (actually 351 K). Similarly, the result for the freezing point and the boiling point of water is  $T_F = 274 \text{ K}$  and  $T_V = 370 \text{ K}$ . We can obtain the pressure dependence of the transition points in the first approximation if we substitute  $\mu_0 + \beta \cdot \Delta p$  in the last equation for  $\mu_0$ . The equation for the fusion curve is for example:

$$T_F = T_0 - \frac{\Delta \mu_0 + \Delta \beta \Delta p}{\Delta \alpha} \quad (8)$$

<sup>10</sup> Symbol  $|\text{w}$  read "dissolved in water" or abbr. "in water"

(3) **Prediction of Reactions:** Procedures during which gases are formed out of condensed substances are favoured by a temperature increase and handicapped by a pressure increase. In the first case, the motivity increases, in the latter it decreases. This is a result of the previously mentioned rules (5),  $\alpha_{\text{B|c}} > \alpha_{\text{B|l}} \gg \alpha_{\text{B|g}}$  and  $\beta_{\text{B|c}} < \beta_{\text{B|l}} \ll \beta_{\text{B|g}}$ , according to which the temperature coefficient of the chemical potential of gases is distinctly lower than that of condensed substances, whereas the pressure coefficient is very much higher. This is why any changes in this parameters have an especially strong effect on gases. The decomposition process



does not proceed at room temperature due to the negative motivity. We expect the process to commence at a sufficiently high temperature, because in this case a gas is produced. The temperature coefficient  $\alpha$  and the pressure coefficient  $\beta$  of the motivity  $\mathcal{A} = -\sum_{\text{B}} \nu_{\text{B}} \mu_{\text{B}}$  of a reaction  $0 = \sum_{\text{B}} \nu_{\text{B}} \text{B}$  is calculable according to

$$\alpha = -\sum_{\text{B}} \nu_{\text{B}} \alpha_{\text{B}}, \quad \beta = -\sum_{\text{B}} \nu_{\text{B}} \beta_{\text{B}} \quad (9)$$

The reviewed case results in  $\alpha = \alpha(\text{CaCO}_3) - \alpha(\text{CaO}) - \alpha(\text{CO}_2) = 161 \text{ G K}^{-1}$ . The temperature  $T_Z$  at which motivity  $\mathcal{A}$  changes its sign, and at which the carbonate begins to decompose, can be obtained out of the equation

$$\mathcal{A} = \mathcal{A}_0 + \alpha \cdot \Delta T = 0 \quad \text{oder} \quad T_Z = T_0 - \frac{\mathcal{A}_0}{\alpha}. \quad (10)$$

If the  $\mathcal{A}_0$ - and the  $\alpha$ -values are substituted into the equation, the result is  $T_Z = 1110 \text{ K}$  (measured 1195 K). The decomposition is promoted by lowering the pressure. To calculate the influence of pressure it is sufficient to substitute  $\mathcal{A}_0$  in the last equation by  $\mathcal{A}_0 + \beta \cdot \Delta p$ . However, if gases are involved in the reaction, the range of application for this linear formula is only very limited:  $\Delta p \ll p_0$ .

(4) **Dissolving Processes:** The solution tendency of a gas B in a solvent A is strongly increased by pressure, due to the rule (5)  $\beta_{\text{B|A}} \ll \beta_{\text{B|g}}$ . Similarly, by comparing the  $\beta$ -values, we can see,

$$\beta / (10^{-6} \text{ G Pa}^{-1}) \quad \begin{array}{c} \text{NaCl|c} \rightarrow \text{Na}^+|\text{w} + \text{Cl}^-|\text{w} \\ 27 \quad \underbrace{-2 \quad 18}_{16} \\ \beta = 11 \cdot 10^{-6} \text{ G Pa}^{-1} \end{array} \quad \begin{array}{c} \text{CaCO}_3|\text{c} \leftarrow \text{Ca}^{2+}|\text{w} + \text{CO}_3^{2-}|\text{w} \\ 37 \quad \underbrace{-18 \quad -4}_{-22} \\ \beta = 59 \cdot 10^{-6} \text{ G Pa}^{-1} \end{array}$$

that increased pressure promotes the dissolution of sodium chloride as well as of calcium carbonate. If the rule  $\alpha_{\text{B|A}} \gg \alpha_{\text{B|g}}$  is used, we have to take more care since the tabulated value is only valid for a molality of  $1 \text{ mol kg}^{-1}$ . In contrast to the pressure coefficient  $\beta_{\text{B|A}}$  the temperature coefficient  $\alpha_{\text{B|A}}$  for the solute drops distinctly when the concentration becomes lower, so that the coefficient in question can fall below the temperature coefficient  $\alpha_{\text{B|g}}$  for the gas. Such problems can easily be solved by methods described in the next paragraph.

## 7. Second Basic Assumption, Mass Action

When comparing the values in the table, it is evident that the pressure coefficient  $\beta_{\text{B|g}}$  has the same value for all gases. Equally, the mole fraction coefficients  $\gamma_{\text{B|c}} = \gamma_{\text{B|l}} = \gamma_{\text{B|g}}$  are the same for all substances in their pure state ( $x = 1$ ) also the mole fraction coefficients  $\gamma_{\text{B|A}}$  are equal for all solutes B in the same solvent A.

This regularity is the expression of a common basic structure of the coefficients, in which the same temperature function<sup>11</sup>  $RT$  appears:

$$\beta = RT/p \quad \text{for gases} \quad \left. \vphantom{\beta = RT/p} \right\} \text{for small concentrations,} \quad (11)$$

$$\gamma = RT/x \quad \text{for solutes} \quad \left. \vphantom{\gamma = RT/x} \right\} \quad (12)$$

$$\gamma = RT/x \quad \text{for solvents for } x \approx 1. \quad (13)$$

The quantity  $R = 8.314 \text{ G K}^{-1}$  is to be understood as a natural constant defined by the above equations. Since our intention is to start out from central assumptions which allow quick application, the question whether and how these relations can be summarized or whether they can be led back to a more general principle is deferred here. The validity of the above equations is the basis of all further deductions.

The above relations express the phenomenon, which chemists call *mass action*, as a characteristic of the chemical potential. By integration, we obtain a series of equations which we call the *mass action formulas*:

$$\mu = \mu_0 + RT \ln(p/p_0) \quad \text{for gases} \quad \left. \vphantom{\mu = \mu_0 + RT \ln(p/p_0)} \right\} \text{for small concentrations,} \quad (14)$$

$$\mu = \mu_0 + RT \ln(x/x_0) \quad \text{for solutes} \quad \left. \vphantom{\mu = \mu_0 + RT \ln(x/x_0)} \right\} \quad (15)$$

$$\mu = \mu_0 + RT \ln(x/x_0) \quad \text{for solvents for } x, x_0 \approx 1. \quad (16)$$

These equations are used in many modifications. For example, in ideal gases where, due to the proportionality of pressure and concentration,  $c \sim p$ , the quotient  $p/p_0$  can be substituted by  $c/c_0$  or, in gas mixtures, the variables  $p$  and  $x_{\text{B}}$  can be comprised to a partial pressure  $p_{\text{B}} = p x_{\text{B}}$ ,

$$\mu = \mu_0 + RT \ln(p/p_0) + RT \ln(x/x_0) = \mu_0 + RT \ln(p_{\text{B}}/p_{0,\text{B}}). \quad (17)$$

For small concentrations  $c$  of a dissolved substance, the mole fraction  $x$ , mass fraction  $w$ , molarity  $b$ , etc. are all in proportion to one another,  $c \sim x \sim w \sim b \sim \dots$ . Therefore, the quotient  $x/x_0$  can be substituted by quotients of the other quantities,

$$x/x_0 = c/c_0 = w/w_0 = b/b_0 = \dots \quad \text{for small concentrations.}$$

If  $x_0 = 1$  and  $x = 1 - x_{\text{F}}$  are substituted into equation (16), whereby  $x_{\text{F}} \ll 1$  denotes the mole fraction of all foreign substances contained in the solvent, it becomes a linear relation:

$$\mu = \mu_0 - RT x_{\text{F}}. \quad (18)$$

This equation would have to be used if the osmotic pressure, the lowering of freezing point or other colligative properties are to be calculated.

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<sup>11</sup> If the empirical temperature  $\vartheta$  is chosen to avoid using the thermodynamic temperature  $T$  in advance, the quantity  $RT$  is to be substituted by a coefficient  $R(\vartheta)$  which must be measured and tabulated for different temperatures  $\vartheta$ .

## 8. Application of the Mass Action Formula

(1) **Law of Mass Action:** The most important application is the derivation of the *law of mass action*. Once more, we will look at the dissolution of calcium carbonate as a concrete example, while we will start from the tabulated norm values of the molality  $b_0 = 1 \text{ mol kg}^{-1}$  to calculate the potentials:

	1	→	2	+	3	
	$\text{CaCO}_3 \text{c}$		$\text{Ca}^{2+} \text{w}$		$\text{CO}_3^{2-} \text{w}$	
$\mu_0/\text{kG}$ :	- 1129		- 553		- 528	$\mathcal{A}_0 = - 48 \text{ kG}$
$\alpha/(\text{G K}^{-1})$	262		- 34		501	$\alpha = - 205 \text{ GK}^{-1}$ ,
$\beta/(10^{-6} \text{ G Pa}^{-1})$	37		- 18		- 4	$\beta = + 59 \cdot 10^{-6} \text{ G Pa}^{-1}$ .

As an abbreviation of the notation, we consider the substances as numbered. In equilibrium the motivity vanishes:

$$\begin{aligned} \mathcal{A} &= \mu_1 - \mu_2 - \mu_3 = \mu_{1,0} - [\mu_{2,0} + RT \ln(b_2/b_0)] - [\mu_{3,0} + RT \ln(b_3/b_0)] \\ &= \mathcal{A}_0 - RT \ln(b_2 b_3 / b_0^2) = 0. \end{aligned}$$

Solving for the product  $b_2 b_3$  the law of mass action for this process is derived,

$$b(\text{Ca}^{2+}) \cdot b(\text{CO}_3^{2-}) = \mathcal{K} \quad \text{with} \quad \mathcal{K} = b_0^2 e^{\mathcal{A}_0/RT} = 4 \cdot 10^{-9} \text{ mol}^2 \text{ kg}^{-2}.$$

For the molality  $b_s$  of the saturated solution, the following is valid:

$$b_s = \sqrt{\mathcal{K}} = b_0 e^{\mathcal{A}_0/(2RT)} = 6 \cdot 10^{-5} \text{ mol kg}^{-1}.$$

We get the pressure and temperature dependence of the solubility, if the exponent  $\mathcal{A}_0$  is substituted by  $\mathcal{A}_0 + \alpha \Delta T + \beta \Delta p$ . For boiling water or for a pressure of  $10^8 \text{ Pa}$  found in deep sea rift valleys we calculate the solubility of calcium carbonate to be:

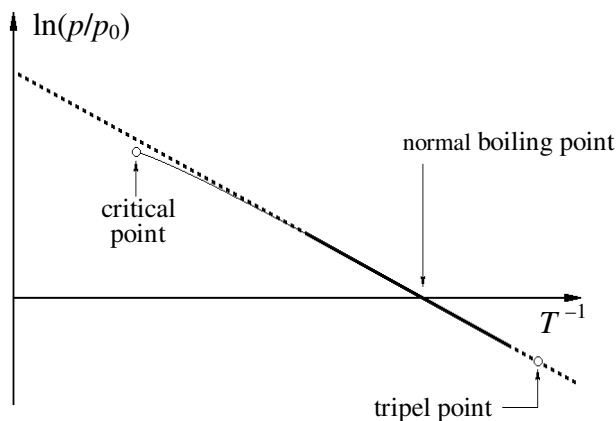
$$\begin{aligned} \mathcal{A} &= - 63 \text{ kG}, & b_s &= 4 \cdot 10^{-5} \text{ mol kg}^{-1} & \text{bei } 100 \text{ }^\circ\text{C}, \\ \mathcal{A} &= - 42 \text{ kG}, & b_s &= 21 \cdot 10^{-5} \text{ mol kg}^{-1} & \text{bei } 1000 \text{ bar}. \end{aligned}$$

(2) **Vapour Pressure Curve:** To calculate the vapour pressure of a liquid, we revert to the condition  $\mu_{\text{ll}}(p) = \mu_{\text{lg}}(p)$ . Because the pressure coefficient  $\beta_{\text{ll}}$  of the liquid is small against the pressure coefficient  $\beta_{\text{lg}}$  of the vapour,  $\beta_{\text{ll}} \ll \beta_{\text{lg}}$ , the potential of the liquid can be regarded as independent of pressure:

$$\mu_{0\text{ll}} = \mu_{0\text{lg}} + RT \ln(p/p_0) \quad \text{or, solved for } p, \quad p = p_0 \cdot e^{-\Delta\mu_0/(RT)}.$$

If the expression  $\Delta\mu_0 = \mu_{0\text{lg}} - \mu_{0\text{ll}}$  is substituted by  $\Delta\mu_0 + \Delta\alpha\Delta T$ , it results in the vapour pressure formula of the common type but of an unusual notation (figure 3).

$$p = p_0 \cdot \exp\left(-\frac{\Delta\mu_0 + \Delta\alpha\Delta T}{RT}\right). \quad (\text{vapour pressure formula}) \quad (19)$$

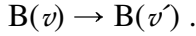


**Figure 3:** Vapour pressure curve as observed (thin line) and as calculated from equation (19) (thick line). The point of intersection with the  $T^{-1}$  axis indicates the normal boiling point, if  $p_0$  is the normal pressure.. To replace  $\mu$  and  $\alpha$  by enthalpies and entropies as usual does neither simplify the formula nor does it extend its range of application.

(3) **Freezing of a molecular vibration:** As a simple example we take a diatomic gas B and consider all gas particles, being in the same state of vibration with the vibrational quantum number  $v$ , as molecules of a substance  $B(v)$  and the entire gas as a mixture of these substances<sup>12</sup>. Since the different substances  $B(v)$  are not distinguishable chemically, we assign to them the same standard potential  $\mu_0$ . The different energies in the different states of vibration  $v$  are taken into account by a corresponding term. For sake of simplicity we regard the vibration as harmonic:

$$\mu_0(v) = \mu_0(0) + N_A h\nu \cdot v .$$

Changes of the state of vibration caused by collisions between the particles appear as reactions of the following type



All these reactions will be in equilibrium within a short period of time. The chemical potential  $\mu$  becomes identical for all substances,  $\mu = \mu(v) = \mu(0)$ , which means, if we take the mass action formula into consideration for  $\mu(v)$  and  $\mu(0)$ :

$$\mu = \mu_0(0) + N_A h\nu \cdot v + RT \ln \frac{c(v)}{c_0} = \mu_0(0) + RT \ln \frac{c(0)}{c_0} . \quad (20)$$

By resolving the equation for  $c(v)$  we obtain  $c(v) = c(0) q^v$  with  $q = e^{-h\nu/kT} < 1$ .

By summing up all  $c(v)$  we derive for the total concentration  $c$  of gas B:

$$c = \sum_{v=0}^{\infty} c(0) \cdot q^v = c(0) \cdot \frac{1}{1-q} = \frac{c(0)}{1-e^{-h\nu/(kT)}} .$$

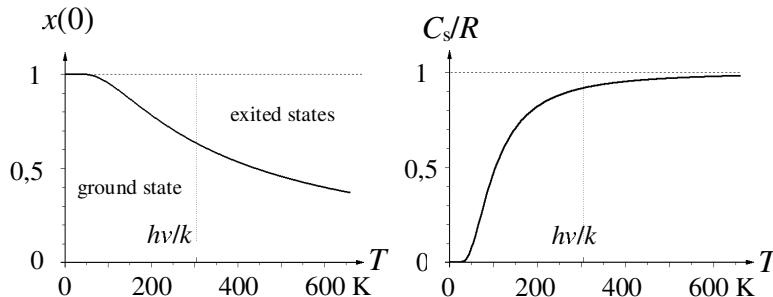
$[1 - e^{-h\nu/(kT)}]^{-1}$  is the partition function for a linear harmonic vibrator. For the fraction  $x(0) = c(0)/c$  of the molecules  $B(0)$  in the ground state we find (figure 4a):

$$x(0) = 1 - e^{-h\nu/(kT)} . \quad (21)$$

If we reversely introduce  $c(0) = c \cdot x(0)$  into equation (20) we obtain beside the two terms  $\mu_0(0)$  and  $RT \ln(c/c_0)$  one term that describes the contribution  $\mu_s(T)$  of the molecular vibration to the chemical potential of B:

$$\mu_s(T) = RT \ln(1 - e^{-h\nu/kT}) .$$

By derivation once or twice with respect to  $T$  we may derive a relation for the contribution of the molecular vibration to the molar entropy  $S_s = -d\mu_s/dT$ , or to the molar heat capacity  $C_s = -T(d^2\mu_s/dT^2)$  respectively (figure 4b). However, in chemical dynamics these quantities are of minor importance and will therefore not be treated within the scope of the course presented here.



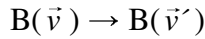
**Figure 4:** Freezing of a molecular vibration. a) Left side: The curve shows for  $I_2$  vapour the fraction  $x(0)$  of the number of molecules in the ground state of vibration ( $v = 0$ ) related to the total number of  $I_2$  molecules. For temperatures below 50 K practically all molecules are in the ground state. b) Right side: Contribution  $C_s$  of the molecular vibration to the molar heat capacity of  $I_2$  vapour.

<sup>12</sup> To regard substances as equilibrium mixtures as above has a long tradition [see for instance A. EINSTEIN, Verhandlungen der Deutschen Physikalischen Gesellschaft **12** (1914) 820].

(4) **Maxwell's Distribution Law of Molecular Velocities:** To determine the distribution of the molecular velocities in a gas, we regard all particles with the same velocity  $\vec{v}$  as molecules of a substance  $B(\vec{v})$  and the entire gas as a mixture of many such substances.<sup>13</sup> Since particles which are moving in different directions are not distinguishable chemically, we assign to them the same standard potential  $\mu_0$ . Different energies in different velocities  $v = |\vec{v}|$  are taken into account by a corresponding term<sup>14</sup>:

$$\mu_0(\vec{v}) = \mu_0(0) + \frac{1}{2}Mv^2.$$

The velocity modifications, caused by multiple collisions between each other or with the walls, appear as a reaction of the following type:



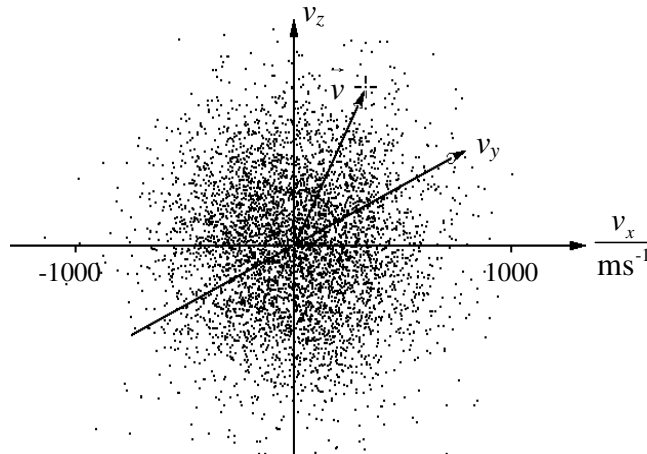
If we do not disturb the gas by stirring it or by other interventions, then all these reactions will be in equilibrium within a short period of time. The chemical potential becomes identical for all substances  $B(\vec{v})$ ,  $\mu(\vec{v}) = \mu(0)$ , which means that if we take the mass action formula into consideration

$$\mu(\vec{v}) = \mu_0(0) + \frac{1}{2}Mv^2 + RT \ln \frac{c(\vec{v})}{c_0} = \mu_0(0) + RT \ln \frac{c(0)}{c_0}.$$

If the equation is resolved for  $c(\vec{v})$ , we attain the distribution law:

$$c(\vec{v}) = c(0) \cdot \exp\left(-\frac{1/2Mv^2}{RT}\right) = c(0) \cdot e^{-\frac{m(v_x^2+v_y^2+v_z^2)}{2kT}}.$$

If we plot the concentration  $c(\vec{v})$  of the particles with equal velocity  $\vec{v}$  as point density in the three-dimensional velocity space, we get a spherical point cloud shown in figure 5.



**Figure 5:** Distribution of Velocities of Nitrogen Molecules at 298 K

<sup>13</sup> To be exact, the number of the particles which have exactly the same velocity  $\vec{v}$  is zero. Therefore, we have to imagine the space of velocity as split up into a cubic lattice with an edge length of  $\Delta v$  in which  $\Delta v$  is to be small against the width of the velocity distribution.  $\Delta v = 1$  m/s for room air is a usable value. We can regard all particles for which the velocity vectors end within such a cube as molecules of the same substance  $B(\vec{v})$ . As argument  $\vec{v}$  the velocity vector which points to the center of the cube is chosen.

<sup>14</sup> Strictly speaking, this potential is no longer purely chemical but a *mechanochemical* one, which corresponds to the electrochemical potential. Impulse  $\vec{p}$  and velocity  $\vec{v}$  appear instead of charge  $q$  and electrical potential  $\phi$ .