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An elementary approach to quantum statistical problems (II)

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Summary: The first subject treated here – namely mono- and multiple-layer adsorption – furnishes a vivid model of the population of single particle quantum states with fermions and bosons. Based on this, an approach to the elementary solution of quantum statistical problems of this kind can be derived as well. The equations describing the translational contributions to chemical potential, entropy, energy and specific heat of a dilute gas are important subsidiary results. Again, as in Part I, we essentially need only the chemical potential and its dependence upon concentration and energy to treat adsorption as well as systems of fermions and bosons. The central aspect of this paper is the problem of the transition from macroscopic to microscopic systems.

Introduction

In many branches of physics and in chemistry especially, we have become used to a constant interplay of macroscopic and microscopic, inter- and intramolecular, viewpoints. In his work, a chemist mentally grasps the processes on the basis of atomistic images. Then he derives rules for his pratical actions from these images (Figure 1). The goal is to combine all the different aspects into a unified image with whose help the transition between various levels can be achieved without stumbling. Sometimes the goal is achieved. The formula H_2O denotes both an unstructured substance, as well as a particle having a certain shape. It describes both an assembly of molecules, as well as a specific union of three atoms. The viewpoint depends upon the setting in which the formula appears, or into which it has been placed mentally. In dynamics, however, the goal is rarely achieved. For phenomena of the macroscopic world, we make use of thermodynamics. Molecular statistics is applied for interactions between molecules, and quantum mechanics describes intramolecular forces. These theories are so different that the transition from one level to another is very cumbersome. Scientists therefore are content often with qualitative rules that allow some orientation. The derivation and application of quantitative relations is left to specialists.
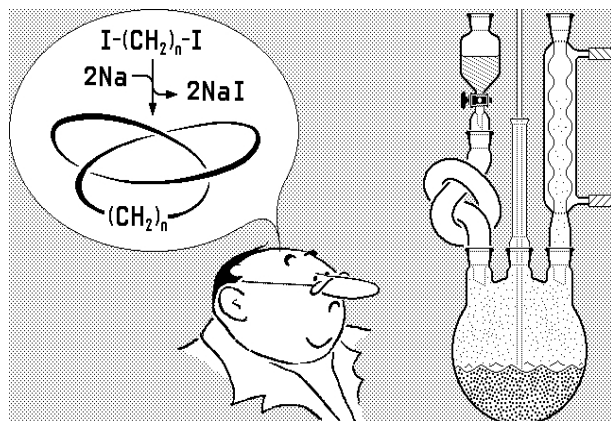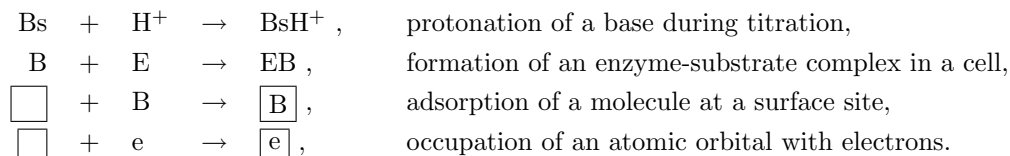

Figure 1: In his work in the lab, a chemist is guided by atomistic models. The success of his work depends largely upon the coherence of his molecular models. A misguided relation between micro-world and macro-world can also lead to failure. In the figure we see a suggestion for an experiment for the WURTZ synthesis of knotted cycloalkanes by dropwise addition of a diluted solution of long-chain ω-ω'-diiodalkanes in a suspension of sodium in xylene. To achieve the formation of knots, at least 50 CH_2 units are needed, as can be shown with the help of calotte models. Knot free cycling and intermolecular polymerization are important competing reactions. The latter can be suppressed by sufficient dilution.

On the other hand, there are transitions in the dynamics between these various levels of description that hint at more commonality than is seen in the typical formulas. As an example, let us consider the following sequence of simple processes that can be described with the help of equivalent reaction formulas. We start with an operation from the lab, and end with a quantum mechanical process in an atom:

$$\begin{array}{rcll}
\text{Bs} + \text{H}^+ & \rightarrow & \text{BsH}^+ \,, & \text{protonation of a base during titration,} \\
\text{B} + \text{E} & \rightarrow & \text{EB} \,, & \text{formation of an enzyme-substrate complex in a cell,} \\
\square + \text{B} & \rightarrow & \boxed{\text{B}} \,, & \text{adsorption of a molecule at a surface site,} \\
\square + \text{e} & \rightarrow & \boxed{\text{e}} \,, & \text{occupation of an atomic orbital with electrons.}
\end{array}$$

The first two processes are commonly described phenomenologically. For the third we use molecular kinetics, for the fourth quantum statistics. All four processes have this in common: a certain type of particle populates a certain type of location. The transition from the first to the last entry in the list is apparently fluid, since we can easily add intermediate entries. The gap between the first (*homogenous*) reaction and the third (*heterogeneous*) is spanned by the second. This reaction can be viewed as either a bimolecular reaction between solved substances E (enzyme) and B (substrate) or as adsorption of B to E. We can get to a contiguous surface in steps by thinking of the E-molecules as being combined into increasingly larger surface-like complexes. In a similar way we can construct elements that mediate between the third and fourth of the processes.

From this viewpoint we cannot see what would hinder us to describe all processes on the basis of the pattern already used in Part I. For instance, we could use chemical potentials to compute the occupation of atomic or molecular orbitals by electrons. On further thought, however, we find reasons that can dampen our expectations somewhat:

- The fact that these processes are dealt with so differently, speaks out against our expectation. It appears absurd to assume that this would happen arbitrarily in such a well thought out subject.

- We know from statistics that many-body systems have properties that are missing from smaller assemblies of the same particles. This makes an equal treatment of an extended aggregate and of molecular or atomic micro-systems an apparent impossibility.

- The occupancy of an atomic orbital with electrons is determined primarily by the PAULI principle. This adds an intrinsically new, quantum-mechanical aspect which does not play a role in the other three cases.

- In quantum statistics, the indistinguishability of equal particles has important consequences for the distribution functions. This aspect does not have to be taken into consideration in normal chemical processes.

To what extent these are good reasons we cannot decide on the spot. We know from the examples of Part I that differing patterns of description often are the expression of differing historical developments, and that prejudices often prevent obvious solutions. Let us disregard the arguments and try to extend the phenomenological description of the first process step by step to the other three. We shall make use of the same few tools that were already applied in Part I. We essentially assume the existence of the chemical potential and fall back on its dependence upon concentration and energy (mass action formula $\mu = \mu_0 + RT ln(c/c_0)$ and excitation formula $\mu(\epsilon) = \mu(0) + \epsilon/\tau$).

Protonation of a base

This section serves to recall the type of description used in chemistry in case of our first example. In the theory of acids and bases, the pH-value (the *proton exponent*) replaces the chemical potential μ_{H^+} of the hydrogen ions[1]. The degree of protonation $\Theta = c_{\mathrm{BsH}^+}/(c_{\mathrm{Bs}} + c_{\mathrm{BsH}^+})$ of a base Bs depends upon the pH-value or the proton potential μ_{H^+} of the solution. Starting with the condition of equilibrium, $\mu_{\mathrm{Bs}} + \mu_{\mathrm{H}^+} = \mu_{\mathrm{BsH}^+}$, the mass action formula leads to

$$\mu_{0,\mathrm{Bs}} + RT \ln(c_{\mathrm{Bs}}/c_0) + \mu_{\mathrm{H}^+} = \mu_{0,\mathrm{BsH}^+} + RT \ln(c_{\mathrm{BsH}^+}/c_0) \quad .$$

Solving for μ_{H^+} and using the notation $\mu_1 = \mu_{0,\mathrm{BsH}^+} - \mu_{0,\mathrm{Bs}}$ yields a relation that is equivalent to a HENDERSON-HASSELBALCH equation where μ_1 replaces the *acidity exponent* pK_{A} (see Figure 2a):

$$\mu_{\mathrm{H}^+} = \mu_1 + RT \ln \frac{c_{\mathrm{BsH}^+}}{c_{\mathrm{Bs}}} = \mu_1 + RT \ln \frac{\Theta}{1-\Theta} \quad .$$

μ_1 graphically describes the 50%-potential, i.e., the proton potential at a degree of protonation $\Theta = \frac{1}{2}$. The index 1 for the attachment of the first proton to the base Bs has been chosen in view of a possible multiple addition of protons. Solving the previous relation for Θ, and making use of $a = \exp[(\mu_{\mathrm{H}^+} - \mu_1)/(RT)]$ as an abbreviation, and $a = \Theta/(1-\Theta)$ and $\Theta = 1/(a^{-1}+1)$ as intermediate steps, leads to the following equation:

$$\Theta = \frac{1}{\exp\left(\frac{\mu_1 - \mu_{\mathrm{H}^+}}{RT}\right) + 1} \qquad \text{(protonation equation)}$$

We shall encounter this equation repeatedly in similar form. Figure 2b shows the relation graphically. We obtain corresponding equations and graphs if we investigate the analogous redox reaction $\mathrm{Ox} + \mathrm{e}^- \to \mathrm{Rd}^-$ instead of the acid-base reaction $\mathrm{Bs} + \mathrm{H}^+ \to \mathrm{BsH}^+$.

The chemical potential of free and occupied sites

The simplest case where we encounter the question of the chemical potential of sites, rather than of substances, is the adsorption of a substance B from a gas or a solution to independent adsorption sites:

$$\boxed{} + \mathrm{B} \to \boxed{\mathrm{B}} \quad .$$
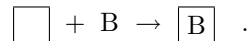
Since the adsorption equilibrium is codetermined by the availability of free and occupied locations, $\boxed{}$ and $\boxed{\mathrm{B}}$, it is obvious that they might be assigned chemical potentials, $\mu(\boxed{})$ and $\mu(\boxed{\mathrm{B}})$, as well. A comparison with the corresponding homogenous reaction discussed in the introduction,

$$\mathrm{A} + \mathrm{B} \to \mathrm{AB} \quad ,$$

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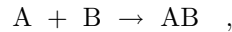
[1] These quantities hardly differ more than Fahrenheit ϑ_{F} and Kelvin T temperatures, as demonstrated by their conversion:

$$\mu_{\mathrm{H}^+} = \mu_{0,\mathrm{H}^+} + f \cdot p\mathrm{H}, \quad \text{where } f = -RT \ln(10), \text{ and } \mu_{0,\mathrm{H}^+} \equiv 0 \ ;$$
$$T = T_{0,F} + f' \cdot \vartheta_{\mathrm{F}}, \quad \text{where } f' = 5\mathrm{K}/9\mathrm{F}, \ T_{0,\mathrm{F}} = 255.37\mathrm{K} \ .$$

The zero point of the chemical potential may be chosen arbitrarily for all temperatures (as long as all partners in the reaction have the same temperature) for a single type of charged particle (electron or ion) without influencing the values of the potential differences which alone are responsible for chemical processes. In the chemistry of aqueous solutions, the standard reference value of the proton potential $\mu_{\mathrm{H}^+}^{\circ}$ lends itself for such fixing of the scale.
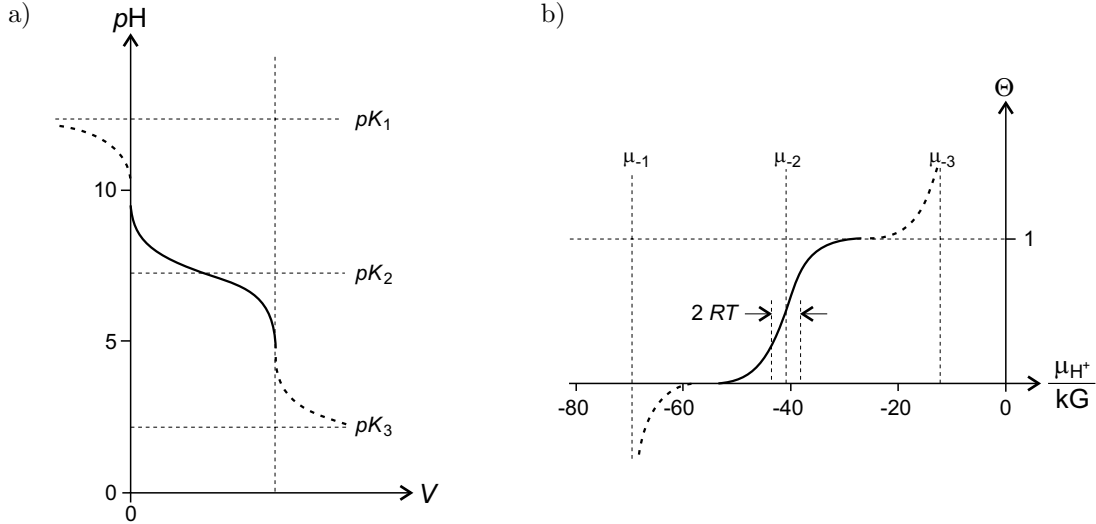
Figure 2: Titration curve of the base hydrogenphosphate, HPO_4^{2-}.

a) conventional: pH-value as a function of used volume V of acid ($V > 0$) or of lye ($V < 0$); solid curve: computed according to the HENDERSON-HASSELBACH equation, $pH = pK_A + \lg(c_{Bs}/c_{BsH+})$; dashed part on the left: result of deprotonation of HPO_4^{2-} forming PO_4^{3-}(and, partially, of H_2O forming OH^-); dashed part on the right: result of protonation of HPO_4^{2-} forming $H_2PO_4^-$ (and, partially, of H_2O forming H_3O^+); pK_i: i-th acidity exponent of phosphoric acid.

b) (corresponds to Graph a rotated by $90°$ counterclockwise): degree of protonation Θ as a function of proton potential μ_{H+}; solid line: calculated course based upon the protonation equation; dashed part: actual course. μ_{-i}: 50%-potential for the i-th level of deprotonation of phosphoric acid.

leads to a plausible suggestion. We can look at a particle A as the carrier of a single adsorption location $\boxed{}$ for B. So that the sites do not interact, the total concentration $c = c(A) + c(AB)$ of free and bound A must remain low. On the other hand, this condition allows us to make use of the mass action formula for $\mu(A)$ and $\mu(AB)$. The condition for equilibrium $\mu(A) + \mu(B) = \mu(AB)$ then takes the form

$$\mu_0(A) + RT \ln[c(A)/c_0] + \mu(B) = \mu_0(AB) + RT \ln[c(AB)/c_0] \quad .$$

We slightly change the requirement for equilibrium in order to achieve a description that is independent of whether or not the sites sit upon separate particles or upon a continuous surface and also independent of the components of the carrier A unimportant for adsorption. $c(A)/c = \Theta(\boxed{})$ is the *fraction of empty sites* and $c(AB)/c = \Theta(\boxed{B})$ the *fraction of occupied sites*. We replace $c(A)$ and $c(AB)$ with $c\,\Theta(\boxed{})$ and $c\,\Theta(\boxed{B})$, respectively, and subtract $\mu_0(A) + RT \ln(c/c_0)$ from both sides:

$$\underbrace{\mu_0(\boxed{}) + RT \ln \Theta(\boxed{})}_{\mu(\boxed{})} + \mu(B) = \underbrace{\mu_0(\boxed{B}) + RT \ln \Theta(\boxed{B})}_{\mu(\boxed{B})}$$

$$\mu(\boxed{}) + \mu(B) = \mu(\boxed{B}) \qquad \text{(equilibrium condition)}$$

We understand $\mu_0(\boxed{B}) \equiv \mu_0(AB) - \mu_0(A)$ to be the *reference value of the chemical potential of the occupied sites*, meaning as the potential $\mu(\boxed{B})$ at full occupation $\Theta(\boxed{B}) = 1$. The term $\mu_0(\boxed{})$ $\equiv 0$ is only inserted for the sake of unity. It takes the role of the *reference value of the chemical potential of empty sites* $\boxed{}$, meaning as the potential $\mu(\boxed{})$ for $\Theta(\boxed{}) = 1$.

A chemical bond between A and B changes both A and B. In larger molecules, the changes affect mostly the atoms near the bonding site while atoms further away are mostly unaffected. Our definition above of the quantity $\mu_0(\boxed{B})$, results in all the changes of the molecules A and B being

formally assigned to the *adsorbed* particle B. In contrast, the contribution of the unchanged parts of the carrier A cancels, especially that of all the atoms of A that do not lie in the bonding site's area of influence.

The *mass action formulas* derived above, $\mu(\boxed{}) = \mu_0(\boxed{}) + RT\ln\Theta(\boxed{})$ and $\mu(\boxed{\text{B}}) = \mu_0(\boxed{\text{B}}) + RT\ln\Theta(\boxed{\text{B}})$, (for sites independent of each other whether or not they are occupied) can be applied widely. We will deal with this in more detail in the following.

Single-layer adsorption

In our first example, we consider the case discussed in the last section. More precisely, we will look at the adsorption of a substance B out of a dilute solution or dilute gas on a solid surface with identical and independent adsorption sites. Taking into account the mass action formula for B, $\boxed{}$ and $\boxed{\text{B}}$, as well as the equations $\Theta(\boxed{\text{B}}) = \Theta$ and $\Theta(\boxed{}) = 1 - \Theta$ with the *degree of coverage* Θ, the condition for equilibrium of adsorption is:

$$\mu_0(\boxed{}) + RT\ln(1 - \Theta) + \mu_0(\text{B}) + RT\ln(c/c_0) = \mu_0(\boxed{\text{B}}) + RT\ln\Theta \quad .$$

We subtract $\mu_0(\text{B})$ from both sides, divide by RT, raise to the power of e and multiply by c_0. Because of $\mu_0(\boxed{}) = 0$, this leads to the relation

$$c(1 - \Theta) = \underbrace{c_0 \cdot \exp\left(\frac{\mu_0(\boxed{\text{B}}) - \mu_0(\text{B})}{RT}\right)}_{c_1 \ 50\%\text{-concentration}} \cdot \Theta \quad .$$

Dividing both sides by $c\,\Theta$ and addition of 1 yields $1/\Theta = 1 + c_1/c$. Going over to the reciprocal and expanding the right hand side by c/c_1 results in the well-known equation for LANGMUIR's adsorption isotherm, in which the parameter c_1 represents the *50%-concentration*, meaning the concentration c for which $\Theta = \frac{1}{2}$:

$$\boxed{\Theta = \frac{c/c_1}{1 + c/c_1}} = \frac{1}{1 + c_1/c} \qquad \text{(LANGMUIR's adsorption equation)}$$

Multi-layer adsorption

If one works at temperatures and pressures near the dew point of a gas B|g that is to be adsorbed, then further gas particles are deposited on the first layer of B molecules on the surface so that the degree of coverage Θ can be greater than 1:

$$\boxed{} + i\,\text{B|g} \;\rightarrow\; \boxed{i\ \text{B}} \qquad i = 1, 2, 3...$$
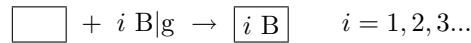
While the undermost layer of the adsorbed B-film is generally bound more strongly to the adsorbing surface, the other layers adhere to each other as if in a fluid. We take this fact into account by assuming that

$$\mu(\boxed{i\ \text{B}}) = \mu(\boxed{\text{B}}) + (i - 1) \cdot \mu(\text{B|l}) \quad .$$

The chemical potential of B in a fluid state is represented by $\mu(\text{B|l})$. If we abbreviate the fraction of sites occupied by i particles by Θ_i, and take into account $\mu(\boxed{}) = 0$, the condition of equilibrium $\mu(\boxed{}) + i\mu(\text{B|g}) = \mu(\boxed{i\ \text{B}})$ for the adsorption process is

$$RT\ln\Theta_0 + i \cdot [\mu_0(\text{B|g}) + RT\ln(c/c_0)] = \mu_0(\boxed{\text{B}}) + (i - 1) \cdot \mu(\text{B|l}) + RT\ln\Theta_i \quad .$$
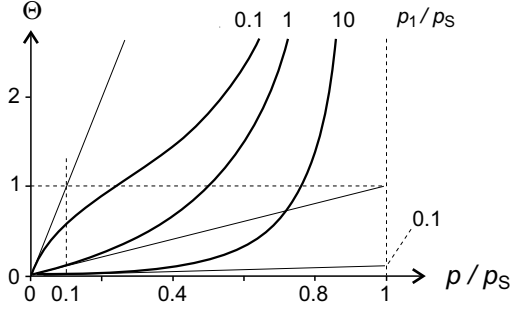
Figure 3: Brunauer-Emmet-Teller adsorption isotherms. The degree of coverage Θ is represented as a function of the reduced pressure p/p_s for various values of the ratio of 50%-pressure p_1 and saturation pressure p_s. The smaller the 50%-pressure the firmer the binding to the surface. $p_1 < p_s$ corresponds to an adsorbing surface, $p_1 = p_s$ to an indifferent surface and $p_1 > p_s$ to a repelling surface.

We subtract $i\mu_0(\mathrm{B}|\mathrm{g})$ from both sides, divide both sides by RT, raise to the power of e and multiply by c_0^i. This yields

$$\Theta_0\, c^i = \underbrace{c_0 \cdot \exp\left(\frac{\mu_0(\boxed{\text{ B }}) - \mu_0(\mathrm{B}|\mathrm{g})}{RT}\right)}_{c_1\ 50\%\text{-concentration}} \cdot \underbrace{\left[c_0 \cdot \exp\left(\frac{\mu(\mathrm{B}|\mathrm{l}) - \mu_0(\mathrm{B}|\mathrm{g})}{RT}\right)\right]^{i-1}}_{c_s\ \text{saturation concentration}} \cdot \Theta_i \quad .$$

c_1 is the *half-value concentration* of single-layer adsorption, as a comparison to the corresponding formula in the last section shows. The *saturation concentration* is c_s where liquid $\mathrm{B}|\mathrm{l}$ and vapor $\mathrm{B}|\mathrm{g}$ are in equilibrium,

$$\mu(\mathrm{B}|\mathrm{l}) = \mu(\mathrm{B}|\mathrm{g}) \qquad \text{or} \qquad \mu(\mathrm{B}|\mathrm{l}) = \mu_0(\mathrm{B}|\mathrm{g}) + RT\ln(c_s/c_0) \quad .$$

Solving for c_s yields the expression used above. If one divides the equation for $\Theta_0 c^i$ by c_s^i and uses the abbreviations $c/c_s = q$ and $c_1/c_S = a$, one obtains

$$\Theta_0\, q^i = a\, \Theta_i \qquad \text{for } i > 0 \quad .$$

Multiplying the equation on the one hand by the factor 1, and on the other by a factor i and adding up over all $i > 0$, yields for $q < 1$ the two relations

$$\Theta_0 q \underbrace{(1 + q + q^2 + q^3 + ...)}_{(1-q)^{-1}} = a\, \underbrace{(\Theta_1 + \Theta_2 + \Theta_3 + ...)}_{1 - \Theta_0} \quad ,$$

$$\Theta_0 q \underbrace{(1 + 2q + 3q^2 + ...)}_{(1-q)^{-2}} = a\, \underbrace{(\Theta_1 + 2\Theta_2 + 3\Theta_3 + ...)}_{\Theta} \quad .$$

The expression in parentheses below at the left is exactly the derivative with respect to q of the expression in parentheses above at the left. Therefore its sum is identical to the derivative $\mathrm{d}(1-q)^{-1}/\mathrm{d}q = (1-q)^{-2}$. Dividing both sides of the first equation by $a\Theta_0$, addition of 1 and going over to the reciprocal yields an expression for Θ_0 (below left). This can be inserted into the second equation to be solved for Θ. The result is (below right):

$$\left[1 + \frac{q}{a(1-q)}\right]^{-1} = \Theta_0 \quad , \qquad\qquad \Theta = \frac{q}{[a(1-q)+q](1-q)} \quad .$$

If one divides the numerator and the denominator by a, and inserts $q = c/c_s$ and $a = c_1/c_s$, one obtains the equation for the Brunauer-Emmet-Teller adsorption isotherm in which the concentration ratios c/c_1 and c/c_s can be replaced by the corresponding pressure ratios p/p_1 and

p/p_s (Figure 3),

$$\Theta = \frac{c/c_1}{(1 + c/c_1 - c/c_s) \cdot (1 - c/c_s)} \qquad . \qquad \text{(BET adsorption equation)}$$

Generalizing the adsorption equations

One can give the adsorption equations a more general formulation in which the substance to be adsorbed, B, can appear in any form (not only as a dilute gas or dilute solution) if one does not revert to the mass action formula for B when deriving the result. We can easily go back on this step and replace the concentrations with potentials again by use of an approach of the type $\mu = \mu_1 + RT \ln(c/c_1)$ or $c_1/c = \exp[(\mu_1 - \mu)/RT]$. This is interesting for the LANGMUIR equation $\Theta = (c_1/c+1)^{-1}$ and, correspondingly, the BET equation for $c_1 = c_s$, $\Theta = (c_1/c-1)^{-1}$, which describes the "condensation" of the gas B on an "indifferent" surface (neither adsorbing nor repelling and comparable to fluid B in binding behavior). We obtain two important functions, represented in Figure 4. We have already encountered one of these in protonation of a base, and we will encounter them again later:

$$\Theta = \frac{1}{\exp\left(\frac{\mu_1 - \mu}{RT}\right) + 1}$$

LANGMUIR adsorption
(FERMI-DIRAC distribution),

$$\Theta = \frac{1}{\exp\left(\frac{\mu_1 - \mu}{RT}\right) - 1}$$

Condensation on indifferent surface
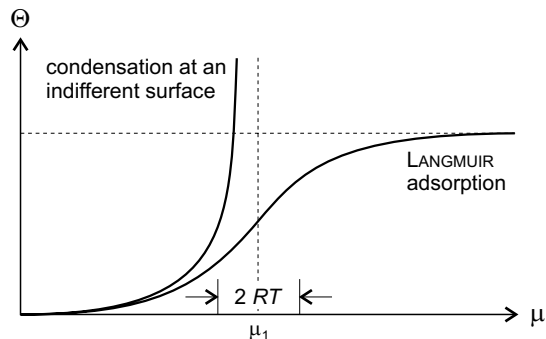(BOSE-EINSTEIN distribution).

Figure 4: Degree of coverage Θ as a function of the chemical potential μ of the substances to be adsorbed, for two theoretically interesting special cases. R gas constant, T temperature, μ_1 "50%-potential" (for which half-occupation of the first adsorption layer is reached).

Contribution of translation to the chemical potential

We wish to calculate the contribution to the chemical potential μ of the different quantum mechanically allowed translation states of the molecules of a *dilute* gas B. This gas is in a container with a volume V. At first we will assume that all the molecules have the same internal state – rotational state, vibrational state, electronic state, nuclear state – having energy ϵ, so that they are all identical. If, for the sake of simplicity, we assume the container to be a cube with edge length a, the additional energy of the individual translation states of the B molecules with mass m, is given by the following equation:

$$\epsilon_{\boldsymbol{n}} = \frac{\boldsymbol{n}^2 h^2}{8ma^2} \qquad \boldsymbol{n} = (n_1, n_2, n_3) \quad \text{and} \quad n_1, n_2, n_3 = 1, 2, 3...$$

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We consider each translation state $\boldsymbol{n}$ as a kind of site $\boxed{}_{\boldsymbol{n}}$ inside the container. This location can be occupied by B particles. In the case of fermions, this would be one particle at the most. In the case of bosons, the number is unlimited,

$$\boxed{}_{\boldsymbol{n}} \; + \; i\mathrm{B} \;\rightarrow\; \boxed{i\,\mathrm{B}}_{\boldsymbol{n}} \qquad \begin{cases} i = 0, 1 & \text{for fermions,} \\ i = 0, 1, 2, 3... & \text{for bosons.} \end{cases}$$

First, in a dilute gas there is no interaction between the particles worthy of mention. Second, the number of locations available is much greater than the particle number N. The first condition means that the locations will be occupied independently of each other, whereas the second means that the *degree of occupation*[2] for all the locations remains small, i.e., $\Theta_{\boldsymbol{n}} \ll 1$, so that multiple occupancy or processes with $i > 1$ can be ignored. Under these circumstances, fermions and bosons behave identically. We revert to

$$\mu(\boxed{}_{\boldsymbol{n}}) = \underbrace{\mu_0(\boxed{}_{\boldsymbol{n}})}_{0} + \underbrace{RT \ln(1 - \Theta_{\boldsymbol{n}})}_{\approx 0} \quad , \qquad \mu(\boxed{\mathrm{B}}_{\boldsymbol{n}}) = \underbrace{\mu_0(\boxed{\mathrm{B}}_{\boldsymbol{n}})}_{(\epsilon_{\boldsymbol{n}} + \epsilon)/\tau} + RT \ln \Theta_{\boldsymbol{n}} \quad .$$

for the chemical potential of an empty and simply occupied site. Because of $\Theta_{\boldsymbol{n}} \ll 1$ in the expression on the left, we can set the logarithmic term practically equal to zero so that $\mu(\boxed{}_{\boldsymbol{n}})$ disappears. On the right, we can express the main term by $(\epsilon_{\boldsymbol{n}} + \epsilon)/\tau$. The substance B is exchanged inside the container between the different locations and between the container and the environment, if the container walls are permeable, until all the processes $\boxed{}_{\boldsymbol{n}} + \mathrm{B} \rightarrow \boxed{\mathrm{B}}_{\boldsymbol{n}}$ are in equilibrium. This means until $\mu(\boxed{}_{\boldsymbol{n}}) + \mu = \mu(\boxed{\mathrm{B}}_{\boldsymbol{n}})$ or, based upon the expressions above, until

$$\mu = (\epsilon_{\boldsymbol{n}} + \epsilon)/\tau + RT \ln \Theta_{\boldsymbol{n}} \qquad \text{for all } \boldsymbol{n}$$

To calculate N, we solve for $\Theta_{\boldsymbol{n}}$ and add up over all $\boldsymbol{n}$:

$$\Theta_{\boldsymbol{n}} = \exp\left(\frac{\mu - \epsilon/\tau}{RT}\right) \cdot e^{-\epsilon_{\boldsymbol{n}}/kT} \quad , \qquad N = \sum_{\boldsymbol{n}} \Theta_{\boldsymbol{n}} = \exp\left(\frac{\mu - \epsilon/\tau}{RT}\right) \cdot \sum_{\boldsymbol{n}} e^{-\epsilon_{\boldsymbol{n}}/kT} \quad ,$$

The sum at the right is in agreement with the *translational partition function* z_{t} of quantum statistics, which we can calculate in the usual way. One cannot call this part of the calculation as elementary, but it is also not too difficult for us to carry it out. Using the abbreviation $q = h/(2a\sqrt{2mkT})$, one obtains:

$$\sum_{\boldsymbol{n}} e^{-\epsilon_{\boldsymbol{n}}/kT} = \sum_{n_1, n_2, n_3 = 1}^{\infty} e^{-q^2(n_1^2 + n_2^2 + n_3^2)} = \left[\sum_{n_1 = 1}^{\infty} e^{-q^2 n_1^2}\right]^3 \approx \left[\underbrace{\int_0^{\infty} e^{-q^2 n_1^2} \mathrm{d}n_1}_{\sqrt{\pi}/2q}\right]^3 = \frac{(2\pi mkT)^{3/2}}{h^3} V \;.$$

The step from the sum to the integral can be carried out if $q \ll 1$, so that the function value $f(n_1) = e^{-q^2 n_1^2}$ changes only slightly with growing integer n_1. This condition is satisfied for usual temperatures and macroscopic dimensions of a. If the "*quantum length*"[3] $\lambda = h/\sqrt{2\pi mkT}$ or the

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"*degeneracy concentration*"[4] $c_e = \tau/\lambda^3$ are introduced as abbreviations, the result simplifies to $\sum e^{-\epsilon_n/kT} = V/\lambda^3 = Vc_e/\tau$. Insertion into the equation for N, solving for μ, and taking into account $N\tau/V = c$, results in the desired contribution of translation:

$$\mu = \frac{\epsilon}{\tau} + \boxed{RT \ln \frac{c}{c_e}} \quad \text{with} \quad \boxed{c_e = \frac{\tau}{\lambda^3} \ , \quad \lambda = \frac{h}{\sqrt{2\pi m kT}}} \quad .$$

In order to put the equation into the usual form $\mu = \mu_0 + RT \ln(c/c_0)$, one needs only to insert $c_e = (c/c_0)/(c_e/c_0)$ and to transform the equation accordingly. Because in gases one prefers the variable to be the pressure p instead of the concentration c, we will continue our considerations in this direction.

Properties of dilute gases

In order to convince ourselves that the substance B distributed upon the sites $\boxed{}_n$ in the container really behaves like a gas, we apply the relation $(\partial\mu/\partial V)_{T,n} = -(\partial p/\partial n)_{V,T}$ known from thermodynamics to the equation for μ which we obtained in the last section. In doing so we observe that $c = n/V$ and that c_e is independent of V:

$$\left(\frac{\partial p}{\partial n}\right)_{V,T} = -\left(\frac{\partial \mu}{\partial V}\right)_{T,n} = 0 + \frac{RT}{V} \quad .$$

Integration over n at fixed V and T yields, as expected, the gas law $p = nRT/V = cRT$. Therefore, we can replace c in the equation $\mu = \frac{\epsilon}{\tau} + RT \ln \frac{c}{c_e}$ by p, $c/c_e = p/p_e$ with $p_e = c_e RT = kT/\lambda^3$ as "*degeneracy pressure*" $\mu = \frac{\epsilon}{\tau} - RT \ln \frac{p_e}{p_0} + RT \ln \frac{p}{p_0}$. By inserting p_e and λ, we obtain

$$\mu = \underbrace{\frac{\epsilon}{\tau}}_{\mu_{\text{inn}}} \underbrace{- RT \ln \left(\frac{(2\pi m)^{3/2}(kT)^{5/2}}{h^3 p_0}\right)}_{\mu_{t,0}(T)} + RT \ln \frac{p}{p_0} \quad .$$

$\mu_{t,0}(T)$ is the reference value of the contribution of translation, meaning the value at the reference pressure p_0. The contribution of the internal state of the molecule is represented by μ_{inn}. Here it is composed only of the term ϵ/τ because we have only assumed a single state. In the case of multiple internal states with energies ϵ_i,

$$\mu_{\text{inn}} = RT \ln \sum_i e^{-\epsilon_i/kT} \quad ,$$

appears instead as one can immediately derive if one again combines all the particles in the same state into a substance B(i) and considers all of these substances as an equilibrium mixture. The expressions derived earlier for the contributions of vibration and rotation, $\mu_s(T)$ and $\mu_r(T)$, are special cases of this equation.

As an acknowledgement of conventions, we finally calculate entropy and heat capacity for a monatomic gas B without internal degrees of freedom, for which we have $\mu_{\text{inn}} = \epsilon/\tau$. Taking the

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[4]A gas must have a concentration of $c \ll c_e = \tau/\lambda^3$ in order to behave normally. It *degenerates* when c is of the order of or larger than c_e, i.e., if one or more particles are found in a volume of the order of λ^3. For electrons at room temperature, $c_e = 21$ mol m^{-3}. The concentration of conduction electrons in a metal is far above this value ($\approx 10^5$ mol m^{-3}).

first derivative with respect to T at constant p yields the molar entropy $S_m = -(\partial\mu/\partial T)_{p,n}$, up to the factor -1. Taking the second derivative, we obtain, up to the factor $-T$, the molar heat capacity at constant pressure $C_{p,m} = -T(\partial^2\mu/\partial T^2)_{p,n}$:

$$S_m = R\left[\ln\left(\frac{(2\,\pi\,m)^{3/2}(k\,T)^{5/2}}{h^3\,p}\right) + \frac{5}{2}\right] \qquad \text{(\textsc{Sackur-Tetrode} equation)}$$

$$C_{p,m} = \frac{5}{2}\,R \quad .$$

The contribution of translation to the molar heat capacity $C_{V,m}$ which is smaller by R, is thus $\frac{3}{2}\,R$ and as a consequence the energy for a translational degree of freedom of a particle $\frac{1}{2}\,k\,T$, as required by the equipartition principle.

Fermi-Dirac, Bose-Einstein and Boltzmanns distributions

We focus once again upon occupation of a single site $\boxed{}$ with a particle B, although we now omit the requirement $\Theta \ll 1$ for the degree of occupancy. We consider a site more generally as a collection of quantum states which vary in *occupation number*, but not in their other quantum numbers. An orbital in the electron shell of an atom or of an atomic union is an example of such a site that can be occupied by electrons as long as one considers states with different spin quantum numbers as belonging to different orbitals. The processes of occupation to be considered are:

$$\boxed{} + i\mathrm{B} \rightarrow \boxed{i\,\mathrm{B}} \qquad \begin{cases} i = 0,1 & \text{for fermions,} \\ i = 0,1,2,3... & \text{for bosons.} \end{cases}$$

For the chemical potential of an i-fold occupied position, we use the approach

$$\mu(\boxed{i\,\mathrm{B}}) = \mu_0(\boxed{i\,\mathrm{B}}) + R\,T\,\ln\Theta_i \qquad \text{with} \qquad \mu_0(\boxed{i\,\mathrm{B}}) = i\cdot\epsilon/\tau \quad .$$

The fact that we have set $\mu_0(\boxed{i\,\mathrm{B}})$ proportional to the occupation number i, means that, as before, we ignore interactions between particles. Here, ϵ comprises the energy of a possible internal excitation of the particle as well as the energy gained by occupation of the site. Because of $\mu_0(\boxed{}) = 0$, the condition for equilibrium $\mu(\boxed{}) + i\cdot\mu = \mu(\boxed{i\,\mathrm{B}})$ takes the following form

$$R\,T\,\ln\Theta_0 + i\cdot\mu = i\cdot\epsilon/\tau + R\,T\,\ln\Theta_i \qquad \text{or solved for } \Theta_i\,,$$

$$\Theta_0\left[\underbrace{\exp\left(\frac{\mu\,\tau - \epsilon}{k\,T}\right)}_{q}\right]^i = \Theta_i \qquad \text{for all } i.$$

Here, q serves as an abbreviation. Multiplication of the equation by 1, on the one hand, and by i on the other, and summing over all i, yields the two relations on the left for fermions. In the case of bosons for $q < 1$, it yields the two relations on the right.

$$\Theta_0(1 + q) = \underbrace{\Theta_0 + \Theta_1}_{1}\,, \qquad \Theta_0\underbrace{(1 + q + q^2 + q^3...)}_{(1-q)^{-1}} = \underbrace{\Theta_0 + \Theta_1 + \Theta_2...}_{1}$$

$$\Theta_0 q = \Theta_1 = \Theta \qquad \Theta_0\,q\,\underbrace{(1 + 2\,q + 3\,q^2...)}_{(1-q)^{-2}} = \underbrace{\Theta_1 + 2\,\Theta_2 + 3\,\Theta_3...}_{\Theta}$$

The expression $1 + 2\,q + 3\,q^2...$ is the derivative of $1 + q + q^2 + q^3....$ Hence, its sum is equal to the derivative $\mathrm{d}(1 - q)^{-1}/\mathrm{d}q = (1 - q)^{-2}$. If we calculate Θ_0 from the equations of the first line, and
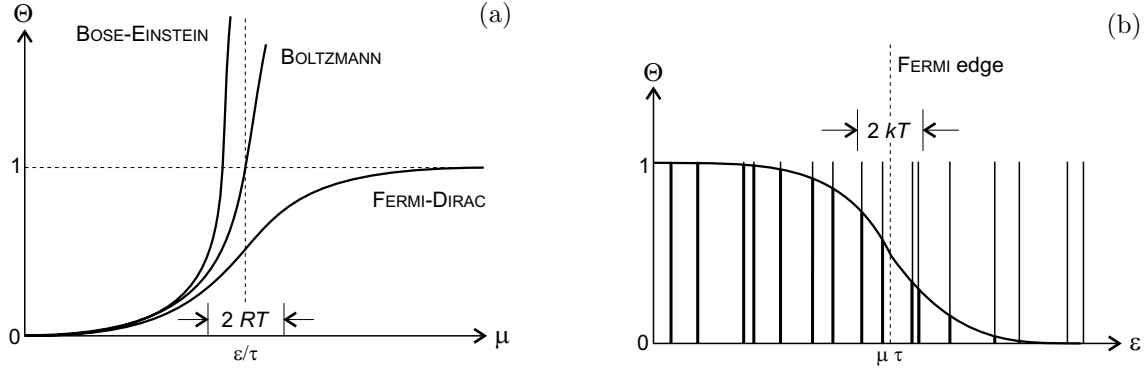
Figure 5: FERMI-DIRAC and BOSE-EINSTEIN distribution

a) Degree of occupation Θ of a site ▭ with fermions or bosons as a function of the chemical potential μ; T temperature, ϵ particle energy on the occupied site; dotted: Extrapolation of the common initial part, which conforms with a Boltzmann distribution. Compare here to Figure 4!

b) Distribution of fermions on sites (thin bars) of different energy ϵ. Degree of occupation Θ (thick bars) as a function of ϵ. Except for a transition zone in the order of $k\,T$, all the sites below the FERMI edge $\mu\,\tau$ are fully occupied. In contrast, the ones above are empty.

insert it into the equations in the second line, we obtain the degree of occupancy

$$\Theta = (q^{-1} + 1)^{-1} \quad \text{for fermions,} \qquad \Theta = (q^{-1} - 1)^{-1} \quad \text{for bosons.}$$

By writing out q we get the distribution functions (left, and middle):

$$\Theta = \frac{1}{\exp\left(\frac{\epsilon - \mu\,\tau}{k\,T}\right) + 1}$$

Fermi-Dirac

$$\Theta = \frac{1}{\exp\left(\frac{\epsilon - \mu\,\tau}{k\,T}\right) - 1}$$

Bose-Einstein

$$\Theta = \exp\left(\frac{\epsilon - \mu\,\tau}{k\,T}\right)$$

Boltzmann

The two functions are illustrated in Figure 5. If the chemical potential decreases below ϵ/τ, and with it the degrees of occupancy Θ become small, the functions have the same form. The 1 in the denominator can then be ignored and one obtains the distribution function valid for small Θ, given above on the right. Numerous sites with the same energy ϵ are often combined into one *energy level*. In this case, the average particle number $\bar{N}$ can be calculated for this purpose by use of the BOLTZMANN-distribution function, even for $\bar{N} > 1$, as long as the degrees of occupancy Θ remain small for a single site.

Review

We have seen that the task we set ourselves, namely to expand the phenomenological description of macrosystems over to microsystems, could be accomplished without much difficulty. The objections that seemed so convincing at the beginning became invalid. In retrospect we are tempted to dismiss them as unfounded prejudices. However, they should not be considered wrong, as they were correct according to the level of knowledge at that time. *Now* – in light of new knowledge – we must review them and adjust our thinking accordingly.

The first argument that differences in the patterns of description in a well thought out field lets us expect that such deviations don't happen arbitrarily, is in itself beyond doubt. Only the assumption that despite their long histories, thermodynamics and chemical dynamics are "well

thought out" doesn't seem to apply. On the contrary, our findings lead us to expect that not all the faults in the conceptual structure have been found, by far.

The second argument pertained to the circumstance that macrosystems can have characteristics which corresponding microsystems do not have, which therefore makes equal treatment impossible. One can associate with an isolated multi-particle gas a temperature T or a chemical potential μ, but not with a closed system of one, two or three gas particles. There is no such limitation in microsystems that are in thermal or chemical equilibrium with their macroscopic environment because T and μ are determined from outside. It is enough here to forgo isolation from the environment, which is uninteresting anyway, in order to achieve the desired equal treatment.

The third argument was that the PAULI exclusion principle introduces a totally new aspect to the considerations. This is a specious argument. In fact, a proton bound to a base excludes binding of a second proton in the same place in the same way that an electron in an orbital holds off a second electron. We make the PAULI principle responsible for the first case and spatial size of atoms for the second one. However, the required space for electrons in the atomic electron shell and the sizes of the atoms and molecules involved are governed by the exclusion principle. This aspect is not new and has been long included without being expressly mentioned.

Similar reasons can be applied to the fourth argument, which states that the indistinguishability of identical particles only comes to bear in quantum statistics and not in common chemical processes. Already in the cases of the simplest chemical equilibria, contradictions can be construed if we disregard indistinguishability. For example, if we consider a dissolved substance B with concentration c and chemical potential $\mu = \mu_0 + R\,T\,\ln(c/c_0)$, to be divided into two identical components made up of B particles with the concentrations $c/2$, then we must assign the chemical potential $\mu_0 + R\,T\,\ln((c/2)/c_0) < \mu$ to the components. If B were in equilibrium with a substance A, then this would not hold for the components in question so that A would have to decay into these and therewith into B. Thinking of a substance as decomposed into components is a mental tool we have often used. It assumes that the components are different from each other in some characteristic. Only artificial violation of this assumption lead to conflicts. Therefore, the indistinguishability of identical particles appears as a special difficulty for us but is rather the specific problem of an approach in which configurations of individual particles are made the starting point of statistical considerations.

Outlook

Up to this point, our means have never failed us in our derivations. On the contrary, we have achieved certain key equations that make a large part of the areas of application of molecular statistics accessible. Since statistical justifications are referred to in many fields of physics and chemistry, a wide field of application opens up here.

However, in order to use the mass action formula, we have always excluded interaction forces between particles of a dissolved, adsorbed or gaseous substance. We have always presupposed "ideal" circumstances. What is to be done when this condition is no longer fulfilled? At first thought, it is hard to imagine how this limitation can be overcome. Again we have the impression of having come to a barrier which is too high for our simple means. On the other hand, we have just observed how misleading such hasty judgements can be and one should not be kept from making an attempt. Indeed, it appears that with some skill, this hurdle can also be overcome. In another paper we wish to investigate the possibilities of including intermolecular interactions, such

as COULOMB's forces between dissolved ions, the required space of gas molecules or the mutual influence of adsorbed particles.