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An elementary approach to quantum statistical problems (I)

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Hamburg University

Summary: In order to derive the relation between macroscopic thermodynamic quantities and the quantum mechanical properties of atoms or atomic unions, statistical thermodynamics is usually applied. It is considered a necessary means of solving problems of this type because "phenomenological thermodynamics as a macroscopic theory is on principle not able to make statements about atomic systems". To correct this entrenched prejudice that is even made relevant by standardized exams, is the aim of this presentation. Various important results of quantum statistics will be derived for which, apart from the well-known relations of quantum mechanics, only the chemical potential and its concentration and energy dependence are needed.

Introduction

The subject dealt with here is a small part of a more extensive project. The purpose of this project is to make a thorough examination of all those areas of chemistry that can be categorized under *chemical dynamics* (or more general *matter dynamics*) with the aim of finding and elaborating the framework of concepts common to all parts of it. Figure 2 gives an overview of the field. If one looks at the individual key words, one sees that almost all the branches of physical chemistry are to be found.

Chemical dynamics has been developed from many sides simultaneously. It therefore has no strictly unified framework like a mono-crystal, but it rather resembles a poly-crystal where differently ordered areas grow together in a more or less coincidental way at historically defined borders (Figure 1). It is no wonder that there are strongly varying ways of describing similar phenomena appearing in different areas. Compare, for instance, the terminology and equations used for describing processes such as the *exchange of chemical substances* on adsorbing surfaces, *exchange of protons* in acid-base reactions, *exchange of electrons* between redox systems and *exchange of photons* in spectroscopy. Common characteristics are hardly to be found here and trying to find them feels contrived.

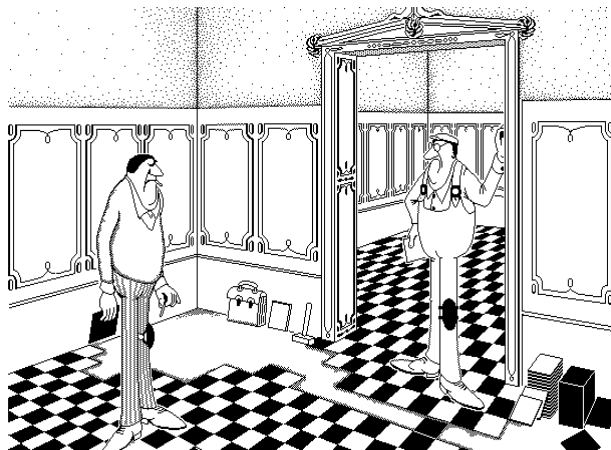


Figure 1: Structures that grow together from different sides are seldom completely ordered. Drawing from a photograph of unknown provenance.

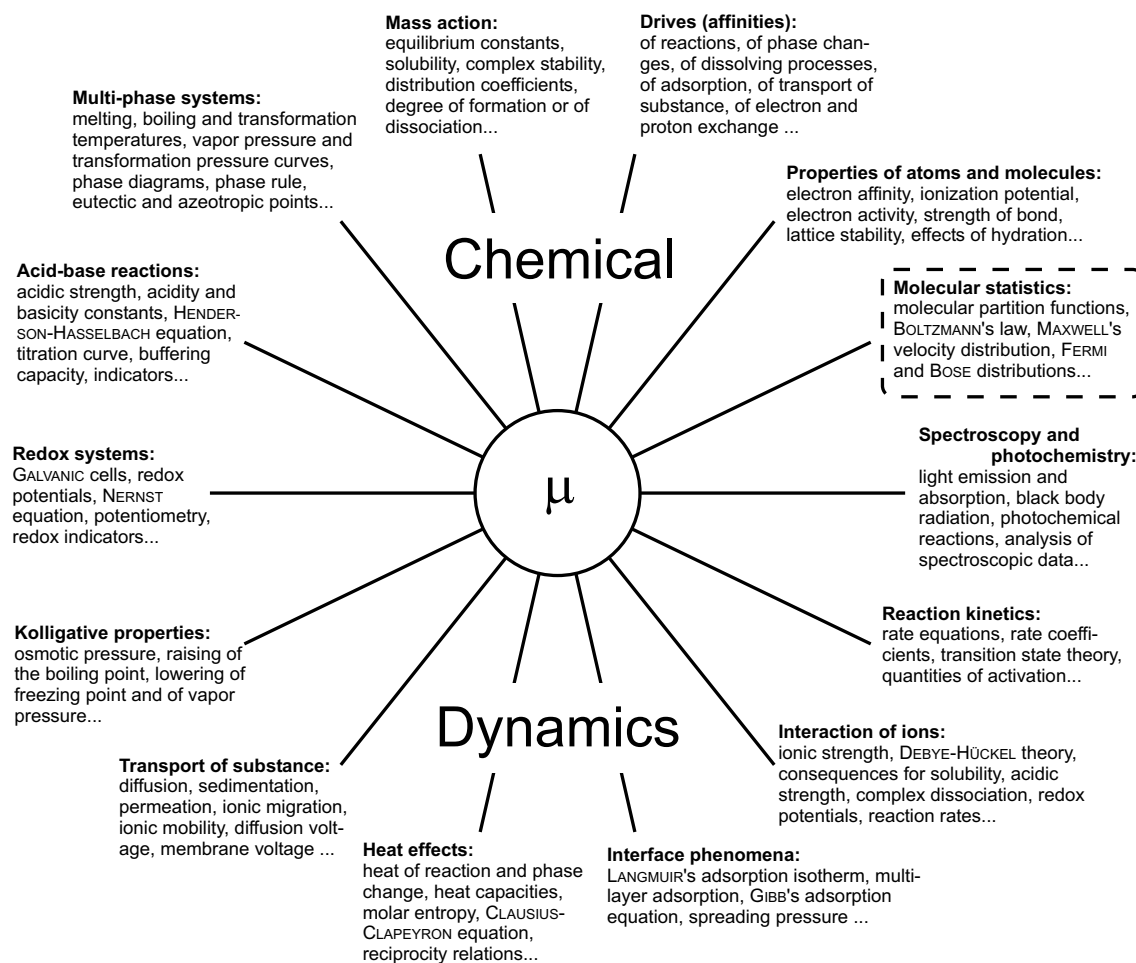


Figure 2: The areas of chemistry that can be categorized under 'chemical dynamics'. The chemical potential μ comprises the central pivot in all of chemical dynamics, where the lever is best applied for solving the problems involved¹. This also holds for the molecular statistics investigated here, in which *partition functions* would otherwise play the key role.

It is obvious that an unnecessary and uncoordinated juxtaposition of various terms is not economical. The transition from one area to another is complicated because one must rethink an old order into a new one.

One tends to accept this condition as natural and therefore, unavoidable. The fact is, though, that the terminology and formulas we use for our descriptions are constructions containing many random elements making it easy to give the appearance of differences when they don't actually appear in nature (Figure 3). A good example of this is "molecular statistics" whose application, if compared to phenomenological thermodynamics, requires a new and specific repertoire of terminology. The problems dealt with can just as easily be solved with previously known methods, as will be demonstrated in the following.

First acquaintance with molecular statistics

A physicist or chemist first encounters molecular statistics in a classic variation, in the kinetic theory of gases. MAXWELL's law of velocity distribution, BOLTZMANN's law, and the equipartition principle of energy are some results of the classical mechanical theory. These are considered to be

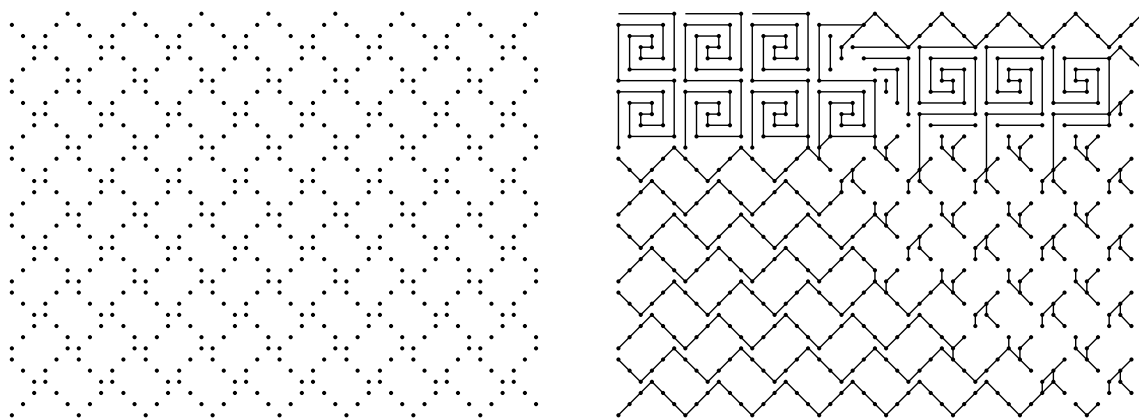


Figure 3: How easily contradicting pictures can be created despite identical basic structures can be seen in the figure. On the left is the predetermined dot pattern. The assignment was to mark the positions of the intersections and breaks of the dots in the most simple and memorable way by use of lines. A selection of the results by various people is pictured on the right. The order of the dots is exactly the same both on the right and on the left. The meandering pattern was basic to the drawing of the points. However, even this pattern is not clearly defined so that differing areas of meandering can be created which have a disordered structure at the edges.

both important enough and simple enough to be presented to students during their first semesters. A statistical derivation is avoided due to its complexity. The barometric formula is often used to give at least some justification for the existence of the BOLTZMANN-Factor $e^{-\epsilon/kT}$.

As the most frequent application of the equipartition principle, the internal energy of an ideal gas and its heat capacity – which is derived on the basis of the temperature dependence of the internal energy – are discussed. While the contribution of the *translational movement* of the gas molecules is totally regular, and the contribution of *rotation* can be comprehended through comparably simple rules, it is difficult to describe *vibrations*. When they are totally "frozen" at low enough temperatures and therefore make no contribution, the conditions are still simple even when incomprehensible from the standpoint of classical theory. The area of somewhat higher temperatures, where vibrations gradually "thaw", is the actual domain of *quantum statistics*, in which quantum theoretical results can be combined with statistical methods. Only when the vibrations are fully stimulated can the equipartition principle be used for calculating the kinetic and potential vibrational energy. It will fail again when even higher temperatures make the vibration anharmonic.

Prerequisite Formulas

It is especially easy here to fall back on phenomenological thermodynamics as an alternative to statistics. In fact – as usual for solving almost all problems of chemical dynamics¹ – we need only the existence and some properties of the chemical potential from the extensive thermodynamic

¹G. Job: "Teaching Thermodynamics: Chemical Potential From the Beginning", lecture at the conference for thermodynamics in Taormina (Sicily) on 20.2.91. Taking into account the numerous special constructs in thermodynamics only increases the length of calculations. Among these constructs are – in addition to the usual energy term E – quantities such as internal energy U , enthalpy H , free energy F , free enthalpy G , or, along with the chemical potentials μ , the activities λ , fugacities f , ionic exponents pH, pOH ... and all the other quantities derived from them. In order to preserve the relationship to previous representations, it will be necessary to deal with these concepts and not to ignore them.

calculus. We will use the formula for its concentration dependence especially often. Because in the following we will limit ourselves to dilute gases and solutions, the following equation is sufficient:

$$\mu = \mu_0 + RT \ln \frac{c}{c_0} \quad . \quad (\text{mass action formula})$$

This formula describes the phenomenon chemists call mass action as a characteristic of the chemical potential of a substance. For this reason we shall call it the *mass action formula*. Due to the proportionality of pressure and concentration in dilute gases of the same temperature, $p \sim c$, we can replace the ratio c/c_0 by the pressure ratio p/p_0 when necessary. Similarly, this holds for other concentration measures – molality b , mass fraction w , mole fraction x , etc. – so that we have slightly differing ways of playing with the mass action formula. The value μ_0 at the reference value of the chosen concentration measures, i.e., c_0, p_0, b_0 etc., we call the reference value of the potential (in an extended sense²) or briefly the reference potential.

Another equation is often used. When the molecules of a substance are put into an excited state which is higher in energy by ϵ , without otherwise altering them or their surround (type of solvent, temperature, pressure, concentrations, field strengths etc.), the chemical potential of the substance increases by the molar energy ϵ/τ :

$$\mu(\epsilon) = \mu(0) + \epsilon/\tau \quad . \quad (\text{excitation formula})$$

(τ indicates the elementary amount of substance^{3,4}). The simplest form of such a 'purely energetic' excitation that leaves the molecules themselves unchanged would be to displace them in an external field to a position having a higher potential energy, by a value of ϵ . By choosing an appropriate point of departure, one can, for example, set $\epsilon = mgh$ in the gravitational field and $\epsilon = ze\varphi$ in the electric field. $\mu(\epsilon) = \mu(0) + Mgh$ is also designated as the *gravi-chemical* potential and $\mu(\epsilon) = \mu(0) + zF\varphi$ as the *electro-chemical* potential, while $\mu(0)$ represents the intrinsic chemical potential (m mass of a molecule, $M = m/\tau$ molar mass, g gravitational field strength, h height, z charge number, e elementary charge, $F = e/\tau$ FARADAY-constant, φ electric potential).

The internal excitation of molecules requires a bit more attention. In general, the initial state of the molecules is not equivalent to any one "quantum state" with a certain energy ϵ_0 , but rather comprises a collective of such states with the energies, $\epsilon_0, \epsilon_1, \epsilon_2 \dots$. Only when an excitation leads to an equal shift of all energy values to $\epsilon, \epsilon_0 + \epsilon, \epsilon_1 + \epsilon, \epsilon_2 + \epsilon \dots$, without changing the number of states, can μ be calculated as given. In the usual approaches, this condition is adhered to unconsciously, needing little thought.

²In practice it is advisable to limit our use of the expression *reference value* (in the narrow sense) to the most common case, namely that the reference values $c_0, p_0, b_0 \dots$ of the chosen concentration measures $c, p, b \dots$ correspond to the norm values $c^\circ = 1 \text{ kmol m}^{-3}, p^\circ = 101 \text{ kPa}, b^\circ = 1 \text{ mol kg}^{-1} \dots$. These reference values – often called standard values – are indicated by a special symbol such as μ° .

³In his "Konzepte eines zeitgemäßen Physikunterrichts", Book 2, Schroedel: Hannover 1978, pg. 9, G. Falk suggests that τ is the reciprocal of the AVOGADRO constant $\tau = N_A^{-1} = 1.6606 \cdot 10^{-23} \text{ mol}$. It marks the *elementary amount* of a substance, meaning exactly the amount that is usually called a particle. This not absolutely necessary and initially strange departure from the usual way of writing gives us more uniform formulas and ways of expression. Particle number N and charge number z or elementary amount of substance τ and elementary charge e become corresponding quantities. The amount of substance n as well as the electric charge q are quantized by integers, where τ and e represent the elementary quanta of these quantities: $n = N \cdot \tau, q = z \cdot e$.

⁴In physics the product $\mu\tau$ is often called chemical potential and abbreviated with the symbol μ . It then happens that the particle number N_i appears in the formulas instead of the amount of substance n_i .

It should be remembered that the first derivative of chemical potential with respect to temperature T at constant values of pressure p and amount of substance n , yields the molar entropy S_m , whereas the second derivative yields the molar heat capacity $C_{p,m}$:

$$S_m = - \left(\frac{\partial \mu}{\partial T} \right)_{p,n} \quad \text{and} \quad C_{p,m} = -T \left(\frac{\partial^2 \mu}{\partial T^2} \right)_{p,n} .$$

If we proceed from chemical potentials to entropies or heat capacities, we already start upon the wrong path, making the descriptions more complicated (except in the case of the effects of heat), the formulas more complex, the proofs more obscure. For these reasons, it is advisable to avoid taking this step if possible. We will take it here on occasion, but only to make better comparisons with previous results.

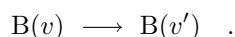
We will, at first, accept the conclusions of quantum theory without question, even though we would only need strongly simplified relations for a number of applications in this field. Some of the derivations below could be further streamlined using this approach.

Contribution of vibrations to the chemical potential

As the simplest example, we consider a bi-atomic gas B, perhaps iodine vapor. We take all the gas particles that are in the same vibrational state with the vibrational quantum number v to be molecules of a substance $B(v)$, and the entire gas to be a mixture of these substances⁵. The differences of energy in the individual vibrational states are taken into account by assuming $\epsilon(v) = v \cdot h\nu$, where we consider the vibrations as approximately harmonic and independent of other kinds of movement of the molecule⁶. As long as this approximation is valid, the excitation formula yields for the chemical potential of the individual substance $B(v)$

$$\mu_0(v) = \mu_0(0) + v \cdot \frac{h\nu}{\tau} \quad \text{for} \quad v = 0, 1, 2, 3... \quad .$$

Since the transformation of potentials into one another must happen under the same conditions, and especially at identical concentrations, the formula contains the reference values. Changes in vibration in the particles through collisions with each other and with the wall, appear as transformations of the following type:



After a short while, all of these processes reach a state of equilibrium where the concentrations of the components $B(v)$ reach their equilibrium values $c(v)$. In this state, the potential μ is the same for all substances $B(v)$. This means that when we take both the mass action and the excitation formula into account, we obtain

$$\mu = \mu_0(0) + v \cdot \frac{h\nu}{\tau} + RT \ln \frac{c(v)}{c_0} \quad \text{and} \quad v = 0, 1, 2, 3... \quad .$$

⁵This device was first used by ALBERT EINSTEIN (Verh. Dtsch. Phys. Ges. **12** (1914) 820) with the expressed note that so used, recourse to BOLTZMANN's principle, and therewith, statistical considerations, become unnecessary.

⁶We therefore assume that the transition from a vibrational state into another, has no influence upon other quantum states of the molecule (translation, rotation, etc.). This is certainly not justified at higher states of rotation because the increase of moment of inertia through an enlarged vibration amplitude and therewith, reaction upon rotational movement, becomes noticeable. This error is unimportant at lower temperatures because the portion of more strongly stimulated particles is very small in the equilibrium mixture.

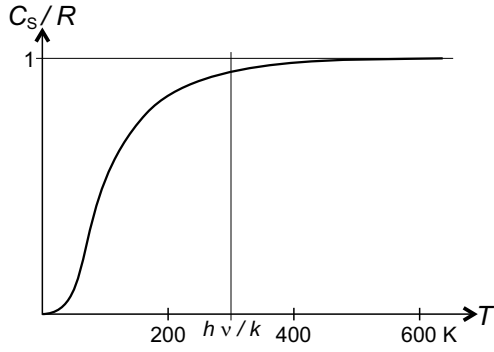


Figure 4: The contribution of molecular vibration to the heat capacity of I_2 -vapor, is $C_s(T)$. The characteristic temperature of vibration Θ_s is 305 K.

The $c(v)$'s are easily calculated from this. By subtracting $\mu_0 + v \cdot h\nu/\tau$ from both sides, dividing by RT , taking into account the power rules $e^{a+b} = e^a \cdot e^b$ and $e^{\ln a} = a$, multiplying by c_0 , and remembering that $R = k/\tau$, we obtain

$$\underbrace{c_0 \cdot \exp\left(\frac{\mu - \mu_0(0)}{RT}\right)}_{c(0)} \cdot \underbrace{\left(e^{-h\nu/kT}\right)^v}_{q < 1} = c(v) \quad .$$

That the expression on the left is equal to $c(0)$ can be seen when one sets $v = 0$. Adding up all the concentrations $c(v)$ gives the total concentration c of the gas B :

$$c = \sum_{v=0}^{\infty} c(v) = c(0) \sum_{v=0}^{\infty} q^v = c(0) \frac{1}{1-q} = c_0 \exp\left(\frac{\mu - \mu_0(0)}{RT}\right) \underbrace{\frac{1}{1 - e^{-h\nu/kT}}}_{z_s} \quad .$$

The fraction on the far right is the well-known quantum statistical expression for the *vibrational partition function* z_s of the harmonic oscillator. Solving for μ results in

$$\mu = \mu_0(0) + \underbrace{RT \ln\left(1 - e^{-h\nu/kT}\right)}_{\mu_s(T)} + RT \ln \frac{c}{c_0}$$

The term $\mu_s(T)$ is the sought after contribution of molecular vibrations to the chemical potential. By taking the second derivative with respect to T and multiplying by $-T$, we can calculate the contribution of vibrations to the molar heat capacity, $C_s = -T(d^2\mu_s/dT^2)$. The result, which is represented in Figure 4, is:

$$C_s = R \cdot \frac{(h\nu/kT)^2 \cdot e^{h\nu/kT}}{[e^{h\nu/kT} - 1]^2}$$

(intermediate steps have been omitted here).

Contribution of rotation to the chemical potential

Calculations for rotational contributions follow the same pattern. This exercise is actually only interesting in the case of hydrogen, where the rotations, like the vibrations, begin to "freeze" at a comparably high temperature. In the following we will limit ourselves to para-hydrogen. Quantum mechanically we obtain for the energy of the hydrogen molecule $\epsilon(J, m_J) = k \Theta_r \cdot J(J+1)$, which holds for the rotational state characterized by the rotational quantum number J and the magnetic quantum number m_J . Θ_r is the *rotational temperature* which can be calculated from the molecular

geometry. Again, we take the total of all the molecules in the same state of rotation as one substance $B(J, m_J)$. According to the excitation formula, the reference value of the potential is:

$$\mu_0(J, m_J) = \mu_0(0, 0) + R \Theta_r J (J + 1) \quad , \quad \begin{cases} J & = 0, 2, 4, 6, 8, \dots \quad , \\ m_J & = -J, -J + 1, \dots, J - 1, J \quad . \end{cases}$$

Of course, we could have combined all the molecules belonging to one rotational level into a substance $B(J)$, i.e., the molecules which have rotational states with the same J , but not necessarily the same m_J , and therefore differ from each other not by their energy, but by their orientation in space. However, since the number of quantum states differing by m_J is $2J + 1$ and therefore changes from one rotational level to another, the requirements for applying the excitation formula were not fulfilled.

In colliding with each other, differing kinds of molecules change into one another so that the concentrations $c(J, m_J)$ alter until – at the same value of the chemical potential – equilibrium is reached for all components $B(J, m_J)$ of the mixture. Because of the mass action formula, the following equation holds in this case for all J and m_J :

$$\mu = \mu_0(0, 0) + R \Theta_r J (J + 1) + RT \ln \frac{c(J, m_J)}{c_0}$$

from which, as seen in the last section, one can calculate the concentrations of all substances

$$c_0 \cdot \exp\left(\frac{\mu - \mu_0(0, 0)}{RT}\right) \cdot \left(e^{-\Theta_r J(J+1)/T}\right) = c(J, m_J) \quad .$$

Adding up over all J and m_J – the latter results in $2J + 1$ equal elements and therewith, a factor $2J + 1$ – yields for the total concentration c of gas B

$$c = c_0 \cdot \exp\left(\frac{\mu - \mu_0(0, 0)}{RT}\right) \underbrace{\sum_J (2J + 1) e^{-\Theta_r J(J+1)/T}}_{z_r}$$

z_r is equivalent to the *rotational partition function* of quantum statistics. If the equation is solved for μ and the sum is written out, one obtains for μ the expression

$$\mu = \mu_0(0, 0) - \underbrace{RT \ln(1 + 5e^{-6\Theta_r/T} + 9e^{-20\Theta_r/T} + \dots)}_{\mu_r(T)} + RT \ln \frac{c}{c_0}$$

where $\mu_r(T)$ represents the desired rotational contribution in the form of a series. Because the series quickly converges at medium and low temperatures, the three elements given are sufficient at around 0 ... 300 K, if the margin of error should be smaller than 0.001 kG.

Again, for a better comparison with conventional representations, one can calculate the rotational contribution to the molar heat capacity C_r , by taking the second derivative of $\mu_r(T)$ with respect to T . By omitting the intermediate calculation, one obtains the formula below which is complicated in comparison to the expression for $\mu_r(T)$. The result is represented grafically in Figure 5.

$$C_r(T) = R \left(\frac{\Theta_r}{T}\right)^2 \left\{ \frac{180 e^{-6\Theta_r/T} + 3600 e^{-20\Theta_r/T}}{1 + 5 e^{-6\Theta_r/T} + 9 e^{-20\Theta_r/T}} - \left[\frac{30 e^{-6\Theta_r/T} + 180 e^{-20\Theta_r/T}}{1 + 5 e^{-6\Theta_r/T} + 9 e^{-20\Theta_r/T}} \right]^2 \right\} .$$

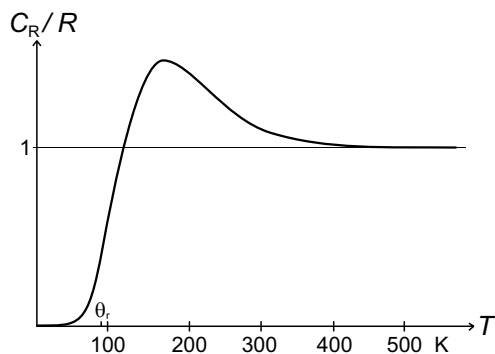


Figure 5: The contribution $C_r(T)$ of molecular rotation to the molar heat capacity of para hydrogen. The rotational characteristic temperature Θ_r is 87.7 K. For calculations up to 300 K, the formula found in the text is used. Only the three lowest levels of rotation ($J = 0, 2, 4$) are taken into account. Above 300 K, the fourth level ($J = 6$) is added.

Molecular velocity distribution

In order to derive the distribution of particle velocities in a gas, we will use the same device as before. We conceive of all the particles with the same velocity vector \mathbf{v} as molecules of a substance $B(\mathbf{v})$, and of the entire gas as a mixture of many such substances. At this point, we run into a difficulty. The number of particles that have exactly the velocity \mathbf{v} is, strictly speaking, zero. For this reason we consider the velocity space to be divided into a lattice of cubes having edges of length Δv , where Δv should be small in comparison to the width of the velocity distribution. All the particles whose velocity vectors end within such a cube will be considered as molecules of the same substance $B(\mathbf{v})$.

Because particles moving in various directions cannot be distinguished from each other on chemical grounds, we assign them the same reference potential μ_0 . Differing values of energy at different absolute values of velocity, $v = |\mathbf{v}|$, are taken into account by the term $\epsilon/\tau = \frac{1}{2}mv^2/\tau = \frac{1}{2}Mv^2$, the *molar kinetic energy* of the substance:

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

In the simplest case of a gas with particles without structure in a volume V , this approach can be justified as follows. All the particles of the substance $B(\mathbf{v})$ lie in a cell of the molecular phase space that has a phase volume of $(m\Delta v)^3V$ and therefore comprises $\zeta = (m\Delta v)^3V/h^3$ quantum states. In the case of small enough Δv , they all belong to the same energy level $\frac{1}{2}Mv^2$ (h : PLANCK constant). Because ζ is the same in all cases, the substance $B(\mathbf{v})$ fulfills the requirements of the excitation formula in regards to number and energy of the molecular quantum state.

Change of velocity of the particles through frequent collisions with each other appears as transformations of a simple type $B(\mathbf{v}) \rightarrow B(\mathbf{v}')$. If we do not disturb the gas by having it stirred, or through other kinds of interference, then all these processes reach a state of equilibrium within a short time. The chemical potential μ will be the same for all substances $B(\mathbf{v})$, so that according to the mass action formula we have

$$\mu = \mu_0 + \frac{1}{2}Mv^2 + RT \ln \frac{c(\mathbf{v})}{c_0} \quad \text{for all } \mathbf{v}$$

where $c(\mathbf{v})$ are the equilibrium values of the concentrations. By solving for $c(\mathbf{v})$, we obtain the desired distribution (compare to Figure 6):

$$c(\mathbf{v}) = \underbrace{c_0 \cdot \exp\left(\frac{\mu - \mu_0(\mathbf{0})}{RT}\right)}_{c(\mathbf{0})} \cdot \exp\left(\frac{-\frac{1}{2}Mv^2}{RT}\right) \Rightarrow \boxed{c(\mathbf{v}) = c(\mathbf{0}) \exp\left(\frac{-m(v_x^2 + v_y^2 + v_z^2)}{2kT}\right)} \quad .$$

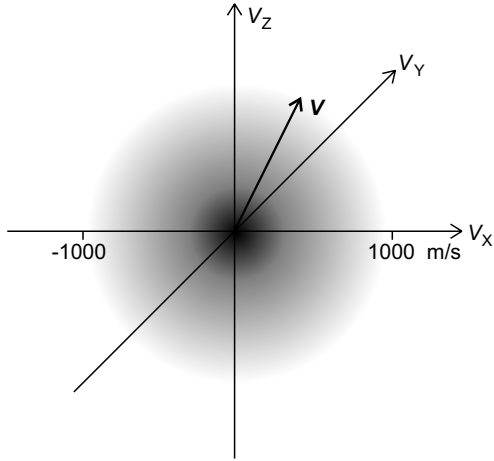


Figure 6: If we represent $c(\mathbf{v})$ according to the equation above as shading in three dimensional velocity space, we obtain the spherical cloud given at the left. The values are valid for nitrogen at 298 K.

Barometric formula

The distribution of a gas in a homogenous gravitational field can be extracted using the same pattern as above. To do this, we consider the particles at a particular altitude h as molecules of a substance $B(h)$ ⁷. The reference potentials $\mu_0(h)$ of the chemically identical substances $B(h)$ differ only by the *molar potential energy* $\epsilon/\tau = Mgh$:

$$\mu_0(h) = \mu_0(0) + Mgh \quad .$$

The exchange of particles between different altitudes is equivalent to the reactions $B(h) \rightarrow B(h')$. If the temperature is homogenous, equilibrium of all the substances is eventually reached. The requirement for equilibrium is

$$\mu = \mu_0 + Mgh + RT \ln \frac{c(h)}{c_0}$$

with the potential μ being independent of h . Solving for $c(h)$ yields the equation

$$c(h) = \underbrace{c_0 \cdot \exp\left(\frac{\mu - \mu_0(0)}{RT}\right)}_{c(0)} \cdot \exp\left(\frac{Mgh}{RT}\right) \quad \Rightarrow \quad \boxed{c(h) = c(0) \cdot \exp\left(\frac{-mgh}{kT}\right)} \quad .$$

Equilibrium of sedimentation in a centrifuge

The centrifugal force upon a particle with a mass m at a distance r from the axis of rotation of a centrifuge spinning with the angular velocity ω , is $F = m\omega^2 r$. It follows that the potential energy relative to a point at a distance r_0 , is

$$\epsilon = \int_{r_0}^r F dr = -\frac{1}{2} m\omega^2 (r - r_0)^2 \quad .$$

Along with the contribution ϵ/τ to the chemical potential, we have to take into account the pressure dependence of the potential due to the high pressures in the solution being centrifuged. A linear

⁷Strictly speaking, in this type of procedure one should consider a layer of finite thickness Δh so that the particle number doesn't vanish. In contrast to the last section where $c(\mathbf{v})$ goes to zero for $\Delta v \rightarrow 0$ (proportional to $(\Delta v)^3$), $c(h)$ is independent of Δh for $\Delta h \rightarrow 0$ and stays finite so that the equations used above remain valid for $\Delta h = 0$ as well.

approach is sufficient here:

$$\mu(p) = \mu(p_0) + V_m \cdot (p - p_0)$$

since the molar volume V_m of the condensed substance is only slightly dependent upon the pressure p . We will now look at a centrifuged dilute solution of a substance B in a liquid A (Figure 7 on the left). As a point of reference, we choose the fluid's surface at a distance r_0 from the axis of rotation. If we neglect the tiny reduction of μ_A by the solved substance B, we have for the potentials μ_A and μ_B of the substances A and B at a location inside the solution ($r > r_0$):

$$\begin{aligned} \mu_A(r) &= \mu_A(r_0) - \frac{1}{2} M_A \omega^2 (r^2 - r_0^2) + V_A \cdot [p(r) - p(r_0)] \quad , \\ \mu_B(r) &= \mu_B(r_0) - \frac{1}{2} M_B \omega^2 (r^2 - r_0^2) + V_B \cdot [p(r) - p(r_0)] + RT \ln \frac{c(r)}{c(r_0)} \quad . \end{aligned}$$

Equilibrium is reached when the potentials have evened out everywhere so that $\mu_A(r)$ as well as $\mu_B(r)$ have the same value everywhere. In this state, the terms $\mu(r)$ and $\mu(r_0)$ in both equations cancel so that we obtain the following quadratic relation for the pressure distribution in the solution from the first one

$$p(r) = p(r_0) + \frac{1}{2} \rho_A \omega^2 (r^2 - r_0^2)$$

Here, $\rho_A = M_A/V_A$ is the density of the fluid A. When this result is inserted into the second equation above, the desired concentration distribution is obtained:

$$[M_B - \rho_A V_B] \cdot \frac{1}{2} \omega^2 (r^2 - r_0^2) = RT \ln \frac{c(r)}{c(r_0)} \quad \Rightarrow$$

$$c(r) = c(r_0) \cdot \exp \left(\frac{[m_B - \rho_A v_B] \cdot \omega^2 \cdot (r^2 - r_0^2)}{2kT} \right) \quad .$$

$v_B = V_B \cdot \tau$ specifies the volume and $\rho_A \cdot v_B$ the mass of fluid displaced by a B particle. In other words, $\rho_A \cdot v_B$ is the apparent loss of mass of a B-particle as a result of buoyancy in the fluid. An interesting point is that this hydro-mechanical correction is a result of the pressure dependence of the chemical potentials. The fact that V_B and v_B can become negative due to denser packing of A-molecules in the solvation sheath does not negate the principle of ARCHIMEDES at all.

Not much is changed if B is not dissolved but only suspended. One can consider particles of the same diameter \varnothing as molecules of a solved substance $B(\varnothing)$, and the entire suspension as a mixture of such substances. For each substance $B(\varnothing)$ the equation derived above again holds.

Probability of an energy state

As the examples which we have observed have shown, the mass action and the excitation formulas, $\mu(c) = \mu_0 + RT \ln(c/c_0)$ and $\mu(\epsilon) = \mu_0 + \epsilon/\tau$, together serve the same purpose as BOLTZMANN's principle. Taken together, they appear to be only a special representation of this principle; they are closer to chemistry and well known in this guise, but badly applied. We obtain the conventional version if we interpret the concentration $c(\epsilon, i)$ of the particle type $B(\epsilon, i)$ as a measure of the probability $p(\epsilon, i)$ to find a particle B in a state with energy ϵ and parameter value i : $p(\epsilon, i) \sim c(\epsilon, i)$. The parameter i , that we take to be discrete, stands for some characteristic (spatial orientation, spin orientation, conformation, etc.) by which – apart from ϵ – the individual types of particle ensembles can be distinguished if applicable. One needs only to insert the second equation

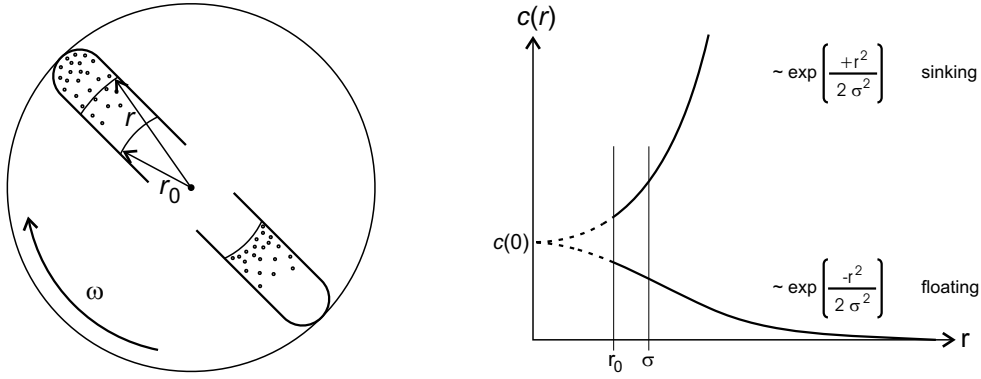


Figure 7: Sedimentation equilibrium in a centrifuge for a substance B (particle mass m_B , particle volume v_B) which is either dissolved or suspended in a fluid with a density of ρ_A . If the centrifugal force becomes larger than the force of buoyancy, the substance B concentrates toward the outside (upper container, upper curve), otherwise toward the inside (lower container, lower curve).

ω angular velocity, r distance from the axis of rotation, r_0 distance of the fluid surface from the axis of rotation, c concentration of B, $c(0)$ the value of c extrapolated to the axis of rotation; the curve parameter σ is the distance from the axis in which the potential energy corrected by the effect of buoyancy is $|m_B - \rho_A v_B| \cdot \frac{1}{2} \omega^2 \sigma^2 = \frac{1}{2} kT$.

into the first one and solve for $c = c(\epsilon, i)$:

$$c(\epsilon, i) = c_0 \cdot \exp\left(\frac{\mu - \mu_0(0)}{RT}\right) \cdot e^{-\epsilon/kT} \quad \Rightarrow \quad p(\epsilon, i) \sim e^{-\epsilon/kT} \quad .$$

Statistical weights do not come up here because application of the excitation formula requires that the individual types of particles are chosen to be equally weighted statistically. The stipulation that the corresponding "quantum states" of differing types of particles may differ by the same energy value ϵ , but not in their number, means exactly this. If the usual question arises about the probability $p(\epsilon)$ of finding a B-particle at the energy level ϵ , i.e., in a state with energy ϵ independent of i , one needs only to add up the appropriate $p(\epsilon, i)$. Since all of these are equal, and if their number is $g(\epsilon)$ (where $g(\epsilon)$ is the statistical weight of the energy level), we obtain

$$\boxed{p(\epsilon) \sim g(\epsilon) \cdot e^{-\epsilon/kT}} \quad . \quad \text{(BOLTZMANN'S principle)}$$

Outlook

Nothing speaks against relying upon BOLTZMANN's principle in the usual way for further considerations. We will, however, stay with the "chemically more adjusted" description using chemical potentials because similarities between the different fields, which usually stay hidden due to differing patterns of description, will become apparent. In order to demonstrate the significance of the approach, additional molecular statistical examples from strongly differing fields of chemical dynamics, will be considered.

The equivalence to BOLTZMANN's principle, stressed in the last section, lets us suspect that our approach must fail at one point. BOLTZMANN based his derivation upon the assumption of individually distinguishable particles, which is unjustified from the view of quantum theory. Conventional teaching says that all particles are either fermions and bosons. These only obey the "BOLTZMANN statistics" when sufficiently diluted. Otherwise, they are subject to special "quantum statistics" as a result of the PAULI principle and the indistinguishability of particles in the same

quantum state. For fermions, this is "FERMI-DIRAC statistics" and for bosons, "BOSE-EINSTEIN statistics". A calculation of the absolute entropy can only be successful upon this basis whereby indistinguishability of like particles also has consequences for highly diluted systems. The number of possible micro-states of a system of N independent equal particles thus changes by a factor $1/N!$ and the entropy by $\Delta S = -k \ln N!$.

We will see that our approach also works with problems of this sort. At this juncture, it is useful to fall back upon surface chemistry because it gives us clear examples of systems with FERMI-DIRAC and BOSE-EINSTEIN distributions. We won't have to waste any words on indistinguishability of particles. We obtain the correct entropy values without even mentioning the factor $1/N!$.

Georg Job

An elementary approach to quantum statistical problems (II)

After a talk given at the Seminar of Surface Chemistry in the Institute of Physical Chemistry
of the University of Hamburg, on May 21, 1991.

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 practical 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.

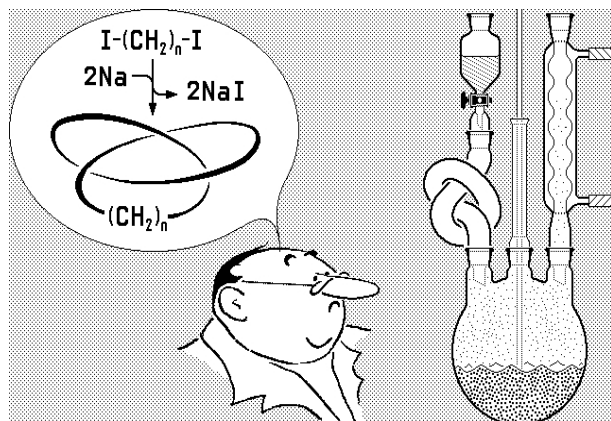
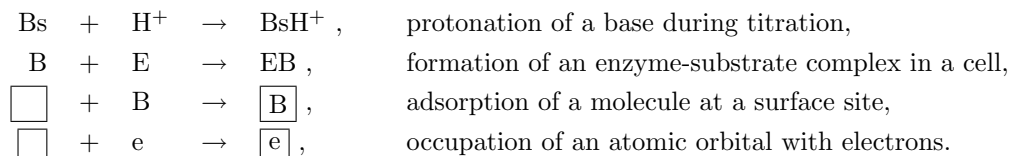


Figure 1: In his work in the lab, a chemist is guided by atomistic models. The success of his work depends largely upon the coherence of his molecular models. A misguided relation between micro-world and macro-world can also lead to failure. In the figure we see a suggestion for an experiment for the 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:



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 ions¹. The degree of protonation $\Theta = c_{\text{BsH}^+}/(c_{\text{Bs}} + c_{\text{BsH}^+})$ of a base Bs depends upon the *pH*-value or the proton potential μ_{H^+} of the solution. Starting with the condition of equilibrium, $\mu_{\text{Bs}} + \mu_{\text{H}^+} = \mu_{\text{BsH}^+}$, the mass action formula leads to

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

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

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

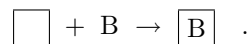
μ_1 graphically describes the 50%-potential, i.e., the proton potential at a degree of protonation $\Theta = \frac{1}{2}$. The index 1 for the attachment of the first proton to the base Bs has been chosen in view of a possible multiple addition of protons. Solving the previous relation for Θ , and making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

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

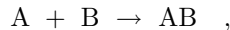
We shall encounter this equation repeatedly in similar form. Figure 2b shows the relation graphically. We obtain corresponding equations and graphs if we investigate the analogous redox reaction $\text{Ox} + e^- \rightarrow \text{Rd}^-$ instead of the acid-base reaction $\text{Bs} + \text{H}^+ \rightarrow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

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:



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



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

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

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 $\mu_{\text{H}^+}^\circ$ lends itself for such fixing of the scale.

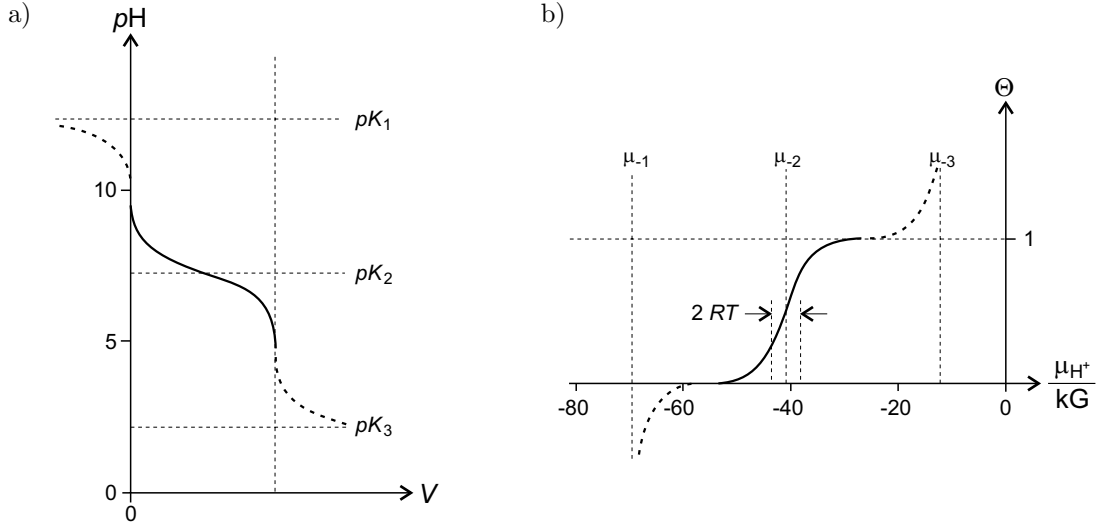


Figure 2: Titration curve of the base hydrogenphosphate, HPO_4^{2-} .

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, $\text{pH} = \text{p}K_A + \lg(c_{\text{Bs}}/c_{\text{BsH}^+})$; 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^+); $\text{p}K_i$: 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 \square for B. So that the sites do not interact, the total concentration $c = c(\text{A}) + c(\text{AB})$ 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 $\mu(\text{A})$ and $\mu(\text{AB})$. The condition for equilibrium $\mu(\text{A}) + \mu(\text{B}) = \mu(\text{AB})$ then takes the form

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

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. $c(\text{A})/c = \Theta(\square)$ is the *fraction of empty sites* and $c(\text{AB})/c = \Theta(\text{B})$ the *fraction of occupied sites*. We replace $c(\text{A})$ and $c(\text{AB})$ with $c \Theta(\square)$ and $c \Theta(\text{B})$, respectively, and subtract $\mu_0(\text{A}) + RT \ln(c/c_0)$ from both sides:

$$\underbrace{\mu_0(\square) + RT \ln \Theta(\square)}_{\mu(\square)} + \mu(\text{B}) = \underbrace{\mu_0(\text{B}) + RT \ln \Theta(\text{B})}_{\mu(\text{B})} \quad (\text{equilibrium condition})$$

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

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 $\mu_0(\text{B})$, 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, $\mu(\square) = \mu_0(\square) + RT \ln \Theta(\square)$ 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, \square and $\boxed{\text{B}}$, as well as the equations $\Theta(\boxed{\text{B}}) = \Theta$ and $\Theta(\square) = 1 - \Theta$ with the *degree of coverage* Θ , the condition for equilibrium of adsorption is:

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

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 $\mu_0(\square) = 0$, this leads to the relation

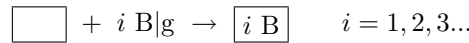
$$c(1 - \Theta) = c_0 \cdot \underbrace{\exp\left(\frac{\mu_0(\boxed{\text{B}}) - \mu_0(\text{B})}{RT}\right)}_{c_1 \text{ 50\%-concentration}} \cdot \Theta \quad .$$

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 $\Theta = \frac{1}{2}$:

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

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:



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 $\mu(\square) = 0$, the condition of equilibrium $\mu(\square) + i\mu(\text{B|g}) = \mu(\boxed{i \text{ B}})$ for the adsorption process is

$$RT \ln \Theta_0 + i \cdot [\mu_0(\text{B|g}) + RT \ln(c/c_0)] = \mu_0(\boxed{\text{B}}) + (i - 1) \cdot \mu(\text{B|l}) + RT \ln \Theta_i \quad .$$

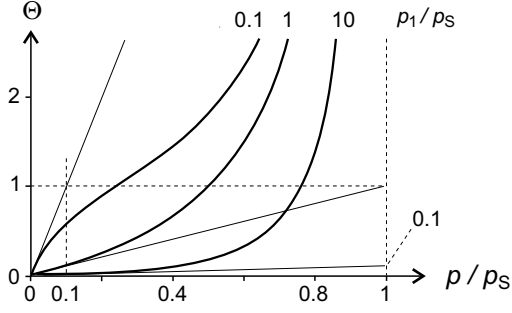


Figure 3: BRUNAUER-EMMET-TELLER adsorption isotherms. The degree of coverage Θ is represented as a function of the reduced pressure p/p_s for various values of the ratio of 50%-pressure p_1 and saturation pressure p_s . The smaller the 50%-pressure the firmer the binding to the surface. $p_1 < p_s$ corresponds to an adsorbing surface, $p_1 = p_s$ to an indifferent surface and $p_1 > p_s$ to a repelling surface.

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

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

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 B|l and vapor B|g are in equilibrium,

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

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

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

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

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

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 $d(1-q)^{-1}/dq = (1-q)^{-2}$. 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):

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

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),

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

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).

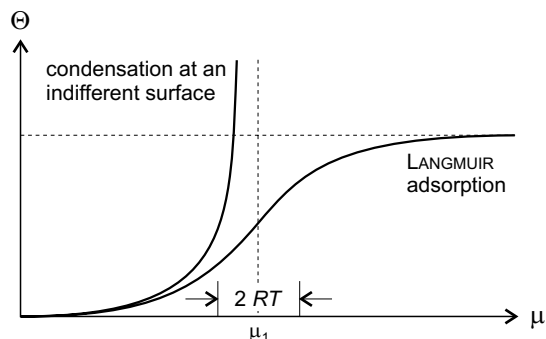


Figure 4: Degree of coverage Θ as a function of the chemical potential μ of the substances to be adsorbed, for two theoretically interesting special cases. R gas constant, T temperature, μ_1 "50%-potential" (for which half-occupation of the first adsorption layer is reached).

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:

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

We consider each translation state \mathbf{n} as a kind of site $\square_{\mathbf{n}}$ 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,

$$\square_{\mathbf{n}} + i\text{B} \rightarrow [i\text{B}]_{\mathbf{n}} \quad \begin{cases} i = 0, 1 & \text{for fermions,} \\ i = 0, 1, 2, 3, \dots & \text{for bosons.} \end{cases}$$

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., $\Theta_{\mathbf{n}} \ll 1$, so that multiple occupancy or processes with $i > 1$ can be ignored. Under these circumstances, fermions and bosons behave identically. We revert to

$$\mu(\square_{\mathbf{n}}) = \underbrace{\mu_0(\square_{\mathbf{n}})}_0 + \underbrace{RT \ln(1 - \Theta_{\mathbf{n}})}_{\approx 0}, \quad \mu([B]_{\mathbf{n}}) = \underbrace{\mu_0([B]_{\mathbf{n}})}_{(\epsilon_{\mathbf{n}} + \epsilon)/\tau} + RT \ln \Theta_{\mathbf{n}}.$$

for the chemical potential of an empty and simply occupied site. Because of $\Theta_{\mathbf{n}} \ll 1$ in the expression on the left, we can set the logarithmic term practically equal to zero so that $\mu(\square_{\mathbf{n}})$ disappears. On the right, we can express the main term by $(\epsilon_{\mathbf{n}} + \epsilon)/\tau$. 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 $\square_{\mathbf{n}} + \text{B} \rightarrow [B]_{\mathbf{n}}$ are in equilibrium. This means until $\mu(\square_{\mathbf{n}}) + \mu = \mu([B]_{\mathbf{n}})$ or, based upon the expressions above, until

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

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

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

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 $q = h/(2a\sqrt{2\pi mkT})$, one obtains:

$$\sum_{\mathbf{n}} e^{-\epsilon_{\mathbf{n}}/kT} = \sum_{n_1, n_2, n_3=1}^{\infty} e^{-q^2(n_1^2 + n_2^2 + n_3^2)} = \left[\sum_{n_1=1}^{\infty} e^{-q^2 n_1^2} \right]^3 \approx \left[\underbrace{\int_0^{\infty} e^{-q^2 n_1^2} dn_1}_{\sqrt{\pi}/2q} \right]^3 = \frac{(2\pi mkT)^{3/2}}{h^3} V.$$

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

²Instead of the term *degree of coverage*, which is based upon surfaces we use the more general term *degree of occupation* here. We reserve the name occupation number for the particle number in specific quantum states. The occupation number is therefore an integer, the degree of occupation (= average occupation number) is a real number.

³ $\sqrt{2\pi mkT}$ describes the momentum uncertainty based upon the thermal motion of the particles, and the quantum length $\lambda = h/\sqrt{2\pi mkT}$ describes the corresponding position uncertainty. The position of the center of mass of a thermally moving gas particle is only determined up to a speck of the length, height and width λ . At room temperature, λ is 100 pm for hydrogen atoms (gas kinetic diameter 250 pm) and 4300 pm for electrons.

"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:

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

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 \square_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 :

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

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

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

$\mu_{t,0}(T)$ 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 ,

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

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

⁴A 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, $c_e = 21 \text{ mol m}^{-3}$. The concentration of conduction electrons in a metal is far above this value ($\approx 10^{23} \text{ mol m}^{-3}$).

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 $C_{p,m} = -T(\partial^2\mu/\partial T^2)_{p,n}$:

$$S_m = R \left[\ln \left(\frac{(2\pi m)^{3/2} (kT)^{5/2}}{h^3 p} \right) + \frac{5}{2} \right] \quad (\text{SACKUR-TETRODE equation})$$

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

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 $\frac{1}{2} kT$, as required by the equipartition principle.

Fermi-Dirac, Bose-Einstein and Boltzmanns distributions

We focus once again upon occupation of a single site \square 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:



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

$$\mu(\boxed{iB}) = \mu_0(\boxed{iB}) + RT \ln \Theta_i \quad \text{with} \quad \mu_0(\boxed{iB}) = i \cdot \epsilon/\tau \quad .$$

The fact that we have set $\mu_0(\boxed{iB})$ 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 $\mu_0(\square) = 0$, the condition for equilibrium $\mu(\square) + i \cdot \mu = \mu(\boxed{iB})$ takes the following form

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

$$\Theta_0 \underbrace{\left[\exp \left(\frac{\mu \tau - \epsilon}{kT} \right) \right]^i}_q = \Theta_i \quad \text{for all } i.$$

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.

$$\Theta_0(1+q) = \underbrace{\Theta_0 + \Theta_1}_1, \quad \Theta_0 \underbrace{(1+q+q^2+q^3\dots)}_{(1-q)^{-1}} = \underbrace{\Theta_0 + \Theta_1 + \Theta_2\dots}_1$$

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

The expression $1+2q+3q^2\dots$ is the derivative of $1+q+q^2+q^3\dots$. Hence, its sum is equal to the derivative $d(1-q)^{-1}/dq = (1-q)^{-2}$. If we calculate Θ_0 from the equations of the first line, and

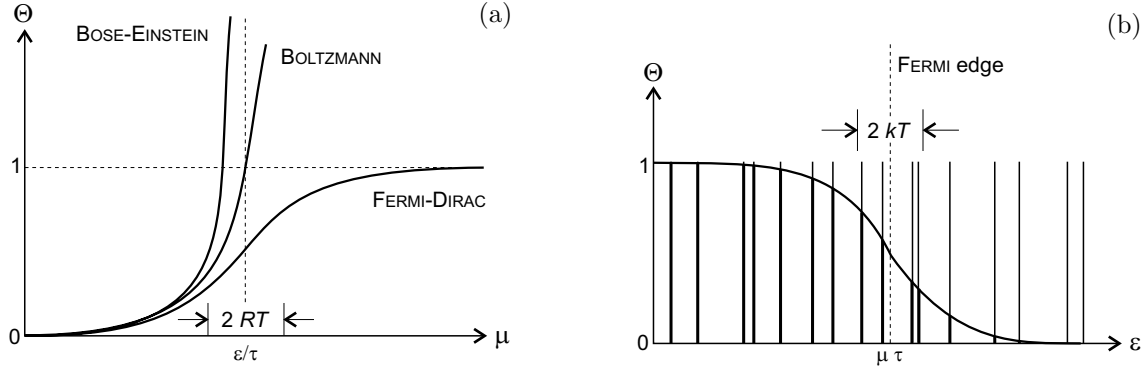


Figure 5: FERMI-DIRAC and BOSE-EINSTEIN distribution

a) Degree of occupation Θ of a site \square 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 kT , 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

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

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

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

Fermi-Dirac

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

Bose-Einstein

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

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.

Georg Job

An elementary approach to quantum statistical problems (III)

Summary: The solution procedures discussed in Parts I and II essentially make use only of the existence of chemical potential, its concentration and energy dependency. However, if cleverly applied, they can also be used in the case of interaction between the dissolved, vaporized or adsorbed particles. For dissolved substances, this will be demonstrated with the help of the DEBYE-HÜCKEL theory of inter-ionic interaction. The van der Waal's equation will serve as the example for gases. For adsorbed substances, we will show the procedure in general.

Introduction

In all of our computational examples, we have mostly used two characteristics of the chemical potential: the concentration dependency and the energy dependency expressed by two equations which we have given names for the sake of convenience. These are the "mass action formula" $\mu(c) = \mu_0 + RT \ln(c/c_0)$ and the "excitation formula" $\mu(\epsilon) = \mu(0) + \epsilon/\tau$. The validity of the first equation necessitates the absence of noticeable interaction between the particles distributed in space. This only applies to ideal gases or ideal solutions, a state that can be approached by sufficiently high dilution. Denser gases and more concentrated solutions are therefore excluded from this treatment.

We know from previous experience how careful one must be with such conclusions. A spontaneous idea can be enough to enable us to jump a hurdle that seemed insurmountable before (Figure 1). Stimulus for solving our problems can be gotten from totally different areas. In order to calculate the deviation from ideal behavior of solved electrolytes, DEBYE and HÜCKEL get by with BOLTZMANN's Principle and POISSON's equation. All we need to do is to take the equivalent steps for chemical potentials to achieve the same objective. An advantage for us here is that we do not have to change from one level to another, i.e., from the statistical to the phenomenological. Rather, we begin immediately with the quantity we are interested in at the end. To keep the math uncomplicated, it is a good idea to study the formation of the ion clouds on flat boundary layers – e.g. in analogy to the barometric equation – before going over to spherically symmetric clouds around the ions.

The insight gained here can, in turn, be used to describe the behavior of real gases. We choose a VAN DER WAAL's gas as our example because the equation of state and the associated physical model are familiar to every physicist and chemist, and therefore immediately comparable

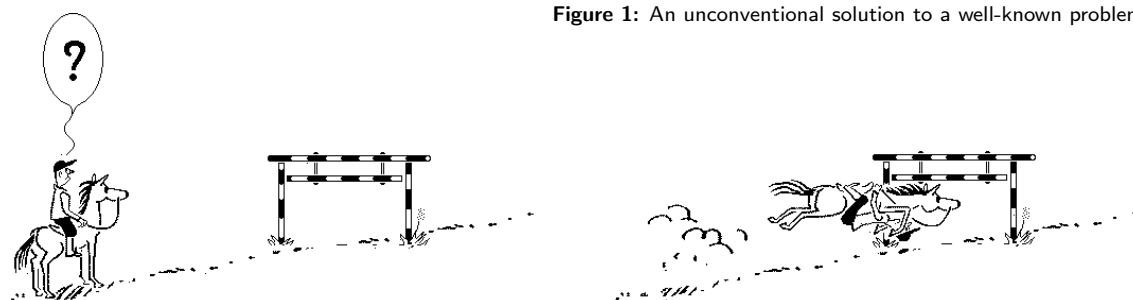


Figure 1: An unconventional solution to a well-known problem

to our assumptions and results. Of course, if one knows how, one can avoid borrowing from electrochemistry and go directly from ideal to real gases.

After having lost our shyness towards micro-systems in Part II, we are able to use these as models for appropriate solution procedures. A base capable of taking several protons, $Bs + i H \rightarrow [BsH_i]$, can serve as a model for a surface having sites for adsorption where strong interactions exist between the adsorbing particles. Nothing hinders us from considering Bs as a very large molecule with correspondingly numerous adsorption sites. If we imagine these spaces distributed inside a homogenous molecule instead of on its surface, we then have a model of a solution with strong interaction between the dissolved particles. We will let this approach play out in an example of surface chemistry. Transferring it to solutions shouldn't present any real difficulties.

Double layers on electrode surfaces

At a charged surface with no charge current in an electrolyte solution, the solution forms a *boundary layer* in which the potential $\varphi(r)$ and the concentrations $c_i(r)$ of the various types of ions deviate from the values $\varphi(\infty)$ and $c_i(\infty)$ dominating far away in the interior of the solution. The distance from the aforementioned flat surface is indicated by r (Figure 2).

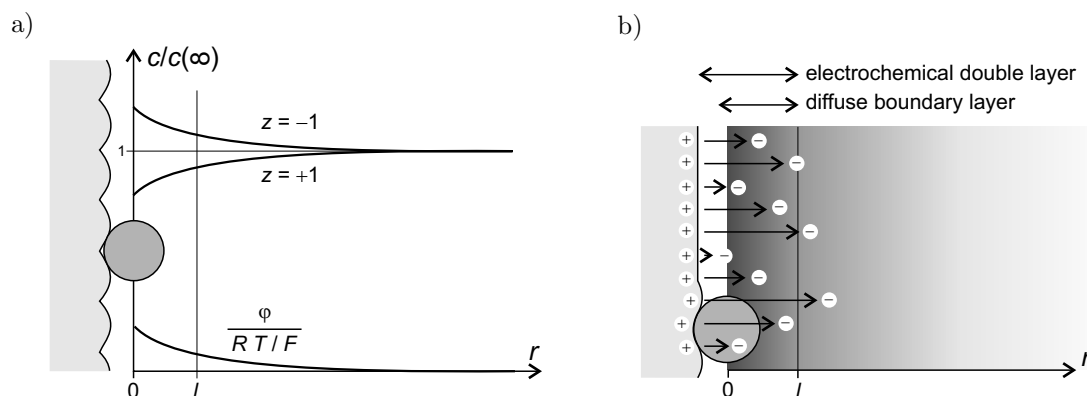


Figure 2: a) Ionic concentration c and electric potential φ in the surface layer of an electrode charged positively relative to the solution. r is the distance from the electrode ($r = 0$ for the centers of the ions when they touch the electrode), z is the charge number, F is the FARADAY constant, R is the gas constant, T is the temperature, l is the shielding length. For small voltages between the electrode and the interior of the solution, $\varphi(0) - \varphi(\infty) \ll RT/F \approx 25$ mV, the c and φ values exponentially approach the values for large r ($\sim \exp(-r/l)$).

b) The field arising in the positive charge of the electrode surface ebbs in the excess negative charge of the boundary layer so that the interior of the solution becomes field-free. The shading on the right symbolizes the charge density.

The boundary layer shields the solution electrically from the charged electrode surface: the field arising there ebbs in the boundary layer. The greater the concentration of ions of the solution, the more effective the *shielding* will be and the thinner the boundary layer will be. The *ional* concentration¹ c_ι offers a natural measure of how "ional" the solution is. Among the three expressions

¹In order to mark the quantities relating to (inter-)ionic interactions, we choose the index ι (lower case iota) which should be carefully distinguished from index i . For historical reasons, instead of c_ι , most authors prefer the *molar* ionic strength $I_c = \frac{1}{2}c_\iota$ which is half as large. In doing so, a factor of 2 is dragged into the formula. For practical reasons (because of independence of pressure and temperature) the *ional* molality $b_\iota = \sum_i z_i^2 b_i$ and respectively, the appropriate *molar* ionic strength $I_b = \frac{1}{2}b_\iota$, is preferred.

$$\underbrace{\sum_i z_i^0 c_i}_c, \quad \underbrace{\sum_i z_i^1 c_i}_{\rho/F}, \quad \underbrace{\sum_i z_i^2 c_i}_{c_l}, \quad \dots$$

the first one expresses the total concentration of all components. The second one describes the *charge density* ρ apart from the factor F^{-1} . The third describes the "ion-ness" of the solution.

In the following, only the simplest case of a double layer consisting of a charged electrode surface and an oppositely charged diffuse boundary layer will be considered. We assume that all the ions have unchanging solvation sheaths of the same diameter and are not adsorbed at the electrode surface. To account for the potential energy in the electric field of an ion with a charge number of z_i , one must, as discussed before, add the term $z_i F \varphi(r)$ to the appropriate chemical potential. Then, based upon the mass action formula, we have:

$$\mu_i(r) = \mu_i(\infty) + z_i F \varphi(r) + R T \ln \frac{c_i(r)}{c_i(\infty)}$$

if we choose $\varphi(\infty) = 0$. As long as there are spatial differences in the potentials $\mu_i(r)$, the ions will migrate and thereby change their concentrations $c_i(r)$. In a state of equilibrium, each of these potentials has the same value μ_i everywhere. In this case, the two terms $\mu_i(r)$ and $\mu_i(\infty)$ cancel each other so that, by solving the equation for $c_i(r)$, we obtain the expression

$$c_i(r) = c_i(\infty) \cdot \exp\left(\frac{-z_i F \varphi(r)}{R T}\right) \approx c_i(\infty) \cdot \exp\left[1 - \frac{z_i F \varphi(r)}{R T}\right] \quad \text{for} \quad \varphi(r) \ll \frac{R T}{z_i F} .$$

The expression on the right results from the series expansion of the exponential function, if the series is broken off after the linear term. This simplification of the calculation means that we must limit ourselves to small voltages between the electrode and the solution, i.e., to $\varphi(0) - \varphi(\infty) \ll R T / F$.

In the boundary layer, even in equilibrium, the charges of the ions do not cancel, but cause a space charge of the density $\rho(r) = F \sum z_i c_i(r)$. According to POISSON's equation, this, in turn, causes the curved shape of the electric potential. With the $c_i(r)$ values calculated above, we find:

$$\underbrace{-\epsilon \frac{\partial^2 \varphi(r)}{\partial r^2} = \rho(r)}_{\text{POISSON'S equation}} = \underbrace{\sum_i z_i F c_i(\infty)}_{\rho(\infty) = 0} - \underbrace{\sum_i z_i^2 c_i(\infty) \cdot \frac{F^2}{R T}}_{c_l} \cdot \varphi(r) .$$

($\epsilon = \epsilon_r \cdot \epsilon_0$ permittivity, ϵ_r relativ permittivity, ϵ_0 permittivity of vacuum, $c_l = c_l(\infty)$). $\rho(\infty)$ vanishes because the solution's interior is electrically neutral. Using the abbreviations $\varphi'' = \partial^2 \varphi(r) / \partial r^2$ and $l^{-2} = c_l F^2 / \epsilon R T$, the equation above becomes:

$$\varphi'' = l^{-2} \cdot \varphi .$$

By taking the second derivative, one is easily convinced that the equation can be solved using $\varphi = a e^{\pm r/l}$, i.e., by $\varphi'' = l^{-2} a e^{\pm r/l}$, where $a = \varphi(0)$. In our case, only the negative sign is useful in the exponent because $e^{+r/l}$ diverges for $r \rightarrow \infty$. With the expressions for $c_i(r)$ found above, with $\varphi(r)$ inserted, we arrive at the result represented in Figure 2:

$$\left. \begin{aligned} \varphi(r) &= \varphi(0) \cdot e^{-r/l} \\ c_i(r) &= c_i(\infty) \cdot \left[1 - \frac{z_i F \varphi(0)}{R T} \cdot e^{-r/l} \right] \end{aligned} \right\} \quad \begin{aligned} &\text{for} \quad \varphi(0) \ll R T / F \\ &\text{with} \quad \boxed{l = \sqrt{\epsilon R T / (c_l F^2)}} . \end{aligned}$$

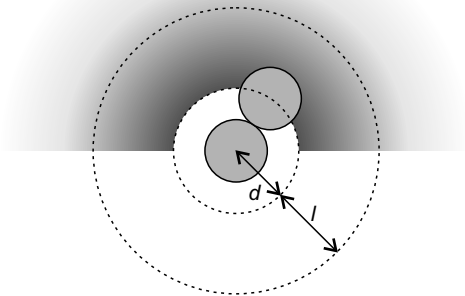


Figure 3: A diffuse boundary layer or "ion cloud" forms around an ion even in a dilute electrolyte solution. It is confined inside by a sphere with a radius of d (d is the ionic diameter) and its thickness is expressed by the shielding length l . The deviation of the electric potential and the ionic concentrations from their average values in the interior of the solution fall as $\sim \exp(-r/l)/r$ with the distance r from the center of the central ion. The shading in the ion cloud shows the charge density in the plane of the figure. Only starting at an ional concentration of 1 kmol m^{-3} will $l \approx d$ formally, as seen in the figure, while l is many times greater in dilute solutions.

We see that the deviations of the potential $\Delta\varphi = \varphi(r) - \varphi(\infty)$ and of the ionic concentrations $\Delta c_i = c_i(r) - c_i(\infty)$ from the values inside the solution subside exponentially in the boundary layer with the distance from the electrode surface. Here, the DEBYE *length* or, *shielding length* l , represents a measure of the thickness of the boundary layer shielding the field.

Theory of interionic interaction

DEBYE and HÜCKEL assumed that around every ion in a dilute electrolyte solution a spherically symmetric boundary layer forms that shields the charge of the central ion. The ion concentrations $c_i(r)$ and the electric potential $\varphi(r)$ can be calculated as functions of the distance r from the center of the central ion the same way as in the last section if analogous prerequisites are assumed. At this point we will pass over the calculation that does not add anything essentially new (except for some special mathematical features as a result of spherical symmetry). We will instead investigate, in a somewhat simplified manner, the most important result of shielding for the chemical behaviour.

Without this shielding effect, the central ion, whose charge number and diameter are z and d , respectively, would be surrounded by a long-range electric field. By forming a boundary layer with the thickness l , calculated according to the equation mentioned in the last section, the field effectively disappears beyond a distance of $r = d + l$, and its energy content ϵ along with it (Figure 3). With the help of the formula for the capacity of a sphere with radius r , $C = 4 \pi \epsilon r$, and the equation for the energy of a capacitor with charge Q , $E = \frac{1}{2} Q^2/C$, the result is $\epsilon = \frac{1}{2} z^2 e^2 / \{4 \pi \epsilon (d + l)\}$. According to the excitation formula, this loss of energy manifests itself in a reduction of the chemical potential μ of the corresponding type of ion by ϵ/τ :

$$\mu = \mu_0 + RT \ln \frac{c}{c_0} - \underbrace{\frac{z^2 e F}{8 \pi \epsilon (d + l)}}_{\mu_i} \quad (\text{DEBYE-HÜCKEL-equation})$$

μ_i is the ionic excess potential which vanishes for uncharged, nonionic substances. If we take the equation for shielding length $l = l_0 \cdot \sqrt{c_0/c_i}$ from the last section, with $l_0 = F^{-1} \sqrt{\epsilon RT/c_0}$, and at the same time keep to such a small ional concentration that d can be neglected compared to l (this is satisfied more or less for $c_i < 10 \text{ mol m}^{-3}$ in watery solutions of the typical ions, that

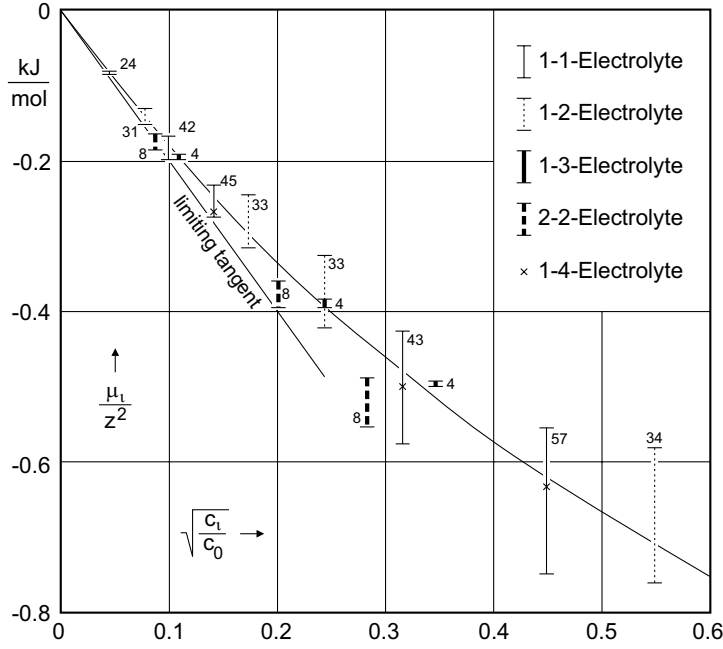


Figure 4: Ionic excess potential μ_l of dissolved electrolytes. The μ_l -value of an electrolyte $A_aB_bC_c\dots$ that is dissociated into the ions A^{z_A} , B^{z_B} , C^{z_C} ..., is composed additively from the contributions of the individual ions. Therefore we have

$$\mu_l = \underbrace{(az_A^2 + bz_B^2 + cz_C^2 \dots)}_{z^2} \cdot \mu_{l0} \sqrt{\frac{c_l}{c_0}}$$

according to the DEBYE-HÜCKEL limiting law for small ionic concentrations c_l . As a result, μ_l/z^2 should yield initially coinciding curves with the initial slope μ_{l0} for all electrolytes. The quantity is plotted as a function of $\sqrt{c_l/c_0}$. Experimental values, averaged for different electrolytes of the same type, are displayed. Error bars denote the standard deviation. The numbers show the number of electrolytes summarized in one bar. The reference value of the concentration is $c_0 = 1 \text{ kmol m}^{-3}$. The limiting tangent and the solid curve have been calculated according to the DEBYE-HÜCKEL equation. For the solid curve, we chose $d = l_0$.

means $d \approx 0.4 \text{ nm}$ including hydration sheaths and $l > 4 \text{ nm}$, we have² (Figure 4):

$$\boxed{\mu_l = \underbrace{\frac{-e F}{8 \pi \epsilon l_0}}_{\mu_{l0}} \cdot z^2 \cdot \sqrt{\frac{c_l}{c_0}}} \quad \text{for } d \ll l \quad . \quad (\text{DEBYE-HÜCKEL limiting law})$$

Van der Waal's gas

In order to explain the behavior of dense gases and their condensation, VAN DER WAAL's gas model is generally used because the physical assumptions can be made evident and the resulting equation of state $(p + an^2/V^2) \cdot (V - nb) = nRT$ is fairly simple, physically clear and more or less applicable even to the condensate. On the other hand, calculating the constants a and b from the molecule

²For water at 298 K and 1 kmol m^{-3} as reference concentration c_0 , we have $\mu_{l0} = -2.062 \text{ kJ mol}^{-1}$. If one replaces μ_l by the appropriate activity coefficient f_l , and the ionic concentration by the ionic strength $I_c = c_l/2$, one obtains the well-known equation $\lg f_l = \mu_l/RT \ln 10 = -\text{const.} \cdot z^2 \sqrt{I_c}$ with $\text{const.} = 0.51 \text{ mol}^{-1/2} \text{ dm}^{3/2}$ for water at 298 K. At this point one should be aware that although this transformation brings us closer to the usual formulations, the general relationships again start to become more complicated.

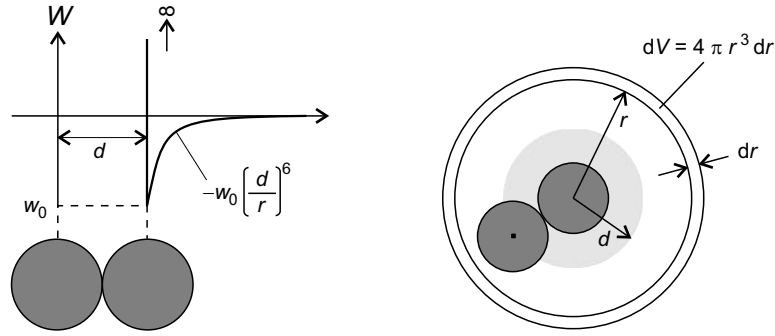


Figure 5: Interaction energy w of rigid, spherical gas particles with a diameter d influenced by dispersion forces. The position of a particle is denoted by the location of its center. The energy is illustrated

a) for a particle pair as a function of their distance r . The figure shows the case of the smallest distance, $r = d$, in which the energy reaches its minimum $-w_0$.

b) for a particle under the influence of all of its neighbors considered as uniformly distributed. The contribution of all of the neighbors in a spherical shell with a radius $r > d$, thickness dr and volume dV , is the same. The particle in consideration excludes all others from the gray zone (radius d).

properties is more difficult and is often omitted. Entropy and the chemically important chemical potential μ are almost always ignored.

Contrary to the usual approach, we will start with μ and calculate the quantity directly from VAN DER WAAL's assumption about molecular interaction without referring to the equation of state. As usual, we imagine the N gas particles as rigid, non-rotating and attracting spheres having a diameter d , distributed in a container of volume V . A slight amount of particle exchange with the environment is expressly allowed, for example as a result of weak diffusion through the walls. If we presume that the attraction is based upon dispersion forces, we can use the LONDON's formula

$$w(r) = -w_0 \cdot \left(\frac{d}{r}\right)^6$$

for the energy of interaction $w(r)$ between two particles as a function of their distance r (Figure 5). To calculate the average energy \bar{w} of an individual particle as a result of interaction with all its neighbors, we imagine the gas particles to be distributed uniformly throughout the volume, leading to a uniform density N/V . The number dN of neighboring particles, which are in a spherical shell of thickness dr at a distance r from the center of the particle in question, is then given by $dN = \frac{N}{V} \cdot 4\pi r^2 dr$. Its contribution to \bar{w} is given by $-w_0 \cdot \left(\frac{d}{r}\right)^6 dN$. Integration over the entire volume where neighboring particles can be found, i.e., from the smallest possible distance $r = d$ to the container walls, which, in molecular dimensions is just about $r = \infty$, leads to the result:

$$\bar{w} = \int_d^\infty -w_0 \cdot \left(\frac{d}{r}\right)^6 \cdot \frac{N}{V} 4\pi r^2 dr = -4\pi w_0 d^6 \frac{N}{V} \left[\frac{-1}{3} r^{-3} \right]_d^\infty = \frac{-4\pi}{3} d^3 w_0 \frac{N}{V} .$$

Related to the amount of substance, which is just τ for a particle, \bar{w} yields the average molar interaction energy

$$\frac{\bar{w}}{\tau} = \frac{-2 a n}{V} \quad \text{where} \quad a = \frac{2\pi d^3 w_0}{3 \tau^2} .$$

A particle occupies a spherical zone with a volume of $\frac{4\pi}{3} d^3$, from which it excludes other particles, more precisely, the centers of other particles. Accordingly, N particles possess N such zones with a total volume of $N \frac{4\pi}{3} d^3$, in which no other particle can exist as long as the particle density is so small that the zones do not overlap noticeably. Hence, the volume V appears to be

reduced for each extra particle intruding from outside. In other words, the gas concentration is correspondingly raised,

$$c^* = \frac{N \tau}{V - N \frac{4\pi}{3} d^3} = \frac{n}{V - 2 n b} \quad \text{where} \quad b = \frac{2 \pi d^3}{3 \tau} .$$

The assumption that the particles may not be too densely packed here means that $V \gg nb$. c^* stands for the concentration relevant for particle interaction with the environment and therefore for the chemical potential. It must be inserted into the mass action formula. At the same time, if we take into account the interaction energy calculated above according to the excitation formula, we obtain

$$\mu = \mu_0 - \frac{2 a n}{V} + RT \ln \frac{n}{(V - 2 n b)c_0} \quad \text{for} \quad V \gg n b .$$

If one sets both a and b equal to zero, then the equation is transformed into the one for ideal gases, $\mu = \mu_0 + RT \ln(c/c_0)$, where μ_0 is the reference value of the potential for the corresponding ideal gas. We can calculate it according to the formulas derived in Parts I and II. Because there is no internal excitation for rigid, non-rotating spherical molecules (mass m), only the translational contribution $\mu_0 = \epsilon/\tau + RT \ln(c_0/c_e)$ is to be considered along with a possible "basic contribution" ϵ/τ . Therefore we have $c_e = \tau/\lambda^3$, where c_e is the *degeneracy concentration*, and $\lambda = h/\sqrt{2 \pi m k T}$ denotes the *quantum length*.

At the moment we are concerned with another question, though. What is the pressure as a result of the approach used above for the chemical potential? We can calculate it as we did for the dilute gases in Part II, with the help of the relation $(\partial\mu/\partial V)_{T,n} = -(\partial p/\partial n)_{V,T}$. Applied to the equation above, we obtain,

$$\left(\frac{\partial p}{\partial n}\right)_{V,T} = -\left(\frac{\partial \mu}{\partial V}\right)_{T,n} = -\frac{2 a n}{V^2} + \frac{R T}{V - 2 n b} \approx -\frac{2 a n}{V^2} + \frac{R T}{V} \cdot \left(1 + \frac{2 n b}{V}\right)$$

since μ_0 is independent of V . The approximation $\frac{1}{1-x} \approx 1+x$ for $x \ll 1$ was used in the last step of the calculation. If we use the same approximation $1+x \approx \frac{1}{1-x}$, integration over n at fixed V and T results in

$$p = \frac{-a n^2}{V^2} + \frac{n R T}{V} \cdot \left(1 + \frac{n b}{V}\right) \approx \frac{-a n^2}{V^2} + \frac{n R T}{V - n b} .$$

Now we have VAN DER WAAL's equation³, which we only need to rewrite into the usual form:

$$\boxed{\left(p + \frac{a n^2}{V^2}\right) (V - n b) = n R T \quad \text{and} \quad a = \frac{2 \pi d^3 w_0}{3 \tau^2}, \quad b = \frac{2 \pi d^3}{3 \tau}}$$

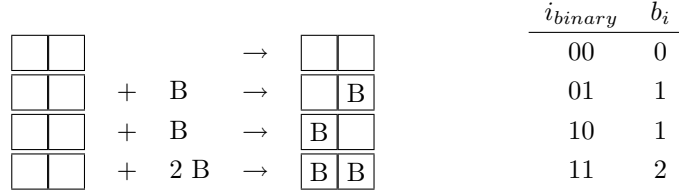
³Only in the case of $V \gg nb$ does the derived expression for the chemical potential yield exactly VAN DER WAAL's equation. One can slightly rewrite it, staying within the limits of validity, so that the relation is strict. In order to replace $V - 2 n b$ in the logarithmic term by the factor $V - n b$ necessary for the VAN DER WAALS equation, we expand the fraction there with $V - n b = V(1 - x)$ where $x = n b/V \ll 1$ and split off the term $\ln[(V - n b)/(V - 2 n b)] = -\ln[(1 - x - x)/(1 - x)] = -\ln[1 - x/(1 - x)] \approx x/(1 - x) = n b/(V - n b)$:

$$\begin{aligned} \mu &= \mu_0 - \frac{2 a n}{V} + RT \ln \frac{n}{(V - 2 n b)c_0} = \mu_0 - \frac{2 a n}{V} + RT \left[\ln \frac{n}{(V - n b)c_0} + \ln \frac{V - n b}{V - 2 n b} \right] \\ &\approx \mu_0 - \frac{2 a n}{V} + RT \left[\ln \frac{n}{(V - n b)c_0} + \frac{n b}{V - n b} \right] . \end{aligned}$$

In order to test our results we form $-(\partial\mu/\partial V)_{n,T}$, on the one hand, and on the other hand $(\partial p/\partial n)_{V,T}$, by use of VAN DER WAAL's equation, we obtain, as it should be, the same expression: $-2 a n/V^2 + [R T/(V - n b)] \cdot [1 + n b/(V - n b)]$.

Adsorption with interaction

If perceptible interactions between the adsorbed particles occur, then the surface may be divided into uniform areas as far as possible. These have to be chosen of such a size that the energy of interaction of the molecules adsorbed at the edges with those outside can be neglected compared to the total energy of interaction on the inside. These areas, comprising z sites, take over the former role of the independent individual sites. In the simplest case, areas with only two adsorption sites, $z = 2$, have no noticeable interaction with the environment when the sites are pair-wise close to each other and the pairs themselves are far enough apart from each other. Starting from an empty area, we have 2^z independent adsorption processes. For $z = 2$ this is:



We consider the sites of an area as numbered, $n = 1, 2, 3, \dots, z$. We number the occupation states as well, with a number $i = 0, 1, 2, \dots, (2^z - 1)$ whose n -th digit is a 0 in z -digit binary syntax i_{binary} , if the n -th site is empty. Otherwise it is 1. The *occupation number* b_i , meaning the number of adsorbed B-molecules in the i -th state, is then simply the cross sum of i_{binary} . In equilibrium, we have

$$\underbrace{\mu_{0,0} + R T \ln \Theta_0}_{\mu(\text{empty area})} + \underbrace{b_i \cdot [\mu_{0,B} + R T \ln(c/c_0)]}_{\mu(B)} = \underbrace{\mu_{0,i} + R T \ln \Theta_i}_{\mu(\text{area in the } i\text{-th state})} \quad \text{for all } i .$$

We subtract $b_i \cdot \mu_{0,B}$ from both sides, divide by $R T$, form the power with and multiply by $c_0^{b_i}$. Since the reference value $\mu_{0,0}$ of the potential for the empty area vanishes, we have

$$\Theta_0 \cdot c^{b_i} = \underbrace{\left[c_0 \cdot \exp \left(\frac{\mu_{0,i} - b_i \mu_{0,B}}{b_i R T} \right) \right]^{b_i}}_{c_i \text{ (50\%-concentration for the } i\text{-th occupation state)}} \cdot \Theta_i \quad \text{for all } i \neq 0 .$$

As the value for the parameter $c_{i=0}$ left undetermined here, we choose the reference concentration c_0 . Except for c_0 , the parameters c_i represent a kind of *50%-concentration* for the respective adsorption process. This means the concentration c for which the fraction Θ_i of areas in the i -th occupation state would become $\frac{1}{2}$ if the process being observed was happening alone. In this case, we would have $\Theta_0 = 1 - \Theta_i$. As above in the case of LANGMUIR adsorption, this allows us to solve the equation for Θ_i :

$$\Theta_i = \frac{(c/c_i)^{b_i}}{1 + (c/c_i)^{b_i}} \quad \text{with } \Theta_i = 1/2 \quad \text{for } c = c_i .$$

Dividing the 2^z equations by $c_i^{b_i}$ and multiplying on the one hand by a factor of 1 and on the other by the factor b_i , and summing over all i , yields two relations,

$$\Theta_0 \cdot \sum_i \left(\frac{c}{c_i} \right)^{b_i} = \sum_i \Theta_i = 1 , \quad \Theta_0 \cdot \sum_i b_i \cdot \left(\frac{c}{c_i} \right)^{b_i} = \sum_i b_i \Theta_i = z \Theta ,$$

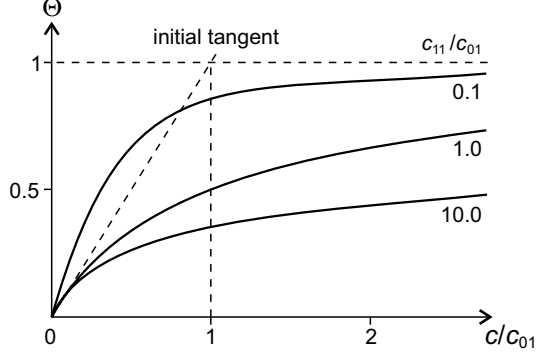


Figure 6: Adsorption isotherms for independent pairs of identical adsorption sites. The figure shows the degree of occupation Θ as a function of the reduced concentration c/c_{01} for various ratios c_{11}/c_{01} . c_{01} is the 50%-concentration for a singly occupied pair of sites. c_{11} means the corresponding value for double occupation. $c_{11} < c_{01}$ represents attracting and $c_{11} > c_{01}$ repelling interactions. $c_{11} = c_{01}$ yields the LANGMUIR-isotherm.

from which, after removing Θ_0 , we obtain the *degree of occupation* Θ of the whole surface as a function of the concentration c :

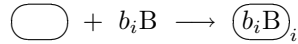
$$\Theta = \frac{1}{z} \sum_i b_i \cdot \left(\frac{c}{c_i}\right)^{b_i} \bigg/ \sum_i \left(\frac{c}{c_i}\right)^{b_i} . \quad (\text{adsorption equation})$$

Applied to the simplest case of $z = 2$ with two identical adsorption positions, i.e. $c_{01} = c_{10}$, for $z = 2$, the equation is (Figure 6):

$$\Theta = \frac{c/c_{01} + (c/c_{11})^2}{1 + 2c/c_{01} + (c/c_{11})^2} .$$

General systems of interacting particles

The adsorption of interacting particles discussed in the last section lends itself to easy generalization in that instead of particles distributed over a flat surface one can consider them distributed in space. Whether or not the space is empty or filled with a material (perhaps a solvent) makes no fundamental difference. In place of a two-dimensional area a three dimensional one, denoted by \bigcirc , appears. We can imagine it separated from the environment by an appropriate envelope. This region represents the *system* being investigated, which exchanges the substance B with its *environment*:



We consider the total of all possible occupation states $\overline{(b_i B)}_i$ of the system to be consecutively numbered (number i). In a concrete case, to keep the math to a minimum, we will attempt to get by with the smallest possible microscopic system. For the case of general equations, smallness basically doesn't matter so the systems can be macroscopic as well.

Because we are no longer interested in the form in which B exists in the environment, we only assume that the chemical potential μ of B has a defined value. The requirement for the occupation equilibrium is then

$$\underbrace{\mu_{0,0} + R T \ln \Theta_0}_{\mu(\text{empty system})} + b_i \cdot \mu = \underbrace{\mu_{0,i} + R T \ln \Theta_i}_{\mu(\text{system in the } i\text{-th state})} \quad \Rightarrow \quad \Theta_i = \Theta_0 \cdot \exp\left(\frac{-\mu_{0,i} \tau + \mu n_i}{k T}\right)$$

for all $i \neq 0$, where $n_i = b_i \tau$ denotes the amount of B in the i -th occupation state. Note that $\mu_{0,0} \equiv 0$. While the sum of all Θ_i results in 1, the sum of all $n_i \Theta_i$ gives us the total amount n of

substance B in the system:

$$1 = \sum_i \Theta_i = \Theta_0 \underbrace{\sum_i \exp\left(\frac{-\mu_{0,i} \tau + \mu n_i}{k T}\right)}_{\Xi}, \quad n = \sum_i n_i \Theta_i = \Theta_0 \underbrace{\sum_i n_i \exp\left(\frac{-\mu_{0,i} \tau + \mu n_i}{k T}\right)}_{k T \cdot (\partial \Xi / \partial \mu)_T}$$

Θ_i can be understood as the *probability* to find the system in its i -th occupation state for given μ and T . n is correspondingly understood, as the *expectation value* of amount of B in the system. While the n_i are integer multiples of τ , n can be a fractional multiple. The amount of B has some *scatter* about the expectation value, whereby the standard deviation is given by $\sigma = \sqrt{\sum_i \Theta_i (n_i - n)^2}$. σ is only of importance in microscopic systems. If one already has calculated the sum Ξ as a function of μ and T (and, where applicable, of other variables such as the volume V of the system, the amount of solvent n_L , pressure p , etc.), then the calculation of the second sum is unnecessary because it results from the first by taking the derivative with respect to μ . Given that $\Theta_0 = \Xi^{-1}$, as we see from the first of the equations above, and $\partial \ln \Xi / \partial \mu = \Xi^{-1} (\partial \Xi / \partial \mu)$, we can thus express n as follows:

$$\boxed{n = kT \left(\frac{\partial \ln \Xi}{\partial \mu} \right)_{T, \dots} \quad \text{where} \quad \Xi = \sum_i \exp\left(\frac{-\mu_{0,i} \tau + \mu n_i}{kT}\right)} \quad (*)$$

This equation describes the occupation of the region \bigcirc with the substance B similarly to how an adsorption equation describes the occupation of a surface site.

Statistical entropy

If our empty system \bigcirc represents a cavity with volume V , and if we classify an internal excitation by rotation, vibration, etc. of a B-particle in the system as a new occupation state with its own number i , then $\mu_{0,i} \tau$ is identical with the energy⁴ $E_i(V, \dots)$ of the system in its i -th state, where the energy is dependent upon the volume V , and possibly upon further parameters. In this case, $\Xi = \sum_i \exp[(-E_i + \mu n_i)/(kT)]$ corresponds to the *grand partition function* known from the quantum statistics of open systems. The function $\Xi(T, \mu, V, \dots)$ is noteworthy for fully describing the system in thermodynamic equilibrium with its environment so that knowing this function suffices to calculate all relevant quantities (energy E , amount of substance n , pressure p ... and the quantities derived from them concentration c , compressibility χ , heat capacity C ...). This holds not only for their expectation values, but for their standard deviation as well.

The necessary equations can be derived with little difficulty. Let us single out the *expectation value* of the energy, for example, which we can calculate from $\Xi(T, \mu, V, \dots)$ because of $\Theta_i = \Theta_0 \cdot \exp[(-E_i + \mu n_i)/(kT)] = \Xi^{-1} e^{\dots}$ as follows:

$$E = \sum_i E_i \Theta_i = \frac{1}{\Xi} \left\{ \underbrace{\sum_i E_i e^{\dots}}_{k T^2 \cdot (\partial \Xi / \partial T)_{\mu, V, \dots}} - \mu \underbrace{\sum_i n_i e^{\dots}}_{k T \cdot (\partial \Xi / \partial \mu)_{T, V, \dots}} + \mu \underbrace{\sum_i n_i e^{\dots}}_{k T \cdot (\partial \Xi / \partial \mu)_{T, V, \dots}} \right\} = k T^2 \left(\frac{\partial \ln \Xi}{\partial T} \right)_{\mu, V, \dots} + \mu n \quad (**)$$

⁴It is unnecessary here to distinguish between the energy ϵ_i of a particle (or a microsystem of few particles) and the energy E_i of the entire system, because the same formulas are valid for microsystems and for macrosystems.

In order to arrive at the entropy, we calculate the increase of entropy while filling the empty (entropy free) system \bigcirc with the substance B. We imagine slowly raising the chemical potential of B in the environment from $-\infty$ up to the desired end value μ . In doing so, all the other independent variables T, V, \dots should be kept constant. Using $dE = TdS - pdV + \mu dn + \dots$, observing $dV = 0$, and performing the intermediate step $dS = T^{-1}[dE - \mu dn]$, we obtain by applying equations (*) and (**):

$$dS = T^{-1} \left[kT^2 \left(\frac{\partial^2 \ln \Xi}{\partial T \partial \mu} \right)_{V, \dots} d\mu + nd\mu \right] = k \left[T \left(\frac{\partial^2 \ln \Xi}{\partial T \partial \mu} \right)_{V, \dots} + \left(\frac{\partial \ln \Xi}{\partial \mu} \right)_{T, V, \dots} \right] d\mu \quad .$$

Finally, as a result of the integration over μ mentioned above

$$S = k \left[T \left(\frac{\partial \ln \Xi}{\partial T} \right)_{T, V, \dots} + \ln \Xi \right] \quad .$$

Although this is a useful result, our actual goal is a more fundamental equation which we arrive at if we introduce $\Xi = \sum_i \exp[(-E_i + \mu n_i)/(k T)]$ and $\exp[(-E_i + \mu n_i)/(k T)] = \Xi \Theta_i$ in the left term of the expression above:

$$S = k \left[T \Xi^{-1} \sum_i \left(\underbrace{-\frac{-E_i + \mu n_i}{k T^2}}_{\ln(\Xi \Theta_i)/T} \right) \underbrace{\exp\left(\frac{-E_i + \mu n_i}{k T}\right)}_{\Xi \Theta_i} + \ln \Xi \right] = k \left[\sum_i \Theta_i [-\ln \Theta_i - \ln \Xi] + \ln \Xi \right] \quad .$$

Since $\sum_i \Theta_i = 1$, $\ln \Xi$ cancels so that we obtain the familiar equation for statistically defined entropy with Θ_i as a probability:

$$\boxed{S = -k \sum_i \Theta_i \ln \Theta_i} \quad . \quad \text{(BOLTZMANN-SHANNON equation)}$$

Review and outlook

The examples have shown that interactions between particles are no obstacle to our approach. However, it can happen that due to their numerous interaction terms, the complexity of quantum statistical calculations can easily become so great that an equation such as the one derived in the last sections becomes useless. It then depends upon mathematical or physical skill to find simplifications that can yield manageable equations without being too far off the mark.

There is another point worth mentioning. In the last sections it became clear that even fluctuation phenomena lie within the range of our approach. This is in direct opposition to the general view that phenomenological thermodynamics as a kind of summarizing theory is insensitive towards atomic details. And that, these effects can be understood and described correctly only in the context of a more comprehensive statistical theory.

It is more difficult to determine whether or not the achievable results will live up to demands which go beyond time-savings and reduction of the work needed for learning through formal simplification. We are thinking of physical plausibility, compatibility with other views (e.g., statistics) and completeness and elegance of description, etc. One can arrive at certain answers by checking examples from various fields using the aforementioned criteria. Examples of this type will be compiled in a further paper without valuation, so that readers can form their own judgement.

For now we will omit time-dependent phenomena because they – in the general view – are foreign to thermodynamics and quantum statistics and require new tools. We shouldn't let ourselves be

discouraged by this type of argument from at least making a try at a solution, though. The theory of the transition of states gives us examples from which to start. But, this topic is beyond the scope of this work and may be addressed in a forthcoming article.