

Georg Job
An elementary approach to quantum statistical problems (I)

Lecture of 14.5.91 at the "Physical Chemistry Seminar" of the Institute for Physical Chemistry of
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.

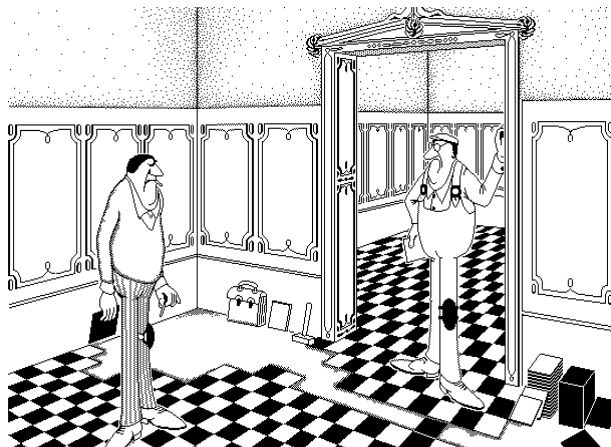


Figure 1: Structures that grow together from different sides are seldom completely ordered. Drawing from a photograph of unknown provenance.

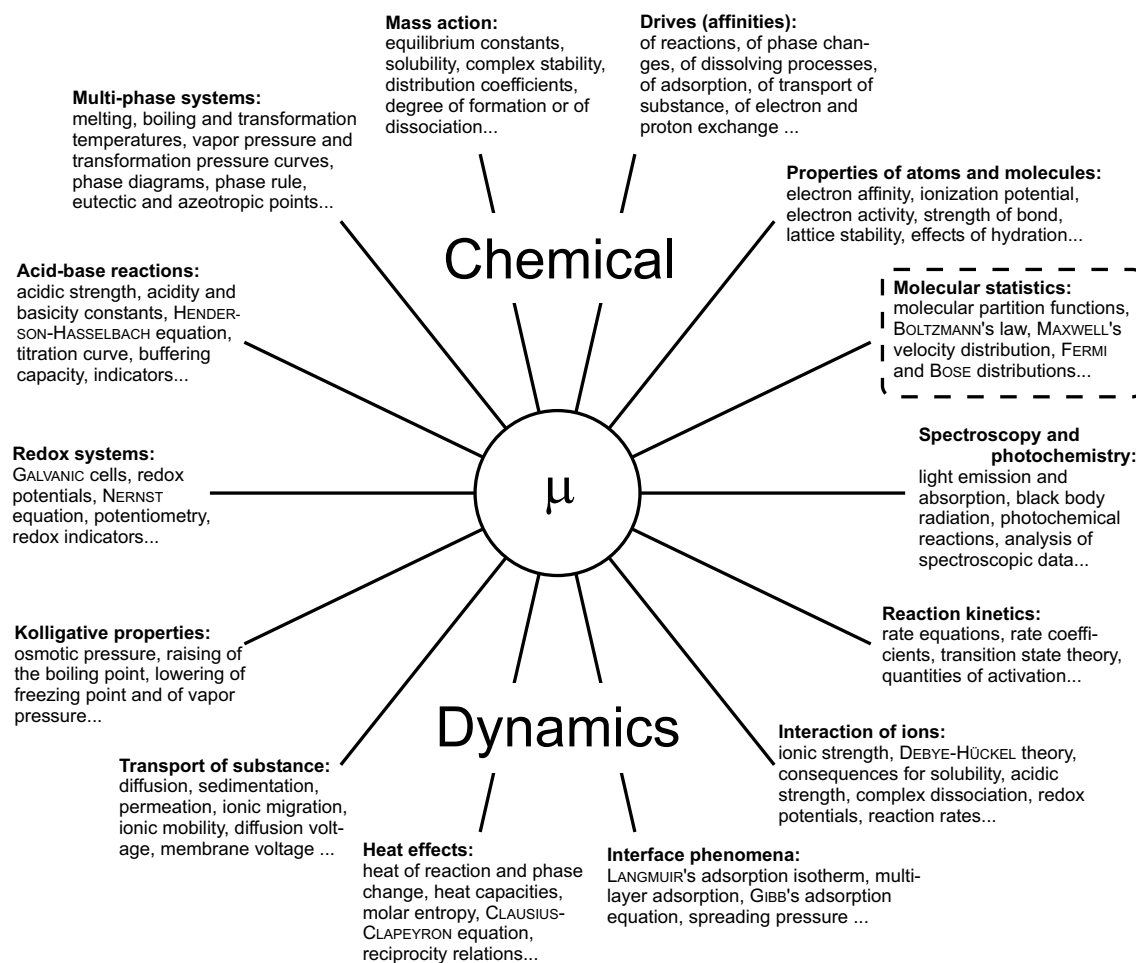


Figure 2: The areas of chemistry that can be categorized under 'chemical dynamics'. The chemical potential μ comprises the central pivot in all of chemical dynamics, where the lever is best applied for solving the problems involved¹. This also holds for the molecular statistics investigated here, in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

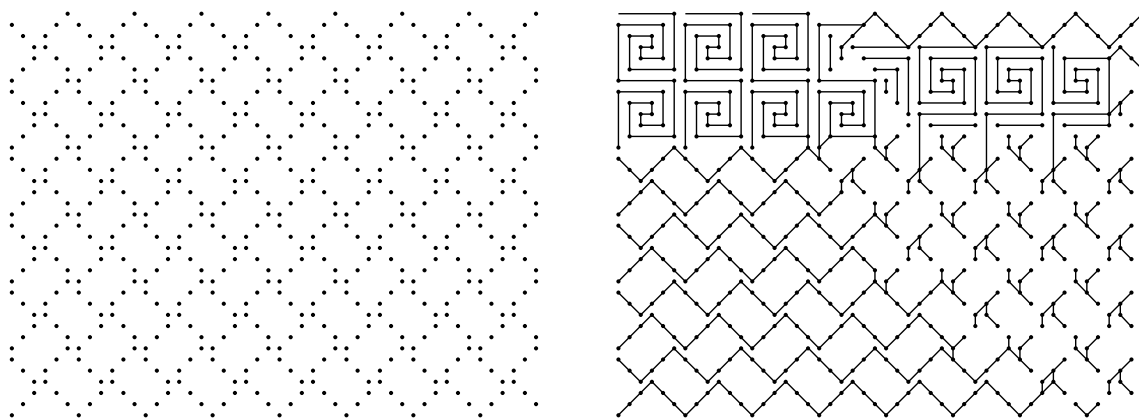


Figure 3: How easily contradicting pictures can be created despite identical basic structures can be seen in the figure. On the left is the predetermined dot pattern. The assignment was to mark the positions of the intersections and breaks of the dots in the most simple and memorable way by use of lines. 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.

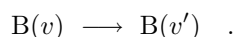
We will, at first, accept the conclusions of quantum theory without question, even though we would only need strongly simplified relations for a number of applications in this field. Some of the derivations below could be further streamlined using this approach.

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.

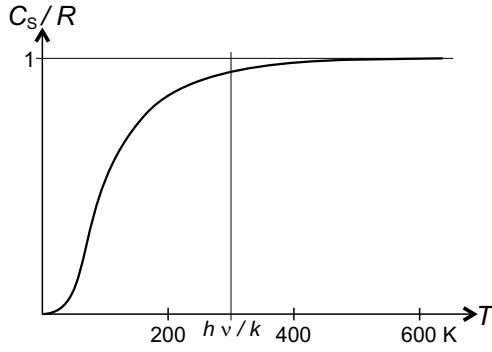


Figure 4: The contribution of molecular vibration to the heat capacity of I_2 -vapor, is $C_s(T)$. The characteristic temperature of vibration Θ_s is 305 K.

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.

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

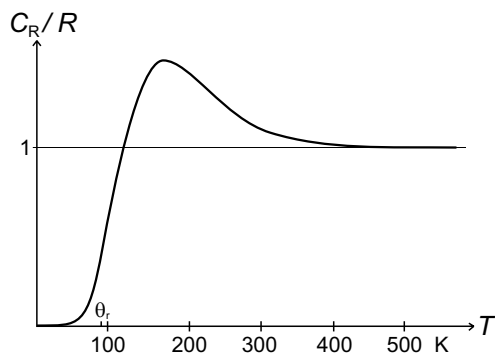


Figure 5: The contribution $C_r(T)$ of molecular rotation to the molar heat capacity of para hydrogen. The rotational characteristic temperature Θ_r is 87.7 K. For calculations up to 300 K, the formula found in the text is used. Only the three lowest levels of rotation ($J = 0, 2, 4$) are taken into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

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

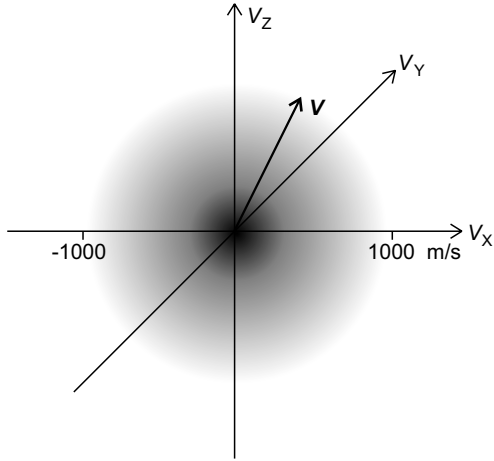


Figure 6: If we represent $c(\mathbf{v})$ according to the equation above as shading in three dimensional velocity space, we obtain the spherical cloud given at the left. The values are valid for nitrogen at 298 K.

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

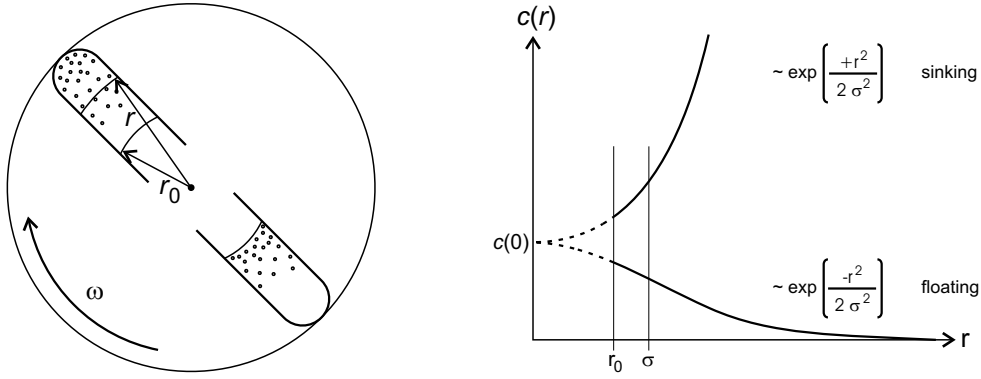


Figure 7: Sedimentation equilibrium in a centrifuge for a substance B (particle mass m_B , particle volume v_B) which is either dissolved or suspended in a fluid with a density of ρ_A . If the centrifugal force becomes larger than the force of buoyancy, the substance B concentrates toward the outside (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 $1/N!$.