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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

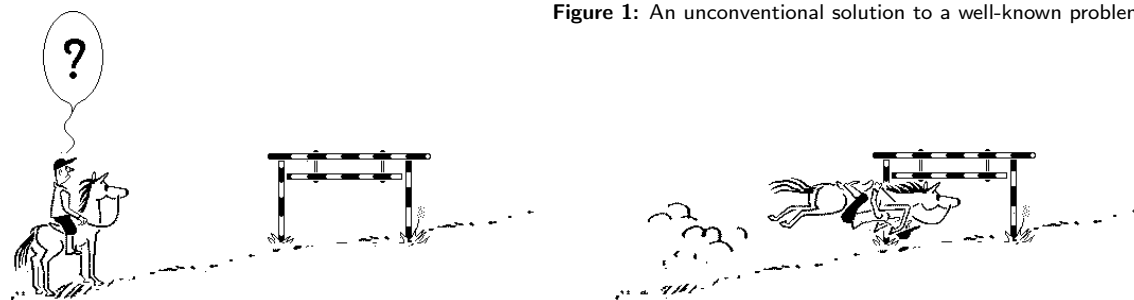


Figure 1: An unconventional solution to a well-known problem

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).

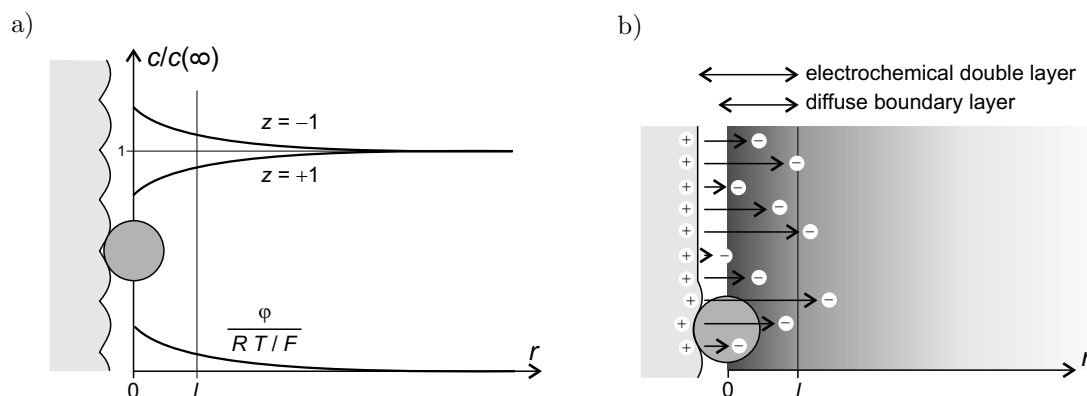


Figure 2: a) Ionic concentration c and electric potential φ in the surface layer of an electrode charged positively relative to the solution. r is the distance from the electrode ($r = 0$ for the centers of the ions when they touch the electrode), z is the charge number, F is the FARADAY constant, R 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:

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

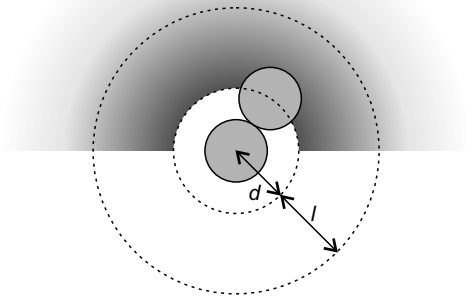


Figure 3: A diffuse boundary layer or "ion cloud" forms around an ion even in a dilute electrolyte solution. It is confined inside by a sphere with a radius of d (d is the ionic diameter) and its thickness is expressed by the shielding length l . The deviation of the electric potential and the ionic 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

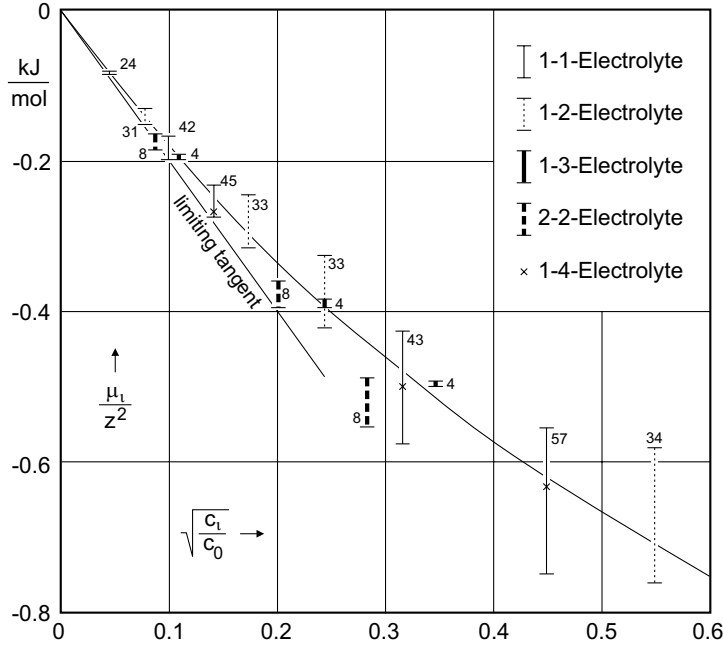


Figure 4: Ionic excess potential μ_l of dissolved electrolytes. The μ_l -value of an electrolyte $A_aB_bC_c\dots$ that is dissociated into the ions A^{z_A} , B^{z_B} , C^{z_C} ..., is composed additively from the contributions of the individual ions. Therefore we have

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

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.

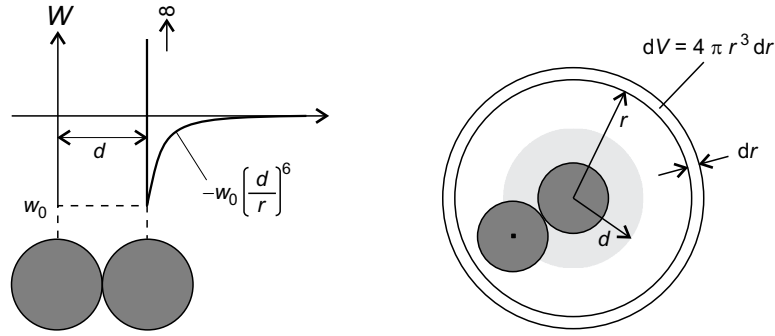


Figure 5: Interaction energy w of rigid, spherical gas particles with a diameter d influenced by dispersion forces. The position of a particle is denoted by the location of its center. The energy is illustrated

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:

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

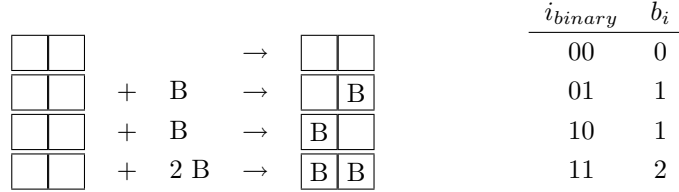
³Only in the case of $V \gg nb$ does the derived expression for the chemical potential yield exactly VAN DER WAAL's equation. One can slightly rewrite it, staying within the limits of validity, so that the relation is strict. In order to replace $V - 2 n b$ in the logarithmic term by the factor $V - n b$ 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 RT , 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,

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

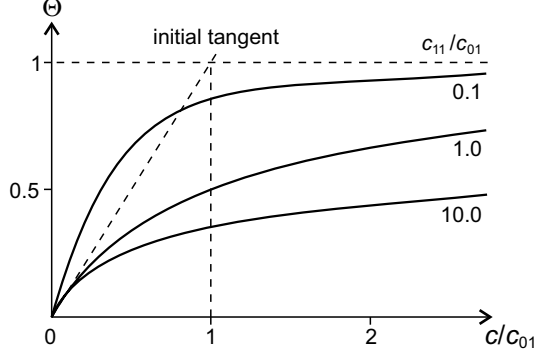


Figure 6: Adsorption isotherms for independent pairs of identical adsorption sites. The figure shows the degree of occupation Θ as a function of the reduced concentration c/c_{01} for various ratios c_{11}/c_{01} . c_{01} is the 50%-concentration for a singly occupied pair of sites. c_{11} means the 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 :

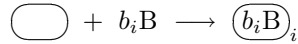
$$\Theta = \frac{1}{z} \sum_i b_i \cdot \left(\frac{c}{c_i}\right)^{b_i} \bigg/ \sum_i \left(\frac{c}{c_i}\right)^{b_i} . \quad (\text{adsorption equation})$$

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.