A toy model solved by statistical mechanics for teaching reaction kinetics beyond ideality.

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Abstract

Chemical equilibrium is fully characterized by thermodynamics, while the rates of chemical reactions can be calculated for ideal solutions by using mass-action equations. The evaluation of the rates of reactions in a non-ideal system is instead much more complex, even at equilibrium, being dependent on the microscopic features of the interactions: no universal theory exist. Here we propose a toy model to help students understand such complexity. It is formulated by means of statistical mechanics and aims at the evaluation of the exchange reaction rate at equilibrium. The toy model can be solved by the students, with various types of interactions, as an exercise. The results prove that no general rule connects the reaction rates to the thermodynamic quantities, such as the activity coefficients, dramatically proving the complexity and richness of the field.

Keywords: Reaction kinetics, non-ideal system, thermodynamics, statistical mechanics

1 Introduction

In the chemistry courses, the kinetics of chemical reactions is mostly discussed for ideal solutions [1], for which the rate $r$ of the reaction

$$n_A A + n_B B + \cdots \rightarrow \cdots$$

(1)

is characterized by the mass-action equations:

$$r = k c_A^{n_A} c_B^{n_B} \cdots$$

(2)

where the $c_j$ are the concentrations of the reactants, $n_j$ are the stoichiometric coefficients of the reaction, and $k$ is the reaction rate constant. This kind of equations is based on several assumptions, which are however valid in significant cases.
Figure 1: Classification of theories describing reaction equilibrium and kinetics.

The possible non-ideal behaviour of the system, i.e., the presence of interactions between particles, is instead easily handled by thermodynamics, thus at chemical equilibrium, e.g.

\[ n_A A + n_B B + \cdots \rightleftharpoons n_C C + n_D D + \cdots \]  

(3)

For such a reaction, the equilibrium is expressed in terms of the chemical potentials \( \mu_j \):

\[ n_A \mu_A + n_B \mu_B + \cdots = n_C \mu_C + n_D \mu_D + \cdots \]  

(4)

Figure 1 schematically shows these concepts. The theory of ideal systems deals with systems in which there is no particle interaction. It enables the calculation of the reaction rates and time-dependence of the concentrations, even outside equilibrium (regions E and F, respectively). Under equilibrium, where the net reaction rate vanishes, the theory predicts the exchange reaction rates (region C) together with the equilibrium concentrations (region A). Thermodynamics holds at equilibrium and enables the calculation of the concentrations of chemical species, even in the presence of interactions (regions A and B).

The two calculation schemes overlap nicely within their shared validity range (region A), i.e. for systems that are both at equilibrium and ideal, when dealing with concentrations. In ideal solutions, the chemical potentials are:

\[ \mu_j = \mu^0_j + k_B T \ln \frac{c_j}{c_0}, \]  

(5)

where \( k_B \) is the Boltzmann constant, \( T \) is the temperature, \( \mu^0_j \) is the standard chemical potential of the \( j \)th species, and \( c_0 \) is the standard concentration. Using this expression, the thermodynamic equilibrium condition (Eq. 4) and the mass-action equations (Eq. 2) merge to give:

\[ R = k_f c_A^{n_A} c_B^{n_B} \cdots = k_b c_C^{n_C} c_D^{n_D} \cdots \]  

(6)
where $R$ is the exchange reaction rate, equal to both the forward and backward reaction rates; $k_f$ and $k_b$ are the forward and backward reaction rate constants, respectively, related by:

$$\frac{k_f}{k_b} = e^{-\frac{\Delta G^0}{k_BT}}$$

(7)

where

$$\Delta G^0 = n_C\mu_C^0 + n_D\mu_D^0 + \cdots - (n_A\mu_A^0 + n_B\mu_B^0 + \cdots)$$

(8)

is the standard Gibbs free energy of reaction.

We now focus on region D of Fig. 1, where chemical equilibrium holds but the system is not ideal, i.e. the interactions are not negligible. Under these conditions, the thermodynamic quantities, including concentrations and their fluctuations, can be calculated, but there is no general theory for calculating the reaction kinetics (exchange rate). The reason is that thermodynamics has the concept of “sequence” but no concept of time. A fundamental tool in statistical mechanics, also valid in region D, is the fluctuation-dissipation theorem [2], which will be shortly discussed below. Rigorous treatments for the evaluation of rates are only valid in specific cases. This lack of a general scheme represents an obstacle not only in research, but also in teaching; the message that must be conveyed is that care must be taken to use the right tool for each case and to avoid misleading generalizations and simplifications. A good understanding of the region D is also a useful training before facing the so-called non-equilibrium thermodynamics, outside the regions A, B, C and D, which presents additional challenges and is outside the scope of this paper.

The first problem that we encounter in extending Eq. 6 outside ideality is that the second equality fails. Indeed, we know that the correct relation is:

$$k_f a_A^n a_B^n \cdots = k_b a_C^n a_D^n \cdots$$

(9)

where $a_j$ is the activity of the $j$th species. This equation could thus suggest to extrapolate Eq. 6 to the questionable (and erroneous in general) equation:

$$R = k_f a_A^n a_B^n \cdots = k_b a_C^n a_D^n \cdots$$

(10)

Undoubtedly, there are two good points in favour of this equation: i) it approaches the ideal equation for vanishing concentrations; ii) the net reaction rate (the difference between second and third term) vanishes at equilibrium. However, the first equality of Eq. 10 is only an extrapolation, which is not correct in general. The main question discussed in this paper is if Eq. 10 provides an evaluation of the exchange rate $R$ that is better than Eq. 6 when applied outside ideality; in general, the answer is negative.

Education in chemistry should prevent the above-described unjustified extrapolations. The courses should clarify that the correct evaluation of the effect of interactions (non-ideality) on the reaction rates requires a suitable approach, lying outside the realm of thermodynamics: chemical potentials, activities, and activity coefficients are not enough to characterize the chemical kinetics. The substitution of concentrations, like in Eq. 6 with activities, like in Eq. 10 does
not lead to a better evaluation of the effects of interactions; taken alone, this substitution can lead even more far from the correct result.

A successful approach for predicting reaction rates is the transition state theory \cite{3,4}, which models the passage of a barrier. In this theory, the Gibbs free energy of the states and of the so-called transition state are taken into consideration, and thus activities play a role in determining the net reaction rate \cite{5}, at least, under the hypothesis needed for the application of this theory. This notwithstanding, this approach does not justify the evaluation of the exchange reaction rate Eq. \ref{exchange} outside ideality.

Fundamental results, valid at equilibrium, have been obtained by means of the fluctuation-dissipation theorem \cite{2}. In general, the theorem relates fluctuations, which are thermodynamic quantities, to kinetic properties. In the case of chemical reactions \cite{6}, it relates the exchange rate and the concentration fluctuations to the decay rate of concentration fluctuations; the latter rate can be used to roughly evaluate the net reaction rate around equilibrium. Notwithstanding the importance of such results, the theorem does not enable the independent determination of the two rates; a microscopic description of the system remains necessary.

In this paper, we develop a toy model that represents a reaction at equilibrium in the presence of interactions, described in terms of statistical mechanics. We propose it as an educational tool for undergraduate students in chemistry with a minimal knowledge of statistical mechanics.

We derive general expressions of the exchange reaction rate and of the chemical potentials in terms of averages on the ensemble distribution. Then, we apply them to various forms of interaction among particles. The applications of the general formula to specific cases can be carried out, as an exercise, by the students. The prerequisite is a minimal knowledge of statistical mechanics; students with a background in numerical calculation can also easily perform Monte Carlo simulations.

The aim is to show that both the chemical potentials (and thus the activity coefficients) and the reaction rate depend on the interactions, but the mathematical expression of this dependence strongly changes among the various examples. The results dramatically prove that the thermodynamic parameters (chemical potentials or activity coefficients) are not able to characterize the kinetics in general, not even close to equilibrium.

2 Description of the toy models and general solution

2.1 Description of the system and notations

We consider an equilibrium between two species A and B:

\[
A \rightleftharpoons B \tag{11}
\]
Figure 2: Sketch of the model system. Panel (a): each cell can contain any number of particles, indexed by $j$. Panel (b): value of Hamiltonian (dotted) and discrete states A and B, representing the different chemical species.
Figure 2a shows a sketch of the system. The two species A and B are in a lattice with \( N \) cells; in general there can be any number of particles in each cell. We will focus on interactions among particles in the same cell, thus the physical, geometrical arrangement of the cells (e.g. cubic lattice) does not play a role. A single index \( j \) runs along all the cells of the lattice.

A configuration of the system is represented by an entity \( s \) consisting in two arrays, \( s^T \) and \( s^P \): \( s^T_i \) is either A or B and represents the type of the \( i \)th particle, and \( s^P_i \) is the position of the \( i \)th particle in the lattice, i.e. a natural number between 1 and \( N \). We denote \( |s| \) the number of elements of the arrays; \( N_A(s) \) and \( N_B(s) \) are the number of particles A and B, respectively, in the state \( s \).

The calculations will be done in a canonical setup, with a fixed \( N_T \) number of particles. Hence, the possible states of the system are represented by states \( s \) such that \( |s| = N_T \). It must be remarked that, during the calculations, states with different length \( |s| \) will appear.

The notation \( s + \langle A, j \rangle \) represents a state \( s \) to which an additional particle A has been added at position \( j \). An analogous notation is used for adding a particle B. It must be noticed that the number of particles increases by 1, i.e. \( |s + \langle A, j \rangle| = |s| + 1 \). The notation \( s|s^T_i = A \) means that the \( i \)th particle is substituted by a particle A, while keeping its position in cell \( s^P_i \). In this latter case, the number of particles does not change, i.e. \( |(s|s^T_i = A)| = |s| \).

The system is specified by giving the Hamiltonian function \( H(s) \). This Hamiltonian treats A and B as discrete states and can be seen as an approximation of a continuous model, smoothly interpolating between the two states A and B along a reaction coordinate. As an example, Fig. 2b shows the dependence of the Hamiltonian energy on the reaction coordinate, with a barrier between A and B.

According to Boltzmann equation, the average on the canonical ensemble of \( N_T \) particles of a variable \( a \) is:

\[
\langle a \rangle_{N_T} = \frac{1}{Z_{N_T}} \sum_{s, |s| = N_T} a(s) e^{-\frac{H(s)}{k_B T}}
\]  

(12)

where \( k \) is the Boltzmann constant and \( T \) is the temperature of the system, and \( Z_{N_T} \) is the partition function:

\[
Z_{N_T} = \sum_{s, |s| = N_T} e^{-\frac{H(s)}{k_B T}}
\]

(13)

2.2 Definition of reaction rate

The reaction that we are taking into account has a single step and does not pass through intermediate states, such as activated chemical species. This assumption is not a limitation; rather, it means that we focus on a single step of a reaction, while the overall process could involve multiple steps and intermediate (possibly transition) states.
We model the reaction as the passage of a barrier. Our approach is based on the Arrhenius law [7, 8, 9], which provides an empirical evaluation of the dependence of the reaction constant on the temperature:

\[
k = \Lambda e^{-\frac{\Delta E}{k_BT}},
\]

(14)

where \( \Lambda \) and the energy barrier \( \Delta E \) are two empirical parameters.

Two different approaches have been proposed in order to justify the Arrhenius law: i) in the collision theory [10], \( \Delta E \) is interpreted as a mechanical potential energy barrier; ii) in the transition state theory [3] (or activated state theory), \( \Delta E \) is interpreted as a free energy barrier, separating the reactants from an activated state. The two approaches are rigorously incompatible with each other, since they attribute a different nature to the same empirical parameter \( \Delta E \).

In our model, the barrier is described by a Hamiltonian, representing the mechanical energy. The forward and backward reaction rates are expressed as:

\[
r_{A\rightarrow B} = \delta_{s_i^{A}} \Lambda \frac{N_A}{N} e^{-\frac{\Delta E_A(s,i)}{k_BT}} N_T
\]

(15)

\[
r_{B\rightarrow A} = \delta_{s_i^{B}} \Lambda \frac{N_B}{N} e^{-\frac{\Delta E_B(s,i)}{k_BT}} N_T
\]

(16)

where \( \delta_{\text{condition}} \) is 1 if “condition” is met, 0 otherwise, \( \Delta E_A(s,i) \) and \( \Delta E_B(s,i) \) are the heights of the energy barrier from the side of the state A and B, respectively, in state \( s \), for the \( i \)th particle (see Fig. 2), and \( \Lambda \) is a linear dependence factor (see Sect. 2.1 for the notation \( s|s_i^{T} = A \)).

The interactions affect the energy of the particles, thus also the height of the energy barriers, \( \Delta E_A(s,i) \) and \( \Delta E_B(s,i) \). We can calculate the difference \( \Delta E_A(s,i) - \Delta E_B(s,i) \) from statistical mechanics, since it equals the difference of energy between states A and B:

\[
\Delta E_A(s,i) - \Delta E_B(s,i) = H (s|s_i^{T} = B) - H (s|s_i^{T} = A)
\]

(17)

In order to separately calculate \( \Delta E_A(s,i) \) and \( \Delta E_B(s,i) \), we assume that the known energy variation \( H (s|s_i^{T} = B) - H (s|s_i^{T} = A) \) is linearly distributed among the two particles A and B:

\[
\Delta E_A = \Delta E + (1 - \alpha) \left[ H (s|s_i^{T} = B) - H (s|s_i^{T} = A) \right]
\]

(18)

\[
\Delta E_B = \Delta E + \alpha \left[ H (s|s_i^{T} = A) - H (s|s_i^{T} = B) \right]
\]

(19)

where \( \Delta E \) is a fixed energy barrier and \( \alpha \) is a linear distribution factor, \( 0 \leq \alpha \leq 1 \). This linear distribution is actually observed in transition state theory [11], in the form of a linear dependence of the height of the barrier on \( \Delta G^0 \), known as the Evans-Polanyi principle. A similar linear dependence also appears in the derivation of the Butler-Volmer equation of electrochemistry [11], where the
coefficient $\alpha$ is called the charge transfer coefficient. The linear splitting can also be justified under the approximation of smooth dependence of the Hamiltonian on the reaction coordinate.

Eqs. 15 and 16 are then rewritten as:

$$
\begin{align*}
\text{r}_{A\rightarrow B} & = \left( \sum_{i=1}^{N_T} \delta_{s_i^T = A} \frac{\Lambda}{N} e^{-\frac{\Delta E_{+(1-\alpha)\left[H(s_i^T = B) - H(s_i]\right]}}{kT}} \right) \langle N_T \rangle\\
\text{r}_{B\rightarrow A} & = \left( \sum_{i=1}^{N_T} \delta_{s_i^T = B} \frac{\Lambda}{N} e^{-\frac{\Delta E + \alpha \left[H(s_i^T = A) - H(s_i]\right]}{kT}} \right) \langle N_T \rangle
\end{align*}$$

(20)

Although this model of reaction rate is quite simple, it is enough to discuss a wide range of phenomena.

2.3 Expression of reaction rates and activity coefficients

The reaction rates and the activity coefficients will be expressed in terms of two quantities, $\Gamma_A(s, j)$ and $\Gamma_B(s, j)$, representing the interactions in the $j$th cell when the system is in state $s$:

$$
\begin{align*}
\Gamma_A(s, j) & = e^{-\frac{H(s + \langle A, j \rangle) - H(s)}{kT}} \\
\Gamma_B(s, j) & = e^{-\frac{H(s + \langle B, j \rangle) - H(s)}{kT}}
\end{align*}
$$

(22)

(23)

(see Sect. 2.1 for the notation $s + \langle A, j \rangle$) Intuitively, the two factors represent the variation of probability of the state $s$ when a particle $A$ or $B$ is inserted in cell $j$. We assume that the result is actually independent of the cell position, so that $j$ can be taken arbitrarily.

We write the chemical potentials $\mu_A$ and $\mu_B$ as:

$$
\begin{align*}
\mu_A & = \mu_A^0 + kT \ln \left( \frac{\gamma_A \bar{N}_A}{N} \right) \\
\mu_B & = \mu_B^0 + kT \ln \left( \frac{\gamma_B \bar{N}_B}{N} \right)
\end{align*}
$$

(24)

(25)

where $\bar{N}_A$ and $\bar{N}_B$ are the average numbers of particles (the actual numbers of particles fluctuate from sample to sample), $\mu_A^0$ and $\mu_B^0$ are the standard chemical potentials, and $\gamma_A$ and $\gamma_B$ are the activity coefficients, representing the deviation of the activities from ideality. In Supporting Information, SI-Sect. A, we give an expression of the standard chemical potentials and of the activity coefficients.
in terms of averages of the functions $\Gamma_A$ and $\Gamma_B$:

$$
\mu^0_A = -k_B T \ln \langle \Gamma_A (s, j) \rangle^j_0
$$

$$
\mu^0_B = -k_B T \ln \langle \Gamma_B (s, j) \rangle^j_0
$$

$$
\gamma_A = \frac{\langle \Gamma_A (s, j) \rangle^j_0}{\langle \Gamma_A (s, j) \rangle^j_{NT}}
$$

$$
\gamma_B = \frac{\langle \Gamma_B (s, j) \rangle^j_0}{\langle \Gamma_B (s, j) \rangle^j_{NT}}
$$

In all the proposed exercises, $\mu^A_0 = \mu^B_0 = 0$; in the following, we assume that this simplifying assumption holds, also implying $\langle \Gamma_A (s, j) \rangle^j_0 = \langle \Gamma_B (s, j) \rangle^j_0 = 1$.

In SI-Sect. B, we calculate the so-called exchange reaction rate $R = r_{A \rightarrow B} = r_{B \rightarrow A}$; the forward and backward reaction rates are indeed equal, as it can be shown from Eqs. 20 and 21 and expected in thermodynamic equilibrium. The exchange reaction rate is:

$$
R = \frac{\Lambda}{2} e^{-\frac{\Delta E}{k_B T}} \vartheta \frac{N_T}{N}
$$

where

$$
\vartheta = 2 \frac{\langle \Gamma_A (s, j) \rangle^j_0 \Gamma_B (s, j)^{1-\alpha} \rangle^j_{NT}}{(\langle \Gamma_A (s, j) \rangle^j_{NT})^2 + (\langle \Gamma_B (s, j) \rangle^j_{NT})^2}
$$

We remark once again that these expressions hold for $\mu^A_0 = \mu^B_0 = 0$, like in the exercises below.

### 2.4 Meaning of the parameter $\vartheta$

From Eq. 31 we notice that $\vartheta = 1$ for an ideal system. This suggests to interpret $\vartheta$ as a factor representing the deviation of the reaction rate from ideality.

For reaction Eq. 11, the equilibrium condition is:

$$
e^{\mu_A^0} e^{\vartheta B T} \gamma_A c_A = e^{\mu_B^0} e^{\vartheta A T} \gamma_B c_B
$$

This equation enables the calculation of the concentrations $c_A$ and $c_B$ as a function of the total concentration $c_T$. In turn, these concentrations can be used to try to evaluate $R$ through Eq. 10:

$$
R = k \frac{\left(\frac{e^{\mu_A^0}}{e^{\vartheta B T}} + \frac{e^{\mu_B^0}}{e^{\vartheta A T}}\right) \gamma_A \gamma_B}{e^{\vartheta B T} \gamma_A + e^{\vartheta A T} \gamma_B}
$$

where

$$
k = k_f \frac{e^{\mu_A^0}}{e^{\vartheta B T} + e^{\vartheta A T}} = k_b \frac{e^{\mu_B^0}}{e^{\vartheta B T} + e^{\vartheta A T}}
$$
is a single constant defining the exchange reaction rate. The comparison of Eq. 33 to Eq. 30 suggests to write \( \vartheta \) as:

\[
\vartheta = \frac{2\gamma_A \gamma_B}{\gamma_A + \gamma_B}
\]

(35)

under the assumption \( \mu^0_A = \mu^0_B = 0 \); it is the harmonic mean of the activity coefficients. Being a consequence of Eq. 10 evaluating the validity of this equation corresponds to investigate the validity of the use of activity coefficients to calculate reaction rates. The equation in question, Eq. 35, depends on the non-ideal effects through the activities, according to Eq. 33 and, in turn, to Eq. 10; the question is if it is a better approximation of \( \vartheta \) than simply taking the value in ideal systems, \( \vartheta = 1 \). The answer will be that it is not, not even qualitatively.

By comparing Eq. 31 with Eqs. 28 and 29, it can be noticed that \( \vartheta \) and the \( \gamma_j \) are expressed in terms of averages of functions of the \( \Gamma_j \). This concept expresses the idea that the reaction rate and the thermodynamic variables are altered by the interactions. However, the averages and the functions are different, thus the expressions suggest that it is impossible to derive \( \vartheta \) from the \( \gamma_j \).

From the definition of \( \vartheta \), Eq. 31, in the case \( \alpha = 1/2 \) (as in the exercises below), we find that \( 0 \leq \vartheta \leq 1 \). The lower bound is trivial; the upper bound is proved in SI-Sect.C. The upper bound is tight, since it is reached by ideal solutions, i.e. in the absence of interactions (constant \( H \)). From these bounds, it is immediately clear that Eq. 35 is not true in general: the right-hand side can be larger than 1, while \( \vartheta \) is smaller than 1.

3 Exercises

In this section, we describe some possible exercises. In each, a specific form of interaction is described, defining a Hamiltonian. The exercises consist in:

- calculating the parameters \( \gamma_j \) and \( \vartheta \);
- qualitatively explaining the trends;
- checking if the equation in question, Eq. 35, holds.

The calculation can be done symbolically or by Monte Carlo numerical methods, depending on the knowledge of the students. In all the cases it can be found that \( \mu^0_A = \mu^0_B = 0 \); moreover the value \( \alpha = 1/2 \) is assumed.

**Exercise 1** (Excluded volume interaction among all the particles). We assume that any particle excludes the presence of other particles in the same cell (whatever is the species). No other interaction is present. We model this behaviour by assuming that the Hamiltonian takes a value 0 on the allowed configurations and a very large value otherwise, such that \( e^{-H} \) vanishes.
Figure 3: Results of Exercise 1 on excluded volume interaction among all the particles. The dashed curve, labelled as “activities”, is the expectation from the equation in question, Eq. 35.

Sketch of solution. We can immediately see that $\Gamma_A(s,j) = \Gamma_B(s,j)$ is 1 on allowed configurations $s$ if the cell $j$ is empty in configuration $s$, and it is 0 otherwise. It is easy to find the following solutions:

$$\gamma_A = \frac{N}{N - N_T} \quad (36)$$

$$\gamma_B = \frac{N}{N - N_T} \quad (37)$$

$$\vartheta = 1 \quad (38)$$

The results are shown in Fig. 3. The increase of the activity coefficient with the number of particles is related to the repulsivity of the force. The reaction rate is not affected by the interaction: the transition of a particle from A to B or vice-versa does not change the interaction energy. The failure of Eq. 35 is dramatic, since $\vartheta$ remains constant as a function of $N_T$, keeping the ideal value, while the equation in question predicts an increase:

$$\frac{2\gamma_A\gamma_B}{\gamma_A + \gamma_B} = \frac{N}{N - N_T} \quad (39)$$

We thus see that, in this case, the correct value of $\vartheta$ equals the ideal one, while the use of activity coefficients, according to Eq. 35, brings the result to a wrong value.
Exercise 2 (Excluded volume interaction among particles of a single species).

At variance with the previous exercise, a particle \( B \) excludes other particles \( B \), but any number of particles \( A \) can be present in the same cell, possibly together with a single particle \( B \).

**Sketch of solution.** For every allowed configurations \( s \), \( \Gamma_A(s,j) = 1 \). Instead, \( \Gamma_B(s,j) = 1 \) if, in configuration \( s \), the cell \( j \) does not contain a \( B \), and it is 0 otherwise. Then we find:

\[
\gamma_A = 1 \tag{40}
\]
\[
\gamma_B = \frac{N}{N - \bar{N}_B} \tag{41}
\]
\[
\vartheta = \frac{N - \bar{N}_B}{N - \frac{\bar{N}_B}{2}} \tag{42}
\]

To find the relation between \( \bar{N}_B \) and \( N_T \), we impose the equilibrium (see Eqs. 24 and 25): \( N_T = (1 + \gamma_B) \bar{N}_B \). The results are shown in Fig. 4: \( \vartheta \), \( \gamma_A \), and \( \gamma_B \) are plotted with horizontal coordinate \( N_T/N \), parametrically in \( \bar{N}_B \).

In this case, \( \vartheta \) is decreased by the interaction: in a cell with one particle \( A \) and one particle \( B \), the transition from \( A \) to \( B \) is prevented by the excluded volume. Only the activity coefficient of the interacting species, \( \gamma_B \), is increased.

Figure 4: Results of Exercise 2 on excluded volume interaction among particles of species B. The dashed curve, labelled as “activities”, is the expectation from the equation in question, Eq. 35.
with respect to the ideal behaviour. With respect to the previous exercise, the failure of Eq. 35 is even more dramatic: $\vartheta$ decreases as a function of $N_T$, while the equation in question predicts an increase:

$$\frac{2\gamma_A\gamma_B}{\gamma_A + \gamma_B} = \frac{N}{N - \frac{N_B}{2}}$$  \hspace{1cm} (43)$$

The actual value of $\vartheta$ is lower than the ideal value, the constant 1, while the prediction through Eq. 35 is a deviation in the opposite direction from the ideal value.

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**Exercise 3** (Repulsive interaction between particles of different type). Any number of particles is allowed to stay in each cell, however, particles A repel particles B in the same cell (and vice-versa, thanks to the third law of mechanics). The Hamiltonian is thus:

$$H (s) = \sum_{j=1}^{N} h n_{A,j} (s) n_{B,j} (s)$$  \hspace{1cm} (44)$$

where $h$ is a positive interaction energy and $n_{A,j}(s)$ (respectively, $n_{B,j}(s)$) is the number of particles A (respectively, B) in the $j$th cell in configuration...
The solution can be obtained by Monte Carlo numerical calculation or by symbolic calculation, by approximating in the limit of small occupancy \( N_T/N \).

**Sketch of solution.** Fig. 5 shows the results of a Monte Carlo numerical calculation. The approximated symbolic solution is obtained as follows.

In the diluted limit, the large majority of the cells contain at most one particle. We can thus neglect cells with multiple particles and approximate:

\[
\Gamma_A(s, j) = \delta_{n_{B, j}(s) \geq 1} e^{-h} + \delta_{n_{B, j}(s) = 0}
\]  

(45)

An analogous expression holds for \( \Gamma_B \). Neglecting the effect of interactions on the particle distribution, we approximate:

\[
\langle \delta_{n_{B, j}(s) \geq 1} \rangle_{N_T} = \frac{\bar{N}_B}{N}
\]

(46)

\[
\langle \delta_{n_{B, j}(s) = 0} \rangle_{N_T} = \frac{N - \bar{N}_B}{N}
\]

(47)

We thus find the quantities needed for the calculation of the activity coefficients \( \gamma_j \):

\[
\langle \Gamma_A(s, j) \rangle_{N_T} = 1 - \frac{\bar{N}_B}{N} (1 - e^{-h})
\]

(48)

\[
\langle \Gamma_B(s, j) \rangle_{N_T} = 1 - \frac{\bar{N}_A}{N} (1 - e^{-h})
\]

(49)

For the calculation of \( \vartheta \), it is useful to notice that:

\[
\Gamma_A(s, j)^\alpha = \delta_{n_{B, j}(s) \geq 1} e^{-\alpha h} + \delta_{n_{B, j}(s) = 0}
\]

(50)

and analogous expressions hold for other powers of \( \Gamma_A(s, j), \Gamma_B(s, j) \), and their products.

By imposing the equilibrium through Eqs. 24 and 25, we find \( \bar{N}_A = \bar{N}_B = N_T/2 \). The results are:

\[
\gamma_A = \gamma_B = \frac{1}{1 - \frac{N_T}{2N} (1 - e^{-h})}
\]

(51)

\[
\vartheta = \frac{1 - \frac{N_T}{2N} (2 - e^{-\alpha h} - e^{-(1-\alpha) h})}{1 - \frac{N_T}{2N} (1 - e^{-h})}
\]

(52)

These approximated results are shown in Fig. 5; they approach the results of the Monte Carlo calculation in the limit of small occupancy \( N_T/N \).

The activity coefficients \( \gamma_j \) are larger than 1 due to the repulsive nature of the interaction: the interaction of each particle participates with a positive additional term to the Hamiltonian and hence to the free energy. Instead, \( \vartheta \) decreases: if two particles are present in a cell, they are more likely of the same type (both A or both B), and the transition of one of them is hindered, because
it would lead to two different particles in the same cell (one A and one B), repelling each other and eventually increasing the mechanical energy.

Like in the previous cases, we see that Eq. 35 is violated. Indeed, the predicted $\vartheta$ from the equation in question is:

$$\frac{2\gamma_A \gamma_B}{\gamma_A + \gamma_B} = \frac{1}{1 - \frac{N_T}{2N} (1 - e^{-h})}$$

which increases as a function of $N_T$, while $\vartheta$ decreases.

**Exercise 4** (Attractive interaction between particles of different type). This exercise is analogous to Exercise 3 but the interaction is an attraction, thus $h < 0$. The solution can be obtained by Monte Carlo numerical calculation or by symbolic calculation, by approximating in the limit of small occupancy $N_T/N$.

**Sketch of solution.** The Monte Carlo calculation and Eqs. 51 and 52 can be applied to this exercise, using $h < 0$. The results are shown in Fig. 6.

The activity coefficients $\gamma_j$ are decreased by the interaction: every particle that interacts introduces a negative interaction term into the mechanical energy, in turn appearing in the free energy. The interaction also decreases $\vartheta$: cells with two different types of particles (one A and one B) are more likely than other
combinations, and the transition of one of them is hindered, since it would lead to the loss of an attractive (negative) interaction energy.

In Fig. 6, it can be noticed that the approximations of Eqs. 51 and 52 hold for small occupancy. However, the Monte Carlo results show an abrupt drop in both $\gamma_j$ and $\vartheta$. The reason is that, above a given threshold, it becomes very likely to have almost all the particles collapsing in the same cell. This is an unphysical phenomenon, however, it is similar to the phase transition that can actually take place in attractive systems.

The value of $\vartheta$ predicted by Eq. 35 has the same expression of the previous exercise, Eq. 53; in this case, since $h$ is negative, it predicts a decrease as a function of $N_T$. Actually, $\vartheta$ decreases, however, the equation in question appears to be quantitatively violated, as can be noticed in Fig. 6.

4 Conclusion

We propose a general scheme of a toy model, describing the equilibrium of two types of reacting particles, possibly in the presence of interactions. The interactions are defined by a Hamiltonian and the thermodynamic quantities are evaluated based on statistical mechanics. The exchange reaction rate is evaluated by modelling the system in analogy with the collision theory used to justify the empirical Arrhenius law. We provide general expressions for calculating the activity coefficients and the exchange reaction rates from the mathematical expression of the interactions.

The educational goal is to show that, even in a so simple system, it is not possible to predict the exchange reaction rate from the thermodynamic parameters, in particular, from the activity coefficients. The students are invited to solve exercises, each specifying a different interaction among particles. The exercises can be solved by students having a minimal background in statistical mechanics; knowledge of Monte Carlo numerical calculation can also be exploited.

The results of the exercises show the absence of a general rule connecting the activity coefficients with the exchange reaction rate. In particular, the exercises prove that the substitution of activities in the place of concentrations in mass-action equations is wrong, although it may appear justified in specific cases, e.g. by the transition state theory. The presented toy model can be used to clarify that the activities cannot be thought of as “more precise concentrations”.

During the initial stages of chemistry courses, kinetics is usually introduced for ideal systems, using mass action laws, based on concentrations. The general case (outside ideality) is later explained by using thermodynamics, for chemical equilibrium; the chemical potentials are introduced, clarifying that they can deviate from ideality in the presence of interactions and that, in some cases, the deviation can still be modelled, e.g. under excluded volume interactions or under the Debye-Hückel theory. The activities and the activity coefficients are introduced as useful mathematical shortcuts. We suggest that, at this stage, it is useful to explicitly discuss the kinetics of non-ideal systems, clearly explaining that there are methods to approach the problem, but all of them require some
microscopic model of the reaction and the thermodynamic quantities are not enough to fully characterize the systems. Care should be taken in order to avoid that the students jump to unjustified extrapolations: the activities are not “more precise than concentrations” in general, nor are the activity coefficients “corrections to the concentrations” in the context of kinetics.

From a broader point of view, the proposed toy model can be used to show that thermodynamics does not predict rates. Under equilibrium, the exchange rates are perfectly defined, and they are connected to the behaviour of fluctuations by the fluctuation-dissipation theorems [2]. However, the knowledge of an independent physical quantity, of kinetic nature, is always needed to calculate the rates: thermodynamics does not have the concept of time.

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