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# Proposal of a new principle of thermodynamics

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## Abstract.

Kinetics and thermodynamics are largely disconnected in current theories because Arrhenius activation energies ( $E_a$ ) have strictly no influence on equilibrium distributions. A first step towards the incorporation of rate theories in thermodynamics was the identification of the pre-exponential term of the Arrhenius equation as an entropic quantity. The second step examined here is the possible contribution of  $E_a$  in equilibrium landscapes. Interestingly, this possibility exists if envisioning the energetic exponential term of rates constants as the probability that the energy of the reactant is sufficient for the transition. Under this assumption, the energetic exponent of the equilibrium constant  $K_{ji}$  takes the form  $\left(1 - \frac{H_i}{H_j}\right) \left(1 + \frac{E_a(i \rightarrow j)}{H_i}\right)$  where  $H$  are the mean enthalpies of the reactants. This alternative treatment solves several inconsistencies, predicts that activation energies decrease with temperature, integrates activation energies in the detailed balance and modifies equilibrium relationships in heterogeneous systems, while letting unchanged the Maxwell-Boltzmann distribution. These probabilistic rate constants are then reintroduced in dynamic systems to provide them with the two distinct facets of time: the time step and the time arrow.

*Keywords:* Kinetics; equilibrium; heat capacity; enthalpy; entropy; Gibbs free energy.

*Notes to readers:* The unitless statistical entropy usually written  $H$  will be renamed here  $S$  to avoid confusion with enthalpy. The letter  $C$  will be used for heat capacity but not for concentration.

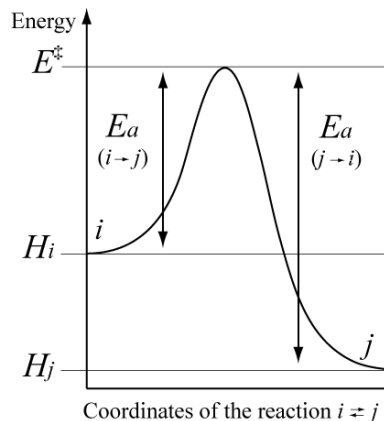
## 1 Introduction

Rate constants are the drivers of all dynamic systems and are widely used in physical chemistry and modeling studies. By the energetic restrictions they impose on chemical transitions, rate constants prevent our organized world from falling directly into its state of weaker free energy and maximal entropy (which might look like something like a mud puddle). Yet the profound nature

of these constants remains obscure and the main focus of this study is to clarify their energetic component. After multiple attempts of description, its most common expression remains the exponential factor of Arrhenius [1, 2]. In its classical version (without tunneling effects), the empirical Arrhenius equation

$$k = A e^{-\frac{E_a}{k_B T}} \quad (1)$$

where  $k_B$  is the Boltzmann constant and  $T$  is the temperature, includes a so-called preexponential factor  $A$ , containing the elementary vibrational frequency and configurational restrictions, and a unitless exponential function containing an energetic barrier called activation energy  $E_a$ . In the present paper, the exponential factor will be reformulated as the probability to reach a threshold energy. This simple hypothesis will lead to major changes in thermodynamic relationships.



**Figure 1.** Representation of the energetic barrier according to the Arrhenius principle. The barrier is supposed to restrict reaction kinetics but to have no influence on equilibrium ratios.  $E^\ddagger$  is a fixed energy threshold necessary for crossing the barrier in both directions and  $H$  are the mean enthalpies of reaction of the particles.

Using the notations of Fig.1, the Arrhenius approach reads

$$k_{ij} = A_{ij} e^{-(E^\ddagger - H_i)/k_B T} \quad (2a)$$

and for the reverse reaction

$$k_{ji} = A_{ji} e^{-(E^\ddagger - H_j)/k_B T} \quad (2b)$$

Note that the activation energy  $E_a$  of Eq.(1) corresponds to the difference  $E^\ddagger - H$ , related to  $\Delta G^\ddagger$  in the activated complex theory of Eyring [3]. In equilibrium the forward and reverse fluxes equalize such that

$$n_i k_{ij} = n_j k_{ji} \quad (2c)$$

giving

$$\begin{aligned} \left(\frac{n_i}{n_j}\right)_{eq} &= K_{ji} = \frac{k_{ji}}{k_{ij}} = \frac{A_{ji}}{A_{ij}} e^{(E^\ddagger - H_i - E^\ddagger + H_j)/k_B T} \\ &= \frac{A_{ji}}{A_{ij}} e^{-(H_i - H_j)/k_B T} = \frac{A_{ji}}{A_{ij}} e^{-\Delta H/k_B T} \end{aligned} \quad (2d)$$

$E^\ddagger$  disappears. The equilibrium ratio is independent of the energetic barrier and depends only on the difference of energy between the reactants. Despite their success, these traditional relationships can be naively questioned.

## 2 Few concerns and alternative proposal

### 2.1 On the universality of $k_B T$ as a mean energy

$1/k_B T$  is introduced in statistical mechanics as a constant called  $\beta$  corresponding to a Lagrangian multiplier or a distribution parameter, and finally connected to temperature by analogy with classical thermodynamics.  $k_B T$  is concretely useful to adimension the exponent of the Arrhenius exponential and is usually interpreted as the mean particle energy. This interpretation holds in the kinetic theory of ideal gases but is much less clear for complex chemical systems in which the mean reactional energies are precisely different for each type of particle.

### 2.2 Insensitivity of dynamic equilibria to activation energies

The accepted conclusion that the presence and the height of energetic barriers do not participate to equilibrium ratios between the reactants, can appear not completely intuitive because one could expect that increasing the height of the barrier amplifies the differential capacity of the reactants to jump over, including in equilibrium. In potential energy landscapes, the mountains regulate the populations but their crests are uninhabited unstable states. By contrast in the transition state theory, the activated complexes reside on the crests but their energy level do not participate to the distributions.

## 2.3 A non-probabilistic exponential law

The exponential term of the Arrhenius law has certain appearances of a probability, but as explained in the following section, as it stands it can not correspond to the exponential distribution. The purpose of the present study is precisely to examine the theoretical consequences of the hypothesis that it is a probability of sufficient energy for the transition. This simple hypothesis leads to the novel formulas

$$P(\text{sufficient energy}) = e^{-\frac{E^\ddagger}{H}} = e^{-(1 + \frac{E_a}{H})} \quad (3a)$$

which gives the equilibrium relationship

$$\begin{aligned} \ln\left(\frac{n_i}{n_j}\right)_{eq} &= \ln \frac{A_{ji}}{A_{ij}} + \left(1 - \frac{H_i}{H_j}\right) \frac{E^\ddagger}{H_i} \\ &= \ln \frac{A_{ji}}{A_{ij}} + \left(1 - \frac{H_i}{H_j}\right) \left(1 + \frac{E_a}{H_i}\right) \end{aligned} \quad (3b)$$

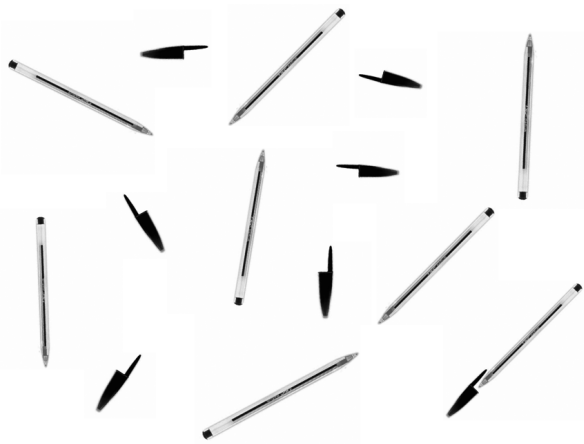
whose structure is completely different from the usual result

$$\ln\left(\frac{n_i}{n_j}\right)_{eq} = \ln \frac{A_{ji}}{A_{ij}} + \frac{H_j - H_i}{k_B T} = \frac{G_j - G_i}{k_B T} \quad (4)$$

In Eq.(4), the pre-exponential terms disappear from the latter form containing the Gibbs free energies  $G$ . This modification results from the identification of the pre-exponential factor as an entropic parameter, which can then be integrated in the Gibbs free energies. This pertinent operation can also be applied to Eq.(3b). The pre-exponential factor can be defined as  $A = \tau^{-1} \Omega^{-1}$  where  $\tau^{-1}$  is the universal thermal frequency (discussed later), giving their time<sup>-1</sup> unit to the rate constants, and  $\Omega^{-1}$  is the reciprocal of the number of possible configurations of the reactant, one of which allowing the reaction to proceed, as simply illustrated in Fig.2. As a consequence,  $\ln(A_{ji}/A_{ij})$  can be identified, after cancellation of the identical frequencies, as the difference of unitless entropies

$$\ln \frac{A_{ji}}{A_{ij}} = \ln \frac{\Omega_{ij}}{\Omega_{ji}} = S_{ij} - S_{ji}$$

Note the inversion of the suffixes between the ratios of  $A$  and  $\Omega$ . Eq.(3b) contrasts with Eq.(4) in that it introduces a role for activation energies in equilibrium distributions. Large  $E_a$  do not inverse but accentuate the extent of the ratios determined in both cases by the relative energy levels.



**Figure 2.** Randomly moving pens and caps simply illustrate the concept of reactional entropy. The set of their equiprobable relative arrangements (which would be much larger in 3D) is noted  $\Omega$ , out of which only one, of probability  $1/\Omega$ , allows the assembly of the caps and the pens, as shown at the bottom right. Even when conveniently arranged, the pen and the cap can stably associate only if the energy of their collision is sufficient. This second condition is quantified from 0 to 1 in the energetic term of rate constants defined here.

### 3 A new probabilistic interpretation of the exponential factor

#### 3.1 The exponential distribution

The exponential component of the Arrhenius law and of the Boltzmann distribution, can be simultaneously derived from the exponential distribution. The probability that a particle from an homogeneous population with an average number of energy quanta per particle  $\langle \mathcal{E} \rangle$ , reaches a fixed threshold number  $\mathcal{E}^\ddagger$ , is

$$P(\mathcal{E} > \mathcal{E}^\ddagger) = e^{-\frac{\mathcal{E}^\ddagger}{\langle \mathcal{E} \rangle}} \quad (5)$$

Since  $\mathcal{E}^\ddagger$  is a temperature-independent threshold and  $\langle \mathcal{E} \rangle$  is temperature dependent, temperature remains at the denominator of the exponent, but the most important difference with current rate equations is the absence of  $k_B T$ .  $k_B T$  is generally considered as the mean single particle energy, acceptable as a mean kinetic energy for purely kinetic gases, but not for all heterogeneous systems containing different kinds of energies. An other problem even more critical with the Arrhenius equation of Eq.(1), is that in absence of energetic barrier ( $E_a = 0$ ), the exponential is equal to 1, suggesting that reactions are no longer energetically restricted but only affected by the pre-exponential factor. In other words, the mean particle energy  $k_B T$  would be fully sufficient for all the

transitions. This result is clearly inconsistent with the view of  $k_B T$  as a mean energy because of a basic principle: the average particle energy in a homogeneous population is no way reached by all the particles. Indeed, even when  $E_a = 0$ , that is to say when the barrier corresponds to the mean particle energy, not all the particles have a sufficient energy. In contrast in the present interpretation,  $E_a = 0$  (equivalent to  $E^\ddagger = H$  in Fig.1 and to  $\mathcal{E}^\ddagger = \langle \mathcal{E} \rangle$ ) predicts a probability of  $1/e$  (0.37).

#### 3.2 The rule for particle interconversion

The present approach also fundamentally differs from the classical one in equilibrium. The relative populations of interconvertible species are determined not only by the difference of their mean energies, but also by the barriers. Interconversion between particles of different nature  $i$  and  $j$  is possible when either a particle  $i$  or a particle  $j$ , has accumulated a minimal number of energy quanta, denoted below by  $\mathcal{E}_{i,j}^\ddagger$ , which is the same for the conversions  $i \rightarrow j$  and  $j \rightarrow i$ . For a particle of type  $i$ , the probability of this accumulation is simply given by the exponential distribution  $P(X_i > \mathcal{E}_{i,j}^\ddagger) = e^{-\mathcal{E}_{i,j}^\ddagger / \langle \mathcal{E}_i \rangle}$  [4]. As the same holds for the particles of type  $j$ , when  $\langle \mathcal{E}_i \rangle > \langle \mathcal{E}_j \rangle$ , the particles of type  $i$  would switch more probably than the reverse. As a consequence, the system spontaneously evolves until the reciprocal fluxes equalize. The number of particles in the sub-populations  $i$  and  $j$  necessarily adjust such that

$$n_i A_{ij} e^{-\mathcal{E}_{i,j}^\ddagger / \langle \mathcal{E}_i \rangle} = n_j A_{ji} e^{-\mathcal{E}_{i,j}^\ddagger / \langle \mathcal{E}_j \rangle} \quad (6a)$$

or

$$\left( \frac{n_i}{n_j} \right)_{eq} = \frac{A_{ji}}{A_{ij}} e^{\mathcal{E}_{i,j}^\ddagger \left( \frac{1}{\langle \mathcal{E}_i \rangle} - \frac{1}{\langle \mathcal{E}_j \rangle} \right)} \quad (6b)$$

Returning to the correspondence between the unitless pre-exponential term and entropy, this equation takes the elegant form

$$\ln \left( \frac{n_i}{n_j} \right)_{eq} = \underbrace{\mathcal{S}_{ij} - \mathcal{S}_{ji}}_{\text{Entropic term}} + \underbrace{\mathcal{E}_{i,j}^\ddagger \left( \frac{1}{\langle \mathcal{E}_i \rangle} - \frac{1}{\langle \mathcal{E}_j \rangle} \right)}_{\text{Energetic term}} \quad (7)$$

Eq.(7) can be written with the activation energy of Arrhenius  $\mathcal{E}_{a(i \rightarrow j)} = \mathcal{E}_{i,j}^\ddagger - \langle \mathcal{E}_i \rangle$  as follows

$$\begin{aligned} \ln \left( \frac{n_i}{n_j} \right)_{eq} &= \mathcal{S}_{ij} - \mathcal{S}_{ji} + \left( 1 - \frac{\langle \mathcal{E}_i \rangle}{\langle \mathcal{E}_j \rangle} \right) \frac{\mathcal{E}_{i,j}^\ddagger}{\langle \mathcal{E}_i \rangle} \\ &= \mathcal{S}_{ij} - \mathcal{S}_{ji} + \left( 1 - \frac{\langle \mathcal{E}_i \rangle}{\langle \mathcal{E}_j \rangle} \right) \left( 1 + \frac{\mathcal{E}_a}{\langle \mathcal{E}_i \rangle} \right) \end{aligned} \quad (8)$$

## 4 Reconnection of the energetic parameter of rate constants to Boltzmann's energy distribution

### 4.1 Starting from the geometric distribution

One of the main virtues of present proposal is its capacity to unify kinetic and thermodynamic rules under the same law, emerging from a simple discrete treatment. Mix  $E$  white balls and  $N$  black balls,  $E$  and  $N$  being positive integers, into a large bag and draw them at random. The number of balls  $E$  between two balls  $N$  written  $\mathcal{E}$  is supposed to correspond to the number of energy quanta in a particle, whose mean number is naturally  $\langle \mathcal{E} \rangle = E/N$ . Simple probabilities say

$$P(\mathcal{E} > \mathcal{E}^\ddagger) = \left( \frac{E}{E+N} \right)^{\mathcal{E}^\ddagger} = \left( \frac{\langle \mathcal{E} \rangle}{1 + \langle \mathcal{E} \rangle} \right)^{\mathcal{E}^\ddagger} \quad (9a)$$

For  $\mathcal{E}^\ddagger$  and  $\langle \mathcal{E} \rangle$  large and of the same order of magnitude, this discrete geometric distribution can be approximated as the continuous exponential distribution.

$$P(\mathcal{E} > \mathcal{E}^\ddagger) = e^{-\frac{\mathcal{E}^\ddagger}{\langle \mathcal{E} \rangle}} \quad (9b)$$

If we no longer reason in terms of threshold but of exact value, we have

$$\begin{aligned} P(\mathcal{E} = \mathcal{E}^\ddagger) &= \left( \frac{E}{E+N} \right)^{\mathcal{E}^\ddagger} \left( \frac{N}{E+N} \right) \\ &= \left( \frac{\langle \mathcal{E} \rangle}{1 + \langle \mathcal{E} \rangle} \right)^{\mathcal{E}^\ddagger} \frac{1}{1 + \langle \mathcal{E} \rangle} \end{aligned} \quad (10a)$$

switching once again to the continuous distribution,

$$\begin{aligned} P(\mathcal{E} = \mathcal{E}^\ddagger) &\sim e^{-\frac{\mathcal{E}^\ddagger}{\langle \mathcal{E} \rangle}} \left( 1 + e^{-\frac{1}{\langle \mathcal{E} \rangle}} \right) \\ &= \frac{e^{-\mathcal{E}^\ddagger/\langle \mathcal{E} \rangle}}{\sum_{j=1}^{\infty} e^{-j/\langle \mathcal{E} \rangle}} \end{aligned} \quad (10b)$$

which is, when taking  $\langle \mathcal{E} \rangle = k_B T$ , exactly the Boltzmann probability law where the denominator can be understood as the sum of all possible microstates, called the partition function. It was considered by Feynman as the summit of statistical mechanics [5], but is recovered

in two lines from the exponential distribution. As a consequence, the relative subpopulations of energies  $\mathcal{E}_1$  and  $\mathcal{E}_2$  are given by the ratio of two Eq.(10b)

$$\frac{P(\mathcal{E}=\mathcal{E}_1)}{P(\mathcal{E}=\mathcal{E}_2)} = e^{\frac{\mathcal{E}_2 - \mathcal{E}_1}{\langle \mathcal{E} \rangle}} \quad (10c)$$

Note that the approximations used above are based on the following property of the exponential function

$$\lim_{\varepsilon \rightarrow 0} (1 + \varepsilon x)^{1/\varepsilon} = e^x$$

which can also be written

$$\lim_{q \rightarrow 1} (1 + (1 - q)x)^{1/(1-q)} = e^x$$

that is the  $q$ -exponential on which rate theories are also built [6, 7].

### 4.2 Simplified Maxwell-Boltzmann distribution

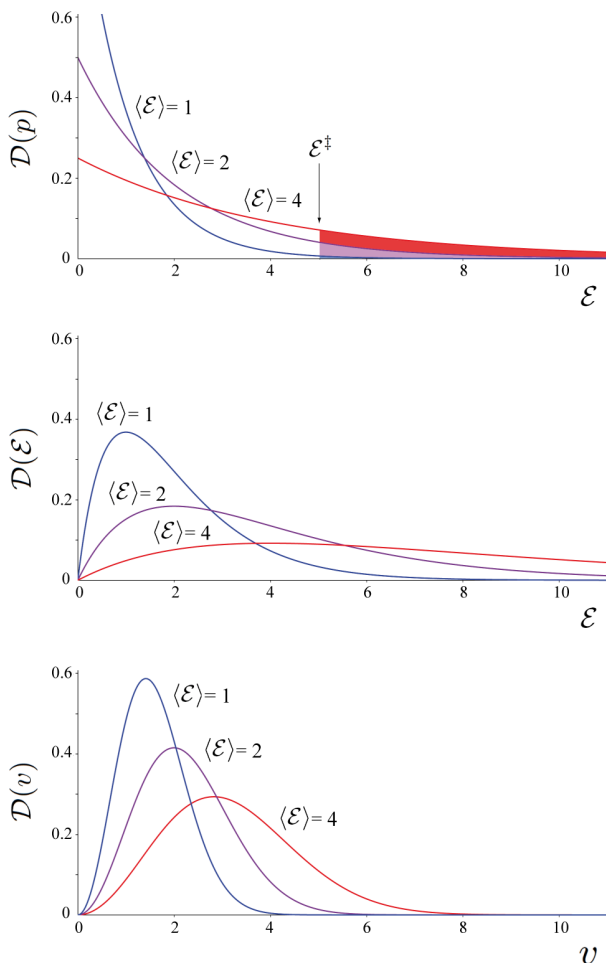
When  $\langle \mathcal{E} \rangle$  corresponds to  $k_B T$  if adding energy units, the structure of Eq.(10b) corresponds exactly to that of the celebrated Boltzmann's energy distribution, which itself simply becomes a particular case of thermal system. The ideal monoatomic gas is the perfect example of a system with a maximal entropy and whose individual components have an energy strictly proportional to temperature. Inversely, most real systems have a certain degree of organization (non-maximal entropy) but are made of molecular components with a certain degree of entropy, which will be examined later. Let us first deepen the analogies between the exponential distribution and Maxwell-Boltzmann results. The particles which have an energy content  $\mathcal{E}_i$  constitute a fraction of the system  $n_i/N$  and bring together in the system a fraction of energy  $P(\mathcal{E}_i) \mathcal{E}_i$ . The most represented particles are, according to the exponential as well as Boltzmann distributions, the low energy particles, which poorly contribute to the total energy of the system, thus generating a peak in the energy density curve at the level of the largest product  $\mathcal{E}_i d(\mathcal{E}_i)$ , where  $d(\mathcal{E}_i)$  is the density function of the exponential distribution

$$d(\mathcal{E}_i) = \frac{1}{\langle \mathcal{E} \rangle} e^{-\frac{\mathcal{E}_i}{\langle \mathcal{E} \rangle}}$$

The normalized expression of  $\mathcal{E}_i d(\mathcal{E}_i)$  is the density of the  $\Gamma_2$  function

$$\mathcal{D}(\mathcal{E}) = \gamma_2(\mathcal{E}) = \frac{\mathcal{E}}{\langle \mathcal{E} \rangle^2} e^{-\frac{\mathcal{E}}{\langle \mathcal{E} \rangle}} \quad (11)$$

whose shape is shown in the middle panel of Fig.4.



**Figure 4.** Fractional densities: of the energetic states of particles ( $\mathcal{D}(p)$ , top panel), of energy ( $\mathcal{D}(\mathcal{E})$ , middle panel), and of velocities ( $\mathcal{D}(v)$ , bottom panel). Curves drawn with arbitrary units and a mass of 1 unit. The fractions of particles with energy higher than  $\mathcal{E}^\ddagger$  correspond to the colored surfaces in the top panel. They are expected to increase with  $\langle \mathcal{E} \rangle$ , itself increasing with temperature. This traditional interpretation of the role of temperature on rate constants supposes that particle energies increase with temperature, contrary to Gibbs free energies. This scheme does not hold for the activated complex theory in which the threshold energy is not fixed, but is itself temperature-dependent.

For a monoatomic ideal gas, the energy content of a particle is exclusively translational. When substituting  $\mathcal{E}_i = \frac{1}{2}mv_i^2$ ,  $\mathcal{E}_i d(\mathcal{E}_i)$  becomes

$$\mathcal{E}_i d(\mathcal{E}_i) = \frac{mv_i^2}{2\langle \mathcal{E} \rangle} e^{-\frac{mv_i^2}{2\langle \mathcal{E} \rangle}}$$

whose integration between  $0 < v < \infty$  is  $\sqrt{\pi \langle \mathcal{E} \rangle / 8m}$ . Multiplying the equation by the inverse of this value di-

rectly yields the normalized velocity density function.

$$\mathcal{D}(v) = \left(\frac{2}{\pi}\right)^{1/2} \left(\frac{m}{\langle \mathcal{E} \rangle}\right)^{3/2} v^2 e^{-\frac{mv^2}{2\langle \mathcal{E} \rangle}} \quad (12)$$

which gives the nice bell-shaped curves shown in the bottom panel of Fig.4, with a mode at

$$v_{mp} = \sqrt{\frac{2\langle \mathcal{E} \rangle}{m}}$$

Therefore, we verify that the most probable values of energy and velocity (tips of the curves of the middle and bottom panels of Fig.4 respectively), naturally coincide through  $\mathcal{E}_{mp} = \frac{1}{2}mv_{mp}^2$ . The mean velocity value  $\int_0^\infty v\mathcal{D}(v)dv$  is

$$\langle v \rangle = \sqrt{\frac{8\langle \mathcal{E} \rangle}{\pi m}}$$

When substituting  $\langle \mathcal{E} \rangle = k_B T$ , Eq.(12) is the Maxwell velocity distribution.

Let us now consider more elaborate systems with different types of particles and energies.

## 5 Comparative influences of temperature in the different treatments

### 5.1 Influence of temperature on rate constants

If the mean reactional energies are proportional to temperature ( $H = CT$ ), the traditional shape of the Arrhenius plot is obtained with the present treatment, but through a different way. Increasing the temperature increases the thermal energy stored in the particles and responsible for their reactional capacity, thus reducing the activation energy  $E_a = E^\ddagger - H$ . By contrast using the conventional formula of Eq.(1),  $E_a$  is the constant steering coefficient of the Arrhenius plot [8] and the effect of temperature comes only from the entity  $k_B T$ , in contradiction with the frequently noticed dependence on temperature of  $E_a$  [9, 10]. It would be preferable in practice to use the fixed thresholds  $\mathcal{E}^\ddagger$  instead of the traditional activation energies which are different for the two interconvertible reactants and depend on temperature.

## 5.2 Influence of temperature in equilibrium

### 5.2.1 Where is the temperature in the different equations?

Equilibrium constants are assumed to vary with temperature according to the equation derived from the van't Hoff relationship.

$$\ln K_{ji} = \frac{G_j - G_i}{k_B T} \quad (13)$$

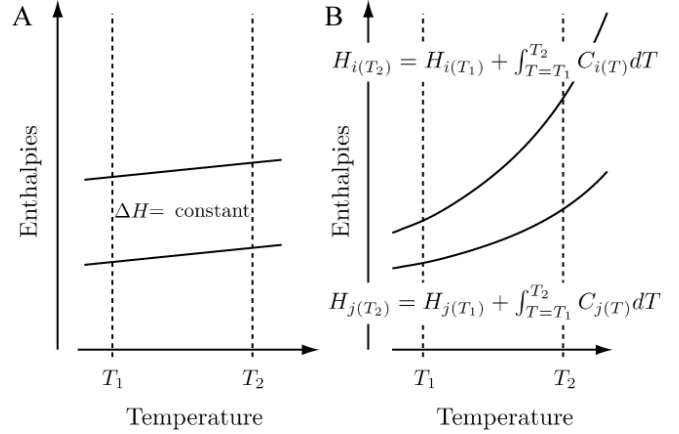
Writing  $\Delta G = \Delta H - T\Delta S$  in this equation and supposing that  $H$  and  $S$  are temperature-independent, has the practical advantage to yield the expected van't Hoff plots linearly dependent of  $1/T$ . In the present treatment, the equilibrium constant remains a function of the energies, which can be considered discretely as a number of quanta in Eq.(7), or translated into classical energies (joules or calories) as follows. Using an energy threshold  $E^\ddagger$  and a mean enthalpy  $H$  for a reactant or a group of reactants according to the Hess's law,

$$\ln K_{ji} = \frac{S_{ij} - S_{ji}}{k_B} + E^\ddagger \left( \frac{1}{H_i} - \frac{1}{H_j} \right) \quad (14a)$$

or, using the activation energy  $E_a$ ,

$$\ln K_{ji} = \frac{S_{ij} - S_{ji}}{k_B} + \left( 1 - \frac{H_i}{H_j} \right) \left( 1 + \frac{E_a(i \rightarrow j)}{H_i} \right) \quad (14b)$$

Temperature is not apparent in this equation but hidden in the variables. The relative temperature-dependence of the enthalpies regulate the equilibrium, as schematized in Fig.3. In Fig.3A, the enthalpies of the reactants are shown to increase in the same proportion with temperature, but note that in fact, the temperature-dependence of the traditional van't Hoff plot would still be obtained even if these enthalpies remain constant, in complete opposition to the other traditional explanation that the effect of temperature on the reactions is due to an increase in the mean energy of the particles.



**Figure 3.** Comparative interpretation of the role of temperature in van't Hoff plots. **(A)** In the classical interpretation, the two reactants are assumed to have identical heat capacities. **(B)** In the present interpretation, temperature affects in a different manner the reactivity of both reactants because of their different heat capacities. As a consequence,  $\Delta H$  depends on temperature.

### 5.2.2 The kinetic formalism using Gibbs free energies is misleading

Temperature is intuitively expected to increase the reaction rates by increasing the energy of the reactants, but the kinetic treatments using free energies say the opposite.  $G$  always decreases with temperature, thereby increasing the difference  $E^\ddagger - G$  and raising the height of the barrier. Using the so-called enthalpies of reaction  $H$  instead of Gibbs free energies, allows to circumvent this contradiction, but if  $H$  is indeed proportional to temperature in certain ranges of temperature, it no longer corresponds to  $G$  used in equilibrium. The energy landscape of Arrhenius is governed by enthalpies whereas thermodynamic landscapes include entropies. In this respect, the activated complex theory [3, 11] may introduce some confusion since it describes the kinetic barrier in term of difference of Gibbs free energies. In this theory, the tip of the barrier is not a temperature-independent threshold but the energy of an activated complex that itself depends on temperature, so that the temperature-dependence of the height of the barrier  $\Delta G^\ddagger$  results from the relative dependences on temperature of the reactant ( $G$ ) and of the activated complex ( $G^\ddagger$ ). The activated complex is an atypical structure stably standing in a crest of the energetic landscape and with the strange property, when it is reached, to only evolve in the direction of the complete transition but can not turn back. Moreover, the forbidden transition is not the same depending to the starting reactant [4].

In the kinetic theory, temperature is the macroscopic manifestation of microscopic motions, that is re-scaled

at the microscopic level through the Boltzmann constant, so that  $k_B T$  is an average index of single particle motion. But temperature is also present in the Gibbs free energy, not only in its most frequent expression  $G = H - TS$ , but also because  $H$  and  $S$  are themselves temperature-dependent [12, 13]. Raising temperature from  $T_1$  to  $T_2$  ( $> T_1$ ) increases enthalpy by  $H(T_2) - H(T_1) = C_P (T_2 - T_1)$  and entropy by  $S(T_2) - S(T_1) = C_P \ln(T_2/T_1)$ , where  $C_P$  is the heat capacity at constant pressure.

### 5.3 Reintroducing temperature in reactional energies

#### 5.3.1 Increasing temperature favors reactions

Using the energy quanta approach, the dependence on temperature is conferred by the ratio  $\mathcal{E}^\ddagger$  (temperature-independent) over  $\langle \mathcal{E} \rangle$  (temperature-dependent). This is in fact less clear for the traditional Eq.(13) where both the numerator and the denominator are temperature-dependent. Reactions are facilitated when the energy of the reactants is higher. Possibly because this reasoning is contradicted for Gibbs free energies which decrease with temperature, teachers prefer drawing the Maxwell velocity distribution to show that increasing the temperature increases the fractional population over the activation energy threshold. This view can be recovered without returning to the ideal gas, using the partial integration of the exponential distribution density, as illustrated by the colored surfaces in the top panel of Fig.4.

$$P(\mathcal{E} > \mathcal{E}^\ddagger) = \int_{\mathcal{E}^\ddagger}^{\infty} \frac{1}{\langle \mathcal{E} \rangle} e^{-\frac{\mathcal{E}}{\langle \mathcal{E} \rangle}} d\mathcal{E} = e^{-\frac{\mathcal{E}^\ddagger}{\langle \mathcal{E} \rangle}}$$

One recovers the energetic form of rate constants proposed here. This rational explanation of a role of temperature mediated by particle energies, corresponds exactly to the present model. On the one hand, it can be understood for enthalpies but not for Gibbs free energies, but on the other hand, even when using enthalpies, the current and present approaches strikingly differ.

#### 5.3.2 Temperature increases the reactional energy of the particles

The dimensionless exponents of the two competing structures of rate constants compared here, contain energies in the numerator and denominator, but beyond this common property, the principles are different. In the usual form, the exponent is  $H/k_B T$ , whereas in the present one, it is  $E^\ddagger/H$ . In the former ratio, the numerator and the denominator both depend on temperature, whereas in the latter one, only the denominator is temperature-dependent. Thermal energy increases the speed of molecules, important for the reactional efficacy

of collisions, but more generally the heat capacity of macromolecules describes how much energy can be stored by a molecule in its internal vibrations or rotations, which are often the triggering factors of chemical transformations, particularly for biological macromolecules whose heat capacity is clearly not negligible. The heat capacity of a monoatomic gas (used in the explanation using Maxwell velocities) is purely translational, but that of more complex particles include the other forms of energy. In the new exponent proposed here, the denominator represents the temperature-dependent reactional energy conceived in all its forms: translational, rotational and vibrational. Since all these forms define the macroscopic notion of temperature, the reactional propensity is naturally expected to follow temperature. This property precisely characterizes enthalpy, which obeys the long established thermodynamic relation

$$\left(\frac{\partial H}{\partial T}\right)_P = m C_P$$

whose integration with the postulated initial value  $H = 0$  at  $T = 0$  simply gives  $H \propto CT$ . The variation of enthalpies with temperature is in fact less simple. It is calculated using Kirchhoff's law in term of a reference state different from  $T = 0$  [14]. In addition, when temperature is far from 298 K, the temperature-dependence of  $C_P$  should be introduced using empirical expressions found in tables like  $C_P = \alpha + \beta T + \gamma T^{-2} + \dots$ . In fact, absolute enthalpies cannot be determined experimentally and only differences of enthalpy can be measured by calorimetry. Hence in the following equations intended to show dependences on temperature, the simple proportionality between  $H$  and  $T$  will be retained as a gross approximation.

For a reaction, the well established relation  $d\Delta H = m \Delta C_P dt$  gives, upon differentiation of  $\ln K = -\Delta H/k_B T$ ,

$$\frac{\partial \ln K}{\partial T} = -\frac{1}{k_B T} \frac{\partial \Delta H}{\partial T} - \frac{\Delta H}{k_B} \frac{\partial (1/T)}{\partial T} = -\frac{\Delta C_P}{k_B T} + \frac{\Delta C_P}{k_B T} = 0$$

which shows that the temperature-dependence of van't Hoff is lost. By contrast, introducing this definition of enthalpy in Eq.(7) gives

$$\ln K_{ji} \sim \frac{S_{ij} - S_{ji}}{k_B} + \frac{E_{i,j}^\ddagger}{T} \left( \frac{1}{C_i} - \frac{1}{C_j} \right) \quad (15)$$

Where  $C_i$  and  $C_j$  are the average heat capacities of the interconvertible reactants weighted by the stoichiometric coefficients. Strikingly, Eq.(15) is expected to yield typical van't Hoff plots. It also shows that at very high temperature, the equilibrium constant becomes essentially a matter of entropy, as expected.

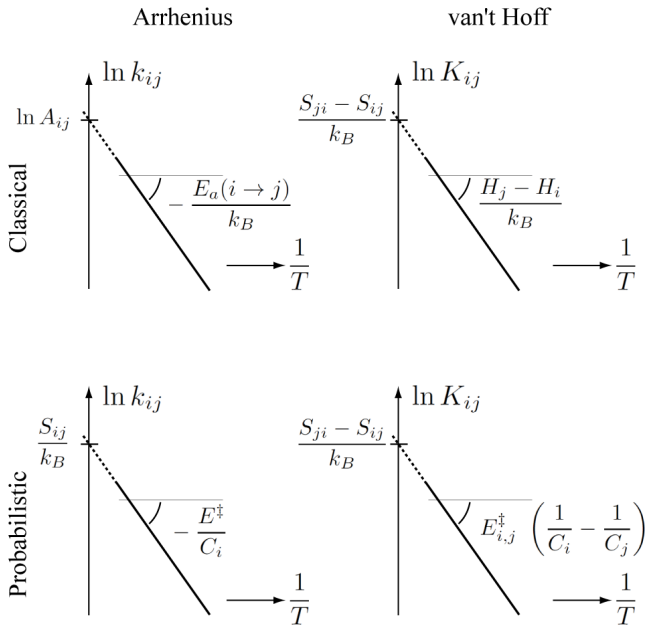


## 5.4 Reinterpretation of experimental plots

Considering the exponential term of rate constants as a probability implies profound conceptual changes but moderate apparent changes in practice, which just imposes to reinterpret the experimental plots.

### 5.4.1 With temperature-independent entropies

At least the slopes of the Arrhenius and van't Hoff plots should be reinterpreted under the new view of rate constants, as schematized in Fig.5. The most striking difference is that in the classical interpretation of the van't Hoff plot, the temperature-dependence of enthalpies is denied, whereas the present probabilistic model is fundamentally based on calorimetric enthalpies. The enthalpies of some mineral substances, solid and liquid, were indeed shown approximately independent of temperature up to 200 degrees, but this behaviour is likely to not hold for all reactional moieties like biological macromolecules in solution.



**Figure 5.** Comparative interpretations of the Arrhenius and van't Hoff plots between the classical and the present treatments of the energetic exponential. The meaning of the entropy intersect (supposed temperature-independent in this version) is unchanged but that of the slopes is completely different.

The equilibrium and kinetic relationships of the two approaches are compared below.

### Equilibrium constants

- In the classical treatment where both enthalpies and entropies are temperature-independent,

$$\frac{\partial \ln K_{ij}}{\partial T} = (H_j - H_i) \frac{1}{k_B} \frac{1}{T^2}$$

and in the new treatment using calorimetric enthalpies,

- $\frac{\partial \ln K_{ij}}{\partial T} = (C_j - C_i) \frac{E_{i,j}^\ddagger}{C_j C_i} \frac{1}{T^2}$

The difference of heat capacity between the reactants is accentuated by the energetic threshold, but alleviated by temperature, in accordance with the principle of Le Chatelier.

### Kinetic constants

- The classical Arrhenius form, with temperature-independent activation energies, gives

$$\frac{\partial \ln k_{ij}}{\partial T} = \frac{E_a(i \rightarrow j)}{k_B} \frac{1}{T^2}$$

and the present form based on the enthalpy of the reactant gives

- $\frac{\partial \ln k_{ij}}{\partial T} = \frac{E_{i,j}^\ddagger}{C_i} \frac{1}{T^2}$

The energy threshold of the new treatment can be deduced from values of  $E_a$  measured classically, through  $E_{i,j}^\ddagger = C_i E_a(i \rightarrow j)/k_B$ .

### 5.4.2 With temperature-dependent entropies

In fact, entropies and enthalpies both depend on temperature according to the basic thermodynamic differentials

$$\frac{\partial S(T)}{\partial T} = \frac{C_p}{T}$$

$$\frac{\partial H(T)}{\partial T} = C_p$$

with the following consequences on equilibrium and kinetic constants.

### Equilibrium constants

- The differentiation of the classical equilibrium relation gives

$$\frac{\partial \ln K_{ij}(T)}{\partial T} = \frac{C_j - C_i}{k_B T} \quad (16a)$$

which is not the van't Hoff formula and gives the temperature-dependence function

$$\ln K_{ij} = \frac{C_j - C_i}{k_B} \ln T + c \quad (16b)$$

- For the present treatment,

$$\frac{\partial \ln K_{ij}(T)}{\partial T} = (C_j - C_i) \left( \frac{1}{k_B T} + \frac{E_{i,j}^\ddagger}{C_i C_j T^2} \right) \quad (17a)$$

giving the temperature-dependence shape

$$\ln K_{ij} = (C_j - C_i) \left( \frac{\ln T}{k_B} - \frac{E_{i,j}^\ddagger}{C_i C_j T} \right) + c \quad (17b)$$

### Kinetic constants

- When ignoring the entropic meaning of the pre-exponential factor in the Arrhenius law,

$$\ln k_{ij} = \ln A_{ij} - \frac{E_a}{k_B T} \quad (18a)$$

and

$$\frac{\partial \ln k_{ij}(T)}{\partial T} = \frac{E_a}{k_B} \frac{1}{T^2} \quad (18b)$$

- For the present treatment,

$$\ln k_{ij} = \ln A_{ij} - \frac{E_{i,j}^\ddagger}{H_i} \quad (19a)$$

interpreted as

$$\ln k_{ij} = -\ln \tau - \frac{S_{ij}}{k_B} - \frac{E_{i,j}^\ddagger}{H_i} \quad (19b)$$

which becomes, when differentiated with respect to temperature,

$$\frac{\partial \ln k_{ij}(T)}{\partial T} = -\frac{C_i}{k_B T} + \frac{E_{i,j}^\ddagger}{C_i} \frac{1}{T^2} \quad (19c)$$

giving a function of temperature of the form

$$\ln k_{ij} = \frac{C_i}{k_B} \ln \frac{1}{T} - \frac{E_{i,j}^\ddagger}{C_i} \frac{1}{T} + c \quad (19d)$$

As explained previously, the dependence on temperature of enthalpies should be further refined in these very approximate equations, using Kirchoff's law, setting the standard values  $H_0$  at  $T = 298K$ , and taking into account the dependence on temperature of heat capacities. Moreover, certain ranges of temperature should not be considered in case of phase transition or of inactivation of certain reactants. For example, most proteins are denatured over 320 K.

### 5.4.3 Deviations from the expected plots

Experimental Arrhenius plots are rarely the straight lines expected from the Arrhenius equation [ $\ln k = \ln A - \frac{E_a}{R} \frac{1}{T}$ ], but can have convex or concave shapes, explained by tunneling effects and other hypotheses [9, 15, 16]. In addition, the intersect with the vertical axis is more guessed than actually existing. Deviations are also the rule for the so-called van't Hoff plots in equilibrium. Moreover, the two types of enthalpy: (i) calorimetric and (ii) determined from the analysis of experimental plots using the currently admitted functions, are always different [12, 13]. Reintroducing the temperature-dependence of enthalpies and entropies may account for certain deviations [17, 18]. In fact, a difference of enthalpy between the interconvertible reactants is synonymous to a heat of reaction, that itself reflects a difference of heat capacity.

## 5.5 Extension of the detailed balance to activation energies

To the properties of the hypothetic rate constants listed above, is added a complication to satisfy the detailed balance rule linking the different rates constants of a system. The traditional form of the energetic exponential obviously complies with this rule since the total difference of energy of a global reaction made of several elementary steps is simply the sum of energy gaps of these steps, with the automatic cancellation of activation energies, as illustrated in Eq.(2d). Things are less simple with the new form since the activation energies should now take part to the detailed balance relationship. Consider for example a triangular circuit. The compounds  $a$  and  $b$  can interconvert either directly, with an activation threshold  $E_{a,b}^\ddagger$ , or indirectly through an intermediate  $c$ . Assuming that the reactional enthalpy and entropy of every reactant is the same for all its transformations, writing  $E_{a,c}^\ddagger$  the activation threshold between  $a$  and  $c$ , and  $E_{c,b}^\ddagger$  between  $c$  and  $b$ , the detailed balance relation

$$\frac{k_{ab} k_{bc} k_{ca}}{k_{ba} k_{cb} k_{ac}} = 1 \quad (20a)$$

implies for the energies

$$\frac{E_{a,c}^\ddagger - E_{a,b}^\ddagger}{H_a} + \frac{E_{a,b}^\ddagger - E_{b,c}^\ddagger}{H_b} + \frac{E_{b,c}^\ddagger - E_{a,c}^\ddagger}{H_c} = 0 \quad (20b)$$

generalizable for all the cycles of the system, with any number of components  $n$

$$\sum_{i=1}^n \frac{E_{i,i-1}^\ddagger - E_{i,i+1}^\ddagger}{H_i} = 0 \quad \text{with} \quad E_{1,0}^\ddagger = E_{n,n+1}^\ddagger = E_{1,n}^\ddagger \quad (20c)$$

These elegant relationships with circular permutations are mutually compatible for all the cycles of a reticulated system. In this new treatment, the activation energies are now envisioned as integral components of the system, whereas in the classical theory they were extra-parameters whose values can be arbitrary.

## 6 Rebuilding discrete thermodynamics

Matter was discretized in the visionary theory of Boltzmann and the same was extended to energy by Planck [19]. Since handling energy as a number of quanta facilitates the formulation of basic equations, let us apply again this recipe to the rudiments of thermodynamics and then reintroduce the new kinetic rules proposed above. Two types of systems will be examined, homogeneous and heterogeneous, but always made of components whose energy is proportional to temperature, like ideal gases. For the heterogeneous system, these particles will be simply assumed to have different heat capacities. The concept of entropy long proved fruitful to begin statistical physics.

### 6.1 Index of uncertainty for a population

Two criteria are sufficient for defining this index equivalent to entropy. It should be: (i) a function of the number of possible configurations (microstates) of the system's components and (ii) additive for uncorrelated systems.

(i) The number of different possible configurations (written  $\Omega$ ) of a macroscopic system are invisible and definitely not measurable in practice, but the number of these theoretical "snapshots" can be deduced statistically. It reflects the uncertainty of the system, a notion closely related to missing information and disorganization. For example, a book is an organized object in which the page 189 is located between the pages 187 and 191 with a good degree of confidence, but if the pages are torn and thrown down, this probability strongly decreases because the number of possible arrangements of the pages increases.

(ii) The other requirement for an index of disorganization is its additivity for independent systems. This can also be easily conceived: For each microstate of a system 1, all the states of a system 2 are possible, so the total number of states of the global system 1 + 2 is the product  $\Omega_1\Omega_2$ . Obviously the function satisfying

$$f(\Omega_1\Omega_2) = f(\Omega_1) + f(\Omega_2) \quad (21)$$

is the logarithmic function ( $\ln \Omega$ ). We will also define a single particle average index  $\mathcal{S} = \frac{1}{N} \ln \Omega$ . Concretely,

the total number of configurations of a system made of  $N$  noninteracting components falling into  $r$  categories is

$$\Omega = \frac{N!}{n_1!n_2!\dots n_r!} \quad (22)$$

Using the Stirling approximation  $x! \sim x^x e^{-x} \sqrt{2\pi x}$  [20] of which a rough approximation is  $x! \sim x^x$ ,

$$\Omega \sim \frac{N^N}{n_1^{n_1} n_2^{n_2} \dots n_r^{n_r}} = \left[ \left(\frac{n_1}{N}\right)^{n_1} \left(\frac{n_2}{N}\right)^{n_2} \dots \left(\frac{n_r}{N}\right)^{n_r} \right]^{-1} \quad (23)$$

so that

$$\ln \Omega = - \sum_{i=1}^r \ln \left(\frac{n_i}{N}\right)^{n_i} \quad (24)$$

giving a single particle average index of

$$\mathcal{S} = - \frac{1}{N} \sum_{i=1}^r n_i \ln \left(\frac{n_i}{N}\right) = - \sum_{i=1}^r p_i \ln p_i \quad (25)$$

with  $p_i = n_i/N$  and  $\sum_i n_i = N$ . With respect to these definitions, the so-called Boltzmann entropy ( $S_B$ ) and Gibbs/Shannon entropy ( $S_G$ ) are not equivalent, but related through  $S_G = S_B/N$ .  $S_G/k_B$  corresponds to  $\mathcal{S}$  whereas  $S_B/k_B$  corresponds to  $N\mathcal{S}$ .

But for deriving a pure theory, using an approximation, as acceptable as it can be, is not satisfactory. To bypass the need for the Stirling approximation, it is of some interest to reconsider Eq.(23), which could simply mean that every fractional state  $n_i/N$  is occupied  $n_i$  times so that  $\Omega$  is simply the reciprocal of the probability of occupancy. Based on the same principle, another equation can be designed by supposing that the system can evolve.

### 6.2 Evolving system

In a first-order network,  $r$  particle states obey a linear evolution system, which has a unique stable solution written  $n_i^{eq}$ . A new state function allows to describe the occupation of the equilibrium proportions  $\left(\frac{n_i^{eq}}{N}\right)^{n_i}$  :

$$\mathcal{U} = - \frac{1}{N} \sum_{i=1}^r n_i \ln \left(\frac{n_i^{eq}}{N}\right) \quad (26)$$

$\mathcal{U}$  is an index of the mean gap between the current and the equilibrium distributions. This gap can incite the system to evolve, provided it is higher than its degree of disorganization  $\mathcal{U} > \mathcal{S}$ . The difference  $\mathcal{F} = \mathcal{U} - \mathcal{S}$

is

$$\begin{aligned}\mathcal{F} &= \frac{1}{N} \left( - \sum_{i=1}^r n_i \ln \left( \frac{n_i^{eq}}{N} \right) + \sum_{i=1}^r n_i \ln \left( \frac{n_i}{N} \right) \right) \\ &= \frac{1}{N} \sum_{i=1}^r n_i \ln \left( \frac{n_i}{n_i^{eq}} \right)\end{aligned}\quad (27)$$

$\mathcal{F}$  will prove particularly interesting upon derivation.

### 6.2.1 Introducing time

To concretize the notion of system evolution and of interchangeability between single particle states, one should introduce a temporal ingredient, in the form of rate constants  $k$  examined previously of unit  $\text{time}^{-1}$ . As these rates depend on the temperature, the system will be considered closed but not isolated and embedded in a thermal bath (NVT ensemble). As the different states can be interchanged two by two, a simple two-state system can be used to derive the proportions of particles in states  $A$  and  $B$  (or for a single particle, the probability to be at a given moment in state  $A$  or  $B$ ). Let us first derive  $\mathcal{S}$ .

$$\begin{aligned}\frac{d\mathcal{S}}{dt} &= - (P_A \ln P_A + P_B \ln P_B)' \\ &= (P_A k_{AB} - P_B k_{BA})(1 + \ln P_A) \\ &\quad + (P_B k_{BA} - P_A k_{AB})(1 + \ln P_B) \\ &= (P_A k_{AB} - P_B k_{BA}) \ln \left( \frac{P_A}{P_B} \right)\end{aligned}\quad (28a)$$

which can be generalized to the  $r$  nodes

$$\mathcal{S}' = \frac{1}{N} \sum_{i,j} (n_i k_{ij} - n_j k_{ji}) \ln \left( \frac{n_i}{n_j} \right)\quad (28b)$$

Eq.(28) is not particularly illuminating because it can be either positive or negative.  $\mathcal{S}$  decreases when  $n_i/n_j > k_{ji}/k_{ij}$  and increases when  $n_i/n_j < k_{ji}/k_{ij}$ . But things become more interesting when deriving  $\mathcal{F}$ . Taking  $n^{eq}$  as constants,

$$\frac{d\mathcal{F}}{dt} = \frac{1}{N} \sum_{i,j} (n_i k_{ij} - n_j k_{ji}) \ln \left( \frac{n_i k_{ij}}{n_j k_{ji}} \right)\quad (29a)$$

or, written in term of flux ( $J = nk$ ),

$$\frac{d\mathcal{F}}{dt} = \frac{1}{N} \sum_{i,j} (J_{ij} - J_{ji}) \ln \left( \frac{J_{ij}}{J_{ji}} \right)\quad (29b)$$

Contrary to Eq.(28), Eq.(29) can be only zero or negative. For this reason, it remarkably illustrates the free

energy dissipation and can naturally be identified with the arrow of time [21, 22, 23]. The discrete statistical functions described above can be reconnected to traditional thermodynamics by identifying  $k_B T \mathcal{F}$  with the Gibbs free energy of the system,  $k_B T U$  with the internal energy and  $k_B \mathcal{S}$  with the entropy. An increase of entropy (towards equipartition) logically decreases free energy and the possibility to extract some work. Further extensions of this discrete approach to thermodynamics are described in [24, 25]. Now let us look at Eq.(29a) which has the particularity to bring together the two different aspects of time.

### 6.2.2 Time's arrow and time steps

The arrow of time envisioned as the dissipation of free energy described in Eq.(29) has a clear thermodynamic origin out of equilibrium, but even in full equilibrium conditions, the rates constants keep their time units and the particles continue to move as long as temperature is nonzero. This sort of time, completely reversible contrary to the time's arrow, corresponds to the elementary time steps related to another field of physics: quantum physics. Statistical and quantum physics are intimately and necessarily related because enumerating configurations would be infinite in continuous space and time. Accordingly, the quantum of time can be defined as the time necessary to cross the length unit below which successive configurations cannot be distinguished, because of the uncertainty principle. This value can be obtained in multiple ways including in the context of the Maxwell-Boltzmann system. For a single particle, the length unit is the thermal wavelength of de Broglie  $\lambda = h/p = h/\sqrt{2\pi m k_B T}$  and the mean velocity is  $\langle v \rangle = \sqrt{8k_B T/\pi m}$  [26]. The ratio gives the minimal time step

$$\tau = \frac{\lambda}{\langle v \rangle} = \frac{h}{4k_B T} \approx 4 \times 10^{-14} \text{ s at } T = 300 \text{ K}\quad (30)$$

that is close to the reciprocal of the vibrational frequency  $k_B T/h$  considered by Eyring as the most remarkable achievement of his theory [27], and which was already present in the equation of Herzfeld [28]. The temporal unit of the rate constants is  $\tau^{-1}$ , weighted by unitless quantitative terms including the probability of sufficient energy.

The arrow of time is a source of endless debates, particularly interesting when applied to the universe taken as a whole. The free energy of a closed system should necessarily diminish within the limits of residual fluctuations. Then, whence comes the initial free energy of our universe which does not seem very organized in its youth? Did previously latent forces release free energy during the physico-chemical maturation of the universe? or do we live in a local fluctuation in a giant universe in

equilibrium, according to an elegant but contested proposal by Boltzmann [29]. These exciting questions are beyond the scope of this study.

### 6.3 Introducing discrete energy

In addition to their temporal parameter, the rate constants include a hidden energy parameter, that can also be envisioned discretely. Instead of distributing particles into "energy levels", energy units are distributed over particles. Perhaps influenced by what Boltzmann said him in 1891: "I see no reason why energy shouldn't also be regarded as divided atomically", Planck proposed in the founder article which opened the way to quantum physics [19], to discretize energy into quanta of value  $h\nu$ , written more generally  $q$  below.

#### 6.3.1 Homogeneous system

The mean energy of thermal systems can be recovered in a discrete manner from the second law. Returning to the white balls supposed to correspond to energy quanta in Section.4, the number of ways to distribute  $E$  objects in  $N$  boxes is

$$\Omega = \frac{(N + E - 1)!}{(N - 1)! E!} \quad (31)$$

which gives, using the Stirling approximation, a single particle average entropy of

$$\mathcal{S} = \frac{1}{N} \ln \Omega = \left(1 + \frac{E}{N}\right) \ln \left(1 + \frac{E}{N}\right) - \frac{E}{N} \ln \left(\frac{E}{N}\right) \quad (32a)$$

When the system contains a single category of particles, the ratio  $E/N$  is equivalent to the mean number of energy quanta per particle  $U/q$  [19].

$$\mathcal{S} = \frac{S}{k_B} = \left(1 + \frac{U}{q}\right) \ln \left(1 + \frac{U}{q}\right) - \frac{U}{q} \ln \left(\frac{U}{q}\right) \quad (32b)$$

Temperature can now be introduced using the fundamental entropy equation.

$$\frac{dS}{dU} = \frac{1}{T} \quad (33)$$

according to which integration of Eq.(32b) yields

$$\frac{k_B}{q} \ln \left(1 + \frac{q}{U}\right) = \frac{1}{T} \quad (34a)$$

and

$$\langle \mathcal{E} \rangle = \frac{U}{q} = \langle \mathcal{E} \rangle = \frac{1}{e^{q/k_B T} - 1} \quad (34b)$$

The reasoning can be circular in statistical thermodynamics and these results can also be recovered in a reverse way starting from the partition function, as did Einstein [30]. The ratio of Planck ( $q = h\nu$ ) over Boltzmann entities, turns to be the logarithm of the inverse proportion of energy quanta in the mixture.

$$\frac{h\nu}{k_B T} = -\ln \frac{E}{N + E} = \ln \left(1 + \frac{1}{\langle \mathcal{E} \rangle}\right) \quad (35)$$

At the thermal scale,  $q$  is negligible compared to  $k_B T$  and the expansion of Eq.(34b) gives a mean number (unitless) of energy quanta

$$\langle \mathcal{E} \rangle \sim \frac{k_B T}{q} \quad (36a)$$

and a mean energy (joules) per particle of

$$\langle \mathcal{E} \rangle q = U \sim k_B T \quad (36b)$$

#### 6.3.2 Heterogeneous system

When the system is composite and made of  $r$  different categories of particles which have different mean energies  $\langle \mathcal{E}_i \rangle$ , we have to fill  $r$  boxes with  $N = \sum_i n_i$  particles and  $E = \sum_i n_i \langle \mathcal{E}_i \rangle$  energy quanta

$$\Omega = \prod_{i=1}^r \frac{(n_i + E_i - 1)!}{(n_i - 1)! E_i!} \quad (37)$$

giving, for large populations and using the Stirling approximation, an entropy of

$$\ln \Omega = \sum_{i=1}^r n_i \left[ \left(1 + \frac{E_i}{n_i}\right) \ln \left(1 + \frac{E_i}{n_i}\right) - \frac{E_i}{n_i} \ln \left(\frac{E_i}{n_i}\right) \right] \quad (38)$$

Keeping  $N$  and  $E$  constant, this entropy is lower than that of an homogeneous system, showing that the categorization of objects is a first step towards organization. As the derivative of a sum is the sum of the derivatives,

$$\langle \mathcal{E}_i \rangle = \frac{E_i}{n_i} = \frac{1}{e^{q_i/k_B T} - 1} \quad (39)$$

#### First-order particle interconversion

To render this heterogeneous system dynamic, one should introduce the possibility of interconversion between the particles of the different kinds in the form of rate constants. The rule for particle interconversion has been established in Eq.(7) using the exponential law. For unimolecular transconversions which do not modify the total number of particles, let us abandon the ratios of pre-exponential factors. The single particle energy averaged

over the  $r(r-1)/2$  couples of categories in the system is

$$\langle \mathcal{E}_m \rangle = \frac{E}{N} = \frac{\sum_i \sum_{j \neq i} \langle \mathcal{E}_i \rangle e^{-\frac{\mathcal{E}_{i,j}^\ddagger}{\langle \mathcal{E}_i \rangle}}}{\sum_i \sum_{j \neq i} e^{-\frac{\mathcal{E}_{i,j}^\ddagger}{\langle \mathcal{E}_i \rangle}}} \quad (40)$$

in which the inexistent interchanges are characterized by  $\mathcal{E}_{i,j}^\ddagger = \infty$ . One can define the enthalpic transition rate constants introduced in the flux system

$$k_{ij} = \tau^{-1} e^{-\mathcal{E}_{i,j}^\ddagger / \langle \mathcal{E}_i \rangle} \quad (41a)$$

$$k_{ji} = \tau^{-1} e^{-\mathcal{E}_{i,j}^\ddagger / \langle \mathcal{E}_j \rangle} \quad (41b)$$

where  $\tau$  is the time step and  $\langle \mathcal{E}_i \rangle$  is the mean energy of the particles of type  $i$ , both depending on temperature through Eq.(30) and Eq.(39) respectively. The dissipation/time's arrow now depends on the relative values between populations and energies according to

$$\frac{d\mathcal{F}}{dt} = \frac{1}{N\tau} \sum_{i,j} \left[ n_i e^{-\frac{\mathcal{E}_{i,j}^\ddagger}{\langle \mathcal{E}_i \rangle}} - n_j e^{-\frac{\mathcal{E}_{i,j}^\ddagger}{\langle \mathcal{E}_j \rangle}} \right] \left[ \ln \left( \frac{n_i}{n_j} \right) - \mathcal{E}_{i,j}^\ddagger \left( \frac{1}{\langle \mathcal{E}_i \rangle} - \frac{1}{\langle \mathcal{E}_j \rangle} \right) \right] \quad (42)$$

For two categories  $n_1$  and  $n_2$ , the relationships linking energy and particle numbers are

$$\frac{n_1}{N} = \left( 1 + e^{\mathcal{E}_{1,2}^\ddagger \left( \frac{1}{\langle \mathcal{E}_1 \rangle} - \frac{1}{\langle \mathcal{E}_2 \rangle} \right)} \right)^{-1} \quad (43a)$$

$$\frac{n_2}{N} = \left( 1 + e^{\mathcal{E}_{1,2}^\ddagger \left( \frac{1}{\langle \mathcal{E}_2 \rangle} - \frac{1}{\langle \mathcal{E}_1 \rangle} \right)} \right)^{-1} \quad (43b)$$

$$\frac{E_1}{E_2} = \frac{\langle \mathcal{E}_1 \rangle}{\langle \mathcal{E}_2 \rangle} e^{\mathcal{E}_{1,2}^\ddagger \left( \frac{1}{\langle \mathcal{E}_1 \rangle} - \frac{1}{\langle \mathcal{E}_2 \rangle} \right)} \quad (43c)$$

and the mean particle energy in the system is

$$\langle \mathcal{E}_m \rangle = \frac{\langle \mathcal{E}_1 \rangle e^{-\frac{\mathcal{E}_{1,2}^\ddagger}{\langle \mathcal{E}_1 \rangle}} + \langle \mathcal{E}_2 \rangle e^{-\frac{\mathcal{E}_{1,2}^\ddagger}{\langle \mathcal{E}_2 \rangle}}}{e^{-\frac{\mathcal{E}_{1,2}^\ddagger}{\langle \mathcal{E}_1 \rangle}} + e^{-\frac{\mathcal{E}_{1,2}^\ddagger}{\langle \mathcal{E}_2 \rangle}}} \quad (43d)$$

### Circular equilibria

Only three categories of particles are sufficient to establish the famous detailed balance relationship of Wegscheider linking the constants of a cycle [31]. The relation

$$\frac{n_1 n_2 n_3}{n_2 n_3 n_1} = 1 \quad (44a)$$

is obviously always true, in particular at equilibrium, so the constants are necessarily related through

$$\frac{k_{12} k_{23} k_{31}}{k_{21} k_{32} k_{13}} = 1 \quad (44b)$$

The activation energies, which were completely arbitrary in previous theories, are now mutually connected through

$$\frac{\mathcal{E}_{1,3}^\ddagger - \mathcal{E}_{1,2}^\ddagger}{\langle \mathcal{E}_1 \rangle} + \frac{\mathcal{E}_{1,2}^\ddagger - \mathcal{E}_{2,3}^\ddagger}{\langle \mathcal{E}_2 \rangle} + \frac{\mathcal{E}_{2,3}^\ddagger - \mathcal{E}_{1,3}^\ddagger}{\langle \mathcal{E}_3 \rangle} = 0 \quad (45)$$

Circular equilibria are particularly relevant with respect to catalysts. Contrary to the widespread representation of catalysis as a deformation of the energy landscape along the coordinates of a single transition, it should rather be envisioned as a circuit, at least triangular and letting unchanged the uncatalysed single step reaction.

### 6.3.3 Possible source of confusion for modeling the relationships between fractional populations and energy

The enthalpic particles of the toy systems described above are sufficient to visualize the important differences of representation of the degree of formulation of particles, depending on whether they belong to the same category or not. For a single type of particle  $n_1$  of mean energy  $\langle \mathcal{E}_1 \rangle$ , the concentration ratio of particles with energies  $\mathcal{E}_a$  and  $\mathcal{E}_b$  follows the familiar ratio

$$n_1(a)/n_1(b) = e^{\frac{\mathcal{E}_a - \mathcal{E}_b}{\langle \mathcal{E}_1 \rangle}} \quad (46)$$

whereas interchangeable particles of different categories with different mean energies  $\langle \mathcal{E}_1 \rangle$  and  $\langle \mathcal{E}_2 \rangle$ , are related through

$$n_1/n_2 = e^{\mathcal{E}_{1,2}^\ddagger \left( \frac{1}{\langle \mathcal{E}_1 \rangle} - \frac{1}{\langle \mathcal{E}_2 \rangle} \right)} \quad (47)$$

Eq.(46) is valid only for a single phase in the pioneer kinetic theory, because  $\langle \mathcal{E} \rangle = k_B T$  is not generalizable to any system. The next (hard) task will be to implement these rules defined for first order networks to second order and entropic open systems in steady state, like biochemical systems, for modeling the fundamental ingredients of life: nonlinearity, retroactions and multi-stability.

## 7 Conclusions

The present probabilistic treatment based on the exponential distribution does not invalidate the Maxwell-Boltzmann distribution, but encompasses it as a particular case of homogeneous system with temperature-dependent particle energies. Hence, there is no reason to not extend this approach to the energy-dependence of transitions, because rates constants are integral constituents of dynamic systems. The central and original assumption of statistical physics was the modeling of randomness, but randomness is precisely described in the most fundamental way by the exponential law. In fact, the equations of Arrhenius and Boltzmann are two facets of the same law of randomness, unified in the present theory. This is perfectly illustrated by Eqs.(9) and (10) respectively: the first one is the probability that  $\mathcal{E} > \mathcal{E}^\ddagger$  and the second one that  $\mathcal{E} = \mathcal{E}^\ddagger$ .

The relationships established here are simply derived from the single postulate that the exponential term of rate constants has the status of a probability, in line with the profoundly probabilistic spirit of Boltzmann's theory and with the intuition of Maxwell: "The true logic of this world is in the calculus of probabilities". In this respect, the rate constants defined here are entirely probabilistic

$$k = \tau^{-1} \times P(\text{configuration is OK}) \times P(\text{energy is OK})$$

which simply says that the frequency of a transformation follows the probability of favorable conjunctions of configurational and energetic conditions, which is

$$k = \tau^{-1} \times \frac{1}{\Omega} \times e^{-\mathcal{E}^\ddagger/\langle \mathcal{E} \rangle}$$

leading to the equilibrium relationship

$$\ln K_{ji} = \mathcal{S}_{ij} - \mathcal{S}_{ji} + \mathcal{E}_{i,j}^\ddagger \left( \frac{1}{\langle \mathcal{E}_i \rangle} - \frac{1}{\langle \mathcal{E}_j \rangle} \right)$$

where the temperature-dependence is mediated by the variables. The mean reactional energy  $\langle \mathcal{E} \rangle$  can logically be identified with enthalpy. If the starting probabilistic postulate is wrong, the present study would remain a theoretical exercise, but its validity seems however supported by (i) the mathematical rational of the exponential distribution, (ii) its capacity to recover the Boltzmann distribution and to unify kinetics and thermodynamics and (iii) the restoration of the link between the reactional propensity and the heat capacity, which was ignored in the interpretation of the slope of van't Hoff plots as  $\Delta H/k_b$ . In the current formulas, the enthalpies are not responsible for the dependence on temperature that is due only to the division of enthalpies by  $k_B T$ . By contrast, it is proposed here that enthalpies mediate the dependence on temperature. Strangely, the same view is assumed in courses of kinetics, in which the dependence on temperature is explained using populational

energy distributions without realizing that this explanation contradicts the general formula where the enthalpies are at the numerator of the exponent. But although profoundly restructured, the thermodynamic relationships derived from this approach yield resembling behaviours, so that the comparison between the previous and new treatments is more a question of interpretation of the experimental plots than a true discrimination. In the field of rate theories, Laidler already noticed that, surprisingly, the widely different rate equations proposed in the past can give reasonably good fit to the same experimental data [2]. The litterature also shows that the same deviations can be interpreted by different authors in the frame of different theories. In the alternative view examined here, the entropies of the reactants are completely identical to the previous ones; the calorimetric enthalpies and the Hess's law are unchanged; the equilibrium constants remain defined by the ratios of interconvertible reactants concentrations in equilibrium, and the dominant term of the temperature-dependence of equilibrium constants still satisfies the van't Hoff formula. Note in this respect that the original formula of van't Hoff was not the equation currently attributed to van't Hoff in textbooks, since van't Hoff did not use the Boltzmann's constant or the ideal gas constant, and his reasoning was fundamentally calorimetric [32], in line with the changes of heat capacity on which the present theory is based. In addition, van't Hoff indicated that he managed his equation for numerical applications and experimental controls only, but did not enter into the details of thermodynamics necessary for its demonstration [32]. The 19th century formula of Arrhenius also remains an equation of practical convenience, even if experimental data show that it is not valid for most reactions. Precise experimental validations in this field are hindered by numerous problems, including the dependence of enthalpies on temperature, the complex temperature-dependence of heat capacities, the interferences with tunnel effects, the narrow range of temperature testable in practice for macromolecules and the lack of knowledge of many parameters. For instance the present approach makes use of absolute enthalpies which are refractory to experimental measurements contrary to differences of enthalpy calculable by calorimetry. Experimental and calculated values are rarely in good agreement [14] and strikingly, calorimetric and van't Hoff enthalpies never coincide [12, 13], which is not a surprise considering that the enthalpy change for a reaction is commonly known as heat of reaction, whereas the heat capacity of enthalpies is ignored in the current van't Hoff plot approach. Moreover, even a faint difference of heat capacity, and a barely detectable change of this difference upon temperature increase, have exponential consequences on rate constants and equilibrium constants respectively. The elucidation of the nature of rate constants is essential considering their widespread use from chemistry to systems modeling. Rate constants are the

motors of systems and as such allow to introduce the notion of time. If time proves so difficult to conceive, it is probably because it relies on two completely different pedestals belonging to different branches of physics: (i) the step of time, always at work, both out of and in equilibrium and originating from quantum physics and (ii) time arrow, existing only out of equilibrium and which is a populational phenomenon emerging from statistical physics [29]. Dynamic systems clarify this perception because they combine both aspects: the time step included in the preexponential component of the Arrhenius equation, and the time arrow describing the spontaneous evolution of a system of interconvertible particle states.

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