



A probabilistic rate theory connecting kinetics to thermodynamics

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HIGHLIGHTS

- A probabilistic rate theory is proposed.
- The Boltzmann partition function is simply recovered from the exponential distribution.
- The increase in reaction rates by a rise in temperature is mediated by the increase of reactional enthalpies.
- Activation energies are proposed to contribute to equilibrium landscapes.
- A new detailed balance relationship includes activation energies.

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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 is the identification of the pre-exponential term of the Arrhenius equation as an entropic quantity. A 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 Arrhenius rate constants as the probability that the energy of the reactant is sufficient for the transition. This radically new approach encompasses Maxwell–Boltzmann distributions and solves inconsistencies in previous theories, in particular on the role of temperature in kinetics and thermodynamics. 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.

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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 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. 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

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

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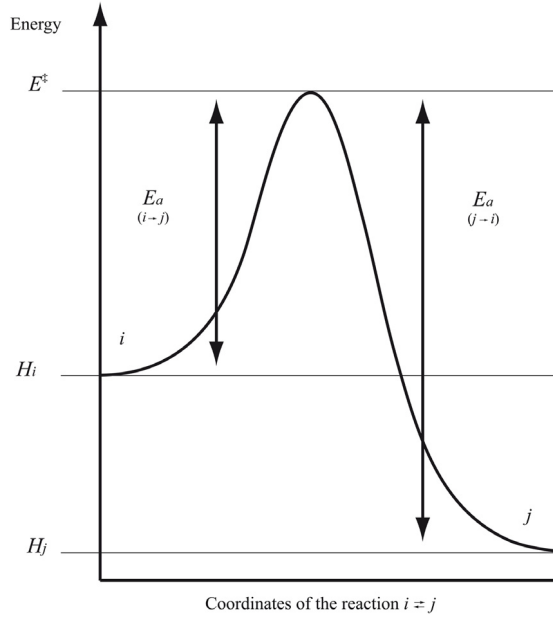


Fig. 1. Representation of the energy barrier according to the Arrhenius principle. The barrier is supposed to restrict reaction kinetics but to have no influence on equilibrium ratios. E^\ddagger is a fixed energy threshold necessary for crossing the barrier in both directions and H are the mean enthalpies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

where k_B is the Boltzmann constant and T is the temperature, includes (i) a so-called preexponential factor A , containing the elementary frequency and configurational restrictions, and (ii) a unitless exponential function containing an energy barrier called activation energy E_a . In the present paper, the exponential factor of Arrhenius will be reformulated as the probability to reach a threshold energy, as initially proposed but incompletely appraised in [3]. This simple hypothesis will lead to major changes in thermodynamic relationships. 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

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

In equilibrium the forward and reverse fluxes equalize such that

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

giving

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

E^\ddagger disappears. The equilibrium ratio is independent of the energetic barrier and depends only on the difference of energy between the reactants. These currently admitted relationships can be naively questioned.

2. Some 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 β corresponding to a Lagrangian multiplier or a distribution parameter, and finally connected to temperature by analogy with classical thermodynamics. This introduction of $k_B T$ is elegant and perfectly rational in this context but could be too restrictive for an extension to more complex systems. $k_B T$ is concretely useful here 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.

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