

A Simple Model to Access Equilibrium Constants of Reactions Type $A \rightleftharpoons B$ Using Monte Carlo Simulation.

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Resumo

Um modelo teórico computacional para descrever propriedades de equilíbrio de reações químicas homogêneas e reversíveis é proposto e aplicado a uma reação do tipo $A \rightleftharpoons B$. Com esta finalidade, as propriedades de equilíbrio são analisadas via simulações de Monte Carlo. Os resultados das simulações mostram que a constante de equilíbrio (K_e) para este tipo de reação exibe distintas características para $E_{ba} < 1$, $E_{ba} = 1$ e $E_{ba} > 1$, onde E_{ba} é a razão entre as energias de ativação reversa e direta. Para $E_{ba} < 1$ ($E_{ba} > 1$) e aumentando (diminuindo) a temperatura nossos resultados recuperam o princípio de Le Châtelier aplicado ao efeito de temperatura. O caso especial e interessante é obtido para $E_{ba} = 1$ desde que $K_e = 1$ para todos os valores de temperatura. Outro importante parâmetro em nossa análise é θ_A , definida como a temperatura medida com relação a energia de ativação da reação direta. Para valores fixos de E_{ba} e para $\theta_A \gg 1$ a constante de equilíbrio tende a 1, mostrando que todas as transições são igualmente prováveis, não importando a diferença de energia entre as barreiras. Os dados obtidos em nossas simulações mostram a bem conhecida relação entre K_e , E_b , E_a and $k_B T$. Por fim, argumentamos que este modelo teórico pode ser aplicado a uma família de reações químicas homogêneas caracterizadas pelo mesmo E_{ba} e θ_A , mostrando a ampla aplicação deste modelo estocástico para o estudo de reações químicas. Alguns deste resultados serão discutidos em termos de teoria das colisões.

Palavras-chave Monte Carlo, Reações Químicas, Equilíbrio, Metropolis.

Abstract

A simple theoretical model to describe equilibrium properties of homogeneous reversible chemical reactions is proposed and applied to an $A \rightleftharpoons B$ type reaction. For this purpose the equilibrium properties are analyzed by usual Monte Carlo simulation. It is shown that the equilibrium constant (K_e) for this kind of reaction exhibits distinct characteristics for $E_{ba} < 1$, $E_{ba} = 1$ and $E_{ba} > 1$, where E_{ba} is the ratio between the reverse and forward activation energies. For $E_{ba} < 1$ ($E_{ba} > 1$) and increase (decrease) the temperature our results recover the principle of Le Châtelier applied to temperature effects. The special and interesting case is obtained for $E_{ba} = 1$ since $K_e = 1$ for all range of temperature. Another important parameter in our analysis is θ_A , defined as temperature measured with relation the activation energy of the forward reaction. For fixed values of E_{ba} and for $\theta_A \gg 1$ the equilibrium constant approaches 1, showing that all transitions are equally likely, no matter the difference in the energy barriers. The data obtained in our simulations show the well known relationship between K_e , E_b , E_a and $k_B T$. Finally we argue that this theoretical model can be applied to a family of homogeneous chemical reactions characterized by the same E_{ba} and θ_A showing the broad application of this stochastic model to study chemical reactions. Some of these results will be discussed in terms of collision theory.

Keywords Monte Carlo, Chemical Reaction, Equilibrium, Metropolis.

1 Introduction

With the advent of rapid computers the computational simulation became an important tool in modern physics, arising like a third branch complementary to the traditional experimental and theoretical approaches [1]. In particular, the Monte Carlo Methods (MCM) has been used for solving various kinds of computational problems by using random number [2]. It has been successfully applied in Physics and Chemistry in the study of, for instance, heterogeneous and homogeneous chemical reactions [4]-[7], equilibrium properties of composite particles [3] and of magnetic systems [8]. In particular, this stochastic approach has brought several new ideas and remarks to the field of chemical reactions. With this aim, we introduce a simple mathematical approach, based in the Monte Carlo Method, to study homogeneous reversible chemical reactions. Our simulations are performed using the Metropolis update [1] where we include the temperature as an important parameter. Hereby we study a simple chemical reaction $A \rightleftharpoons B$. A diagram of energy transitions in this kind of chemical reaction is shown in figure (1). In this figure, E_a and E_b represent the activation energies of the forward and reverse reactions while A and B are the reactant and product molecules, respectively. So, in order for each type of molecule to react, each one must possess sufficient kinetic energy to overcome the energy barrier [9, 10]. A given molecule that does not have this kinetic energy amount can gain it by colliding with other molecules. In this scenario, it is analyzed the equilibrium properties of this chemical system when we increase the height of the reverse energy barrier (activation energy) with respect to forward one, i.e. when E_b/E_a increases. In addition, we are interested in verifying some fundamental concepts of this kind of homogeneous reaction by considering some different values for the average thermal energy per particle, i.e. different temperatures, measured with respect to the energy barrier for the forward reaction, i.e. different values of $k_B T/E_a$. It is argued that all results reported herein are in agreement with collision theory [9].

2 Mathematical Model

In the present work we use the standard Monte Carlo Methods (MMC) [1] with the dynamics defined via Metropolis update whose transition probability functions depend as much on the energy barrier as on the temperature [4]. In the present case the energy barrier is the activation energy. So, we define the transition probability, for forward reaction, P_f , and for reverse reaction, P_r , as follows

$$P_f = \exp(-\beta E_a) \quad (1)$$

$$P_r = \exp(-\beta E_b) \quad (2)$$

where $\beta = (k_B T)^{-1}$, k_B the Boltzmann constant, T the temperature, E_a and E_b the activation energies of the forward and reverse reactions, respectively.

For the sake of simplicity we define dimensionless temperature-related variable $\theta_A \equiv \frac{k_B T}{E_a}$

and dimensionless energy-related variable $E_{ba} \equiv \frac{E_b}{E_a}$. So, our analyses will be based in terms of the thermal energy, say $k_B T$, and in the activation energy of reverse reaction, E_b , both measured with respect to the activation energy of forward reaction, E_a .

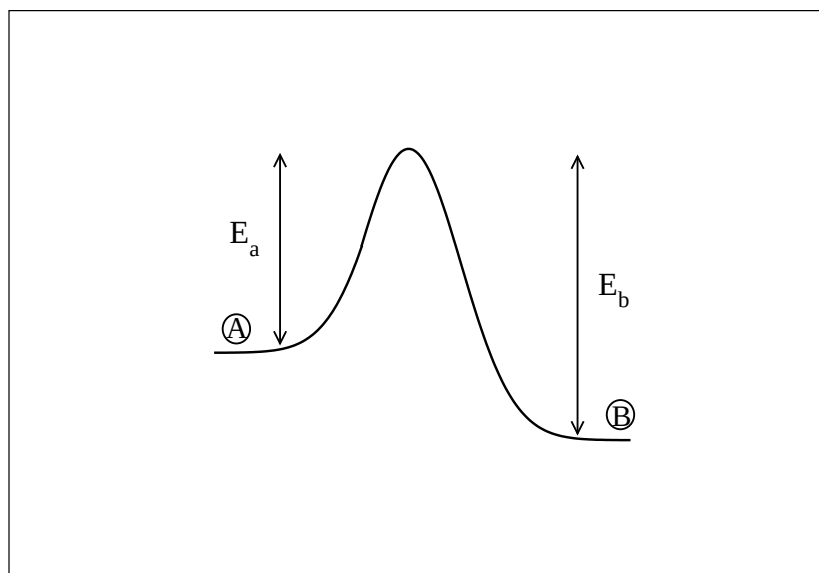


Figura 1: Illustrative diagram of energy transitions in a chemical reaction $A \rightleftharpoons B$. The activation energies for forward and reverse reaction are E_a and E_b , respectively. The symbols A and B represent the reactants and products molecules, respectively. The chemical reaction for any molecule occurs if the kinetic energy suffices for overcoming the energy barrier. In this picture we have considered the case $E_b > E_a$.

Before to perform the dynamics we index all molecules [4, 7]. After that, we carry out the following steps:

(i) we try to select an A type molecule. If the choice fails, we go to the step (ii). If not, a uniform random number $z \in [0, 1]$ is generated and compared with P_f Eq.(1); if $z \leq P_f$ the reaction occurs and A becomes B ; if not, the A molecule remains in this original form;

(ii) we try to select a B type molecule. If the trial fails the step ends. If not, a uniform random number $z \in [0, 1]$ is generated and compared with P_r Eq.(2); if $z \leq P_r$ the reaction occurs and B turns into A ; if not, the B molecule remains in this original form.

Running the steps (i) and (ii) N (number of molecules) times, we define the Monte Carlo Step (MCS) in our simulations. In all the simulations presented here, all samples have the same initial condition which is the system consisting only of molecules of the type A , i.e. the concentration of the reactant $[A] = 1$, and trivially, $[B] = 0$. Hereby we define $[A] = \frac{N_A}{N}$ and

$[B] = \frac{N_B}{N}$ where N_A is the number of molecule of the type A , N_B is the number of molecule of the type B and N the number of molecules, $N_A + N_B$. For the results shown here, we used $N = 10^4$. In order to calculate the equilibrium constant $K_e = \frac{[B]}{[A]}$, we execute 1×10^4 MCS

to reach the initial configuration for each E_{ba} . From this configuration, we carry out 1×10^2 MCS for equilibration and 1×10^4 MC steps to get thermal averages. After the average is made for one E_{ba} we use the last configuration as an initial one of the next sample. In addition, we perform an average over 10^2 different samples. Other values for these parameters do not change

quantitative and qualitatively our results.

3 Results and Discussions

In figure (2) we present the equilibrium constant K_e , in logarithmic scale, as a function of E_{ba} for three different values of θ_A . The inset shows an amplification for $E_{ba} \leq 1$. The arrows point to the horizontal dotted line ($K_e = 1$) showing the behavior of the system for high values of θ_A . First of all, our simulations were carried out up to a maximum $E_{ba} = 8$. In figure (1) we observe that for a fixed value of θ_A the equilibrium constant K_e increases with respect to E_{ba} . This behavior reflects the fact that increasing of the activation energy E_b with E_a fixed, the reverse reaction occurs with minor chance. Indeed, in terms of collision theory [9], for a fixed value of the temperature, the mean kinetic energy per molecule, E_k , which is proportional to thermal energy, $k_B T$, i.e. $E_k \sim k_B T$, is constant. So, the increase of the energy barrier E_b turns the E_k less effective for reverse reaction to occur.

Another interesting result that we observe in figure (1) is that for $E_{ba} > 1$, i.e. $E_b > E_a$, $K_e > 1$, so the reaction is product favored for all values of the temperature. The set of values of E_{ba} that produces a reactant favored reaction, for all values of the temperature is $0 < E_{ba} < 1$, since $K_e < 1$. This fact can be seen in the inset of the figure (1).

Again, this result can be understood via collision theory. For a given temperature, the forward (reverse) reaction takes place with a major chance if the forward (reverse) energy barrier is lower, because any A (B) type molecule has a kinetic energy sufficient to overcome that energy barrier more easily.

The results reported in figure (2) are very well fitted by

$$K_e \sim \exp(-1/\theta_A) \exp(E_{ba}/\theta_A) = \exp((E_b - E_a)/k_B T) \quad (3)$$

recovering the dependence of the equilibrium constant with respect to E_b , E_a and $k_B T$ [10].

From now on, we accomplish our analyses for fixed E_{ba} values and one observe the behavior of the equilibrium constant as a function of θ_A . For $E_{ba} < 1$, we can see in the inset of the figure (1) that increasing θ_A the equilibrium constant increases, exhibiting a widely known Le Châtelier's principle [11], where the increase of the temperature will favor the forward reaction (the direction where the reaction is endothermic). An analogous scenario could be seen for $E_{ba} < 1$ where the reduction of the temperature disfavors the reaction to the exothermic direction.

A newsworthy characteristic arise for $E_{ba} = 1$. As presented in figure (1) this is a special case where the equilibrium constant does not depend on the temperature. It is an important characteristic of this kind of reaction which is not treated clearly in text books, as far as we know. Once again, we analyze this result in terms of collision theory. Since the energy barriers are the same, both A and B molecules with a given kinetic energy $\sim k_B T$ will jump those barriers with the same chance, implying that at equilibrium the system presents equal amount of reactants and products, which shows $K_e = 1$ in terms of concentration.

With this last analysis in terms of collision theory, we can understand the behavior of the equilibrium constant for high values of temperature. As depicted in figure (1) K_e approaches 1 for high values of θ_A , for all the range of E_{ba} analyzed. For very high values of temperature, or thermal energy $k_B T \gg 1$, the forward and reverse barriers practically are often overcome by the highly energetic molecules A and B . So, as a consequence, the constant of equilibrium equals 1.

For completeness an emblematic picture is shown in figure (3), where it can be seen the complete behavior of the equilibrium constant given by Eq. (3), in logarithmic scale, as a function of the dimensionless temperature-related θ_A and the dimensionless energy-related E_{ba} in a perspective 3D plot. As stated earlier, we can see that for $E_{ba} < 1$ ($E_{ba} > 1$) and increasing (decreasing) θ_A the equilibrium constant increases and goes to 1. The curve, on this surface, $E_{ba} = 1$ determine all points with null concavity characterizing the independence of K_e with the temperature. Furthermore, we can observe all features analyzed previously.

Finally it is worth to stress that the results presented herein are not only for a specific homogeneous chemical reaction $A \rightleftharpoons B$, but for a family of chemical reactions $A_1 \rightleftharpoons B_1$,

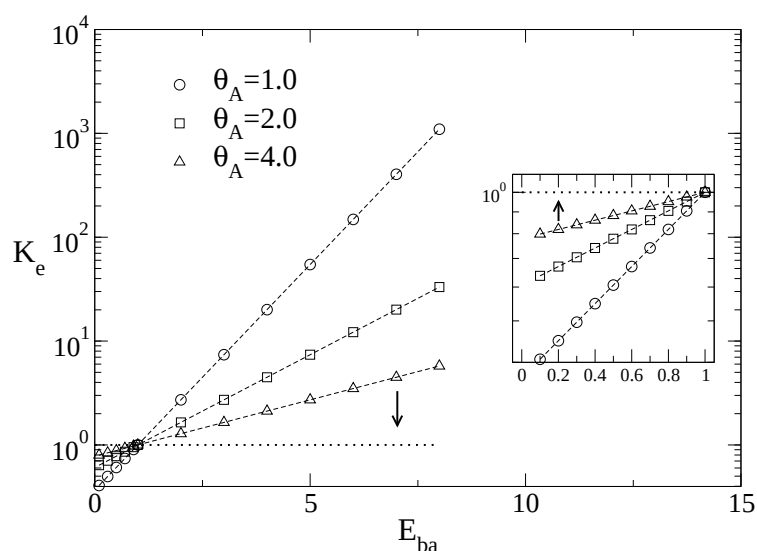


Figura 2: The equilibrium constant K_e , in logarithmic scale, as a function of E_{ba} for three different values of θ_A : $\theta_A = 1.0$ (empty circle), $\theta_A = 2.0$ (empty square) and $\theta_A = 4.0$ (empty triangle). The horizontal dotted line is $K_e = 1$. The inset shows an amplification for $E_{ba} < 1$. In this figure we observe different behavior of K_e for $E_{ba} < 1$, $E_{ba} > 1$ and for $E_{ba} = 1$, as a function of θ_A . The arrows indicate the behavior of K_e for high values of θ_A .

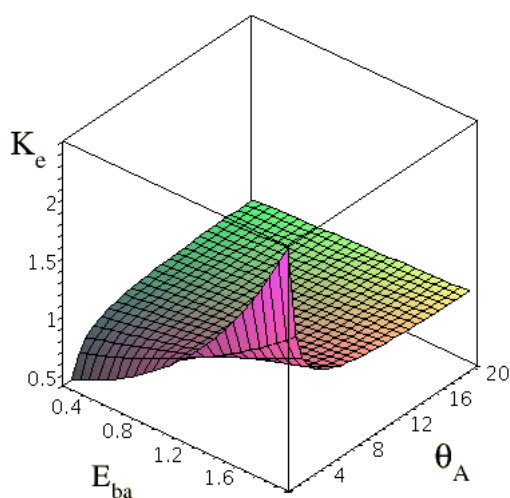


Figura 3: A emblematic figure showing the dependence of K_e with θ_A and with E_{ba} . This plot was done by plotting the Eq. (3) that is the fitting of the our simulated data.

$A_2 \rightleftharpoons B_2$, $A_3 \rightleftharpoons B_3$, and so on, characterized by the same ratio between the energy barrier of forward and reverse reactions, i.e. $E_{ba_1} = E_{ba_2} = E_{ba_3} = \dots$, and for the same temperature measured with respect to the energy barrier of forward reaction, i.e. $\theta_{A_1} = \theta_{A_2} = \theta_{A_3} = \dots$. So, in order to study these kinds of reactions no matter what are the values of the temperatures, and the values of the energy barriers separately, but the relationship among them. Again, we stress that the newsworthy result obtained for $E_{ba} = 1$ for which the equilibrium constant does not depend on the temperature. This result is not for a specific reaction, but for a family of chemical reactions whose the forward energy barrier is equal to the reverse one, at any temperature.

4 Conclusions and Prospects

An appropriate simple mathematical model has been used to investigate equilibrium features for a homogeneous reversible chemical reaction $A \rightleftharpoons B$. This mathematical model consider the standard Monte Carlo Methods whose dynamics is defined via Metropolis update. Defining a dimensionless energy-related $E_{ba} \equiv \frac{E_b}{E_a}$ where E_b and E_a are respectively the forward and reverse energy barriers of the chemical reaction, our simulations exhibit some features of the equilibrium constant for two distinct range for E_{ba} , $0 < E_{ba} < 1$ and $E_{ba} > 1$, and for a special point $E_{ba} = 1$. In these regions the equilibrium constant exhibits different behaviors, as a function of the dimensionless temperature-related $\theta_A \equiv \frac{k_B T}{E_a}$ where $k_B T$ is the thermal energy, in agreement with the Le Châtelier principle applied to temperature effects. A newsworthy result is observed for $E_{ba} = 1$ where the equilibrium constant of the reaction does not depend on the temperature. This feature is not clearly discussed in the text books. The results obtained by our simulations fit well to the widely known dependence of the equilibrium constant with E_b , E_a and $k_B T$. For fixed E_{ba} and θ_A above a certain value, our results indicate that the reaction behaves as if $E_b = E_a$ meaning that the high thermal energy in the system is sufficient to overpass the energy barriers of forward and reverse reactions with the same probability, even if actually those activation barriers are different.

Finally we point out that in order of study these kinds of reactions no matter what are the values of the temperatures, and the values of the energy barriers separately, but the relationship among them. So, all equilibrium features presented in our simulations are not only for a specific homogeneous chemical reaction, but for a family of chemical reaction, characterized by the same values of dimensionless energy-related E_{ba} and for the same dimensionless temperature-related θ_A . Thus, the present mathematical model can be used to help to understand a number of homogeneous chemical reactions, showing its broad application to study chemical reactions.

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