

Article

Fluctuation Theory in Chemical Kinetics

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Received: 12 November 2018; Accepted: 12 December 2018; Published: 17 December 2018

Abstract: In this research, we study the stability properties of chemical reactions of arbitrary orders. In a given chemical experiment, we focus on the formation of a chemical equilibrium by optimizing the reaction rate. Under infinitesimal simultaneous variations of the concentrations of reacting species, the binary component equilibrium is achieved when either one of the orders or concentrations of reactants vanishes. The chemical concentration capacities of the components are calculated to describe the local stability of the equilibrium. The correlation between the components is obtained as the mixed second-order derivative of the rate with respect to concentrations. The global stability analysis is performed by introducing a symmetric matrix with its diagonal components as the chemical capacities and off-diagonal components as the local correlation. We find that the local chemical stability requires the orders of the reactants to be either negative or larger than unity. The corresponding global stability requires the positivity of a cubic factor over the orders of the reactants. In short, our consideration illustrates how a chemical reaction takes place by attaining its activation state and asymptotically approaches the equilibrium when two components are mixed with arbitrary orders. Qualitative discussions are provided to support our analysis towards the formation of an optimized equilibrium. Finally, along with future directions, we discuss verification of our model towards the formation of carbon-based reactions, formation of organic/inorganic chemical equilibria and catalytic oxidation of $CO - H_2$ mixtures in presence of Pt.

Keywords: chemical stability; reaction rate; chemical equilibria; fluctuation theory; kinetic theory

1. Introduction

For several decades, the study of equilibrium in chemical reactions has provided a broad scope for research in the field of chemical physics by exploiting the concept of collision theory [1]. From this viewpoint of chemical kinetics, the equilibrium formation plays an important role in the occurrence of a chemical reaction. According to the concept of collision theory, various atoms, molecules, and ions collide with each other to create a pathway for the completion of the reaction. Thus, the temperature and concentration of reacting species arise as the governing parameters of the corresponding chemical rate. This follows from the notion of the collision energy and molecular structures [1,2]. It is worth mentioning that the rate constant of the reaction varies as an exponential function of the temperature [2]. In this concern, it is well understood that an increase in the temperature increases the rate of the reaction, therefore an enhanced formation of products.

Here, under varying concentrations and orders of reacting species, we focus on analytical solutions of the rate equation of a given chemical reaction. Namely, our investigation allows to access the nature of the chemical equilibrium as a function of input parameters. In the light of the collision theory, this is realized by the existing information that a chemical reaction takes place based on a transition state model [3]. Herewith, a product is formed via an intermediate state [4], when its corresponding energy

crosses the barrier potential, termed as the activation energy, also see [5] for the associated quantum mechanical effects. In the sequel, we illustrate functionalities of the chemical rate of an arbitrary single stage reaction by considering its occurrence at a definite temperature and composition of the reaction, viz. the concentration of constituents. Consequently, the forward and backward rates depend upon the concentration of the reactants and that of the products, respectively. In this context [6], as a function of the concentration of constituents, fluctuations in the chemical rate could explain the formation of an irreversible reaction, as well.

Considering the microscopic aspects, molecular structures of various reacting species contribute towards the happening of a chemical reaction [7,8]. Furthermore, the reaction rate varies with respect to the frequency factor of the products, as well. Notice that the rate is directly related to the structural complexities, viz. the collision frequency and orientation probability factor of the species [9]. Briefly, parameters governing the rate of a chemical reaction are summarized [10] as follows. Firstly, at a constant temperature, the rate generically decreases as a monotonic function with respect to its duration. Secondly, at a given temperature, for an irreversible reaction, the rate largely depends on the concentration of the participating species, see [11]. Thirdly, the rate constant depends on the temperature as per the Arrhenius's first law [6]. In a nutshell, at a constant temperature, the rate of an arbitrary reaction can be factored as a weighted product of the concentrations of the species. Therefore, for a given reversible reaction, the change of the concentration of the reactants per unit time (or that of the product) define its rate.

To examine fundamentals concerning chemical interactions, we require an understanding of the chemical affinity and reactivity of participating species, see [12] for experimental perspectives concerning aqueous solution and its implications. For example, the notion of a chemical bond arises from the concept of chemical affinity [13]. This occupies a key importance in chemistry to rationalize the notion of the reactivity and performance of compounds, in addition to their variations of physical states with respect to the temperature and pressure. We notice that the chemical affinity [12] can be viewed as an electronic property, whereby dissimilar species form new chemical compounds. In this concern, the reason follows from the physical properties of the atoms and molecules [7,8]. Specifically, for a given set of dissimilar reactants, we can describe the tendency of atoms or compounds to form a new state via the corresponding chemical reaction. In this scenario, it is worth stating that certain atoms or molecules possess the ability to aggregate each other to form a definite bonding.

Mostly statistical and thermodynamic factors are used to determine characteristics of a given chemical reaction [14,15]. Fundamentally, such notions emerge as factors affecting the rate of the chemical reaction, see [13] for an introduction towards a universal chemical attraction and combinations. Following the same, we can measure the chemical affinity of the reacting species via their chemical rates [4,13]. Various aspects towards the happening of a chemical reaction are governed via the formation of an equilibrium. As mentioned before, this concept well correlates with the rate of a chemical reaction and its reversibility. Furthermore, Ref. [16] provides theoretical and experimental accounts of chemical kinetics and chemical physics.

In the present study, we emphasize the chemical equilibrium formation by invoking the setup of the fluctuation theory [17–22]. This had various applications in examining the stability properties of condensed matter systems [17], black objects [18], equilibrium thermodynamics [19,20] and optical systems [22]. In this concern, one of the authors [21] has demonstrated the associated geometric perspectives of stability in the light of entropy functions. From this motivation, our primary objective is to examine the nature of the chemical equilibrium and system stabilities when the concentrations of one or more species are varied. Following the above viewpoints, we provide a detailed account of fluctuation theory relations to chemical kinetics towards an optimal happening of chemical reactions.

Following the above observations, we discuss fluctuations of the rate of an arbitrary reaction to offer guidelines towards the modeling of organic and inorganic chemical interactions [23]. Namely, we provide the fluctuation theory analysis of the equilibrium formation under variations of the concentrations $\{c_1, c_2\}$ of reactants $\{A, B\}$ with their partial orders $\{m, n\}$. As per the above analysis,

for any positive concentrations c_1 and c_2 of the reactants A and B , we find that the stability of an equilibrium solely depends on the partial orders m and n of the reactants. In this concern, we provide a comparative analysis of various organic and inorganic chemical equilibrium formations with respect to variations of the concentrations and orders of A and B .

Namely, for the zeroth-order reaction with its order $m + n = 0$, the stability of equilibrium depends on the product of m and n . Similarly, for the first-order reactions, i.e., when $m + n = 1$, we find that the fluctuation determinant vanishes identically. For a second- or higher-order reaction with $m + n \geq 2$, we notice that the sign of the fluctuation determinant varies as the negative of the product of the partial orders m and n of the reactants A and B respectively. Indeed, our analysis remains valid for fractional- and negative-order reactants and their equilibrium formation [24,25]. This is because our analysis is valid for any real valued concentrations c_1 and c_2 and any real values of the partial orders m and n of the reactants A and B forming the equilibrium. Our model is further supported by various inorganic and organic equilibrium formations as well as a catalytic oxidation of $CO - H_2$ mixtures in presence of Pt. This offers a clear-cut classification of the inorganic and organic chemical equilibria, happening of an arbitrary chemical reaction and the formation of new products.

The rest of the presentation is organized as follows. In Section 2, we provide a brief account of reaction mechanism and kinetic rate, viz. the notion of a chemical equilibrium and fluctuation theory. In Section 3, we compute the stability quantities concerning a chemical equilibrium under fluctuations of the reaction rate with respect to concentrations of the reactants. In Section 4, we offer qualitative discussions of the results and their interpretations towards the formation of a chemical equilibrium. In Section 5, we discuss verification of our model towards the formation of an inorganic or organic equilibrium, and catalytic oxidation of $CO - H_2$ mixtures in presence of Pt. The perspective directions and future scope emerging from our proposition are highlighted in Section 6. In Section 7, we briefly summarize by offering the conclusions.

2. Reaction Mechanisms and Kinetic Rates

In this section, we begin by recalling fundamentals of chemical reactions towards the formation of a chemical equilibrium [26]. First, a chemical reaction is said to occur when the reactants change into products. The progress of such a change is governed by the laws of chemical kinetics [2], which deal with the changes that take place in a given reaction. Herewith, we mainly focus on the reaction rate that depends on the concentration of reactants and products. Please note that the concentrations taken here can be expressed either in the unit of the mass, molar or volume depending upon the state of the reacting species.

2.1. Chemical Equilibrium

In this section, we provide a brief overview of the chemical rate to study its fluctuation theory properties. From perspectives of a chemical equilibrium formation [26], we focus on an arbitrary chemical reaction with a given set of reactants and products. From the viewpoints of chemical science, the equilibrium is pictured as an extremal system at which the amount of the species involved remain unchanged unless an external force is applied to it. For reason, a chemical equilibrium is formed at a constant temperature, pressure, volume, and composition of the reacting species. Furthermore, it is worth mentioning that a chemical equilibrium taking place in a closed system [27] can be represented as



where " \rightleftharpoons " represents the chemical equilibrium among the reactants and products. In the sequel, it follows that a chemical equilibrium can be understood based on macroscopic observations [7,8]. Normally, it is achieved when the forward and reverse reactions take place with a constant rate, where the macroscopic amount of chemical species remains the same.

Historically, an explanation for the conversion occurring in a given chemical reaction in an equilibrium condition was proposed by Leopold Pfaundler von Hadermur during 1880's. A priori, von Hadermur hypothesized the concept of a chemical reaction based on his observations following from the kinetic theory of gases with reference to collisions [1] between the molecules as early as 1867. In particular, at a given temperature, he observed that the equal number of molecules were created and dissociated in due course of their collisions. His theory also suggests that there cannot be the same translational and internal energy for all molecules [7,8]. This is because the collisions of the selected molecules can contribute to the formation of reaction, which solely happens by creating or dissociating the molecules. Consequently, the concept of the chemical affinity arises via the kinetic and statistical interactions among all possible molecules.

The concept of the chemical affinity [13] was further examined by equilibrium displacement mechanism by Guldberg, Waage and Berthollet, which indicates that one cannot explain the formation of an equilibrium only by the mass of the species in a given solution, see [28] for a recent account. Thus, to achieve a chemical equilibrium, one eventually exploits the concept of the active masses of the species, viz. their concentrations.

In general, given an arbitrary single component reaction $A \rightarrow B$ with $[A]$ as the concentration of the reactant A , its rate [13] is defined as per the ratio

$$\text{Rate} := -\frac{\Delta[A]}{\Delta t}, \quad (2)$$

where $\Delta[A]$ represents the change in the concentration $[A]$ in the time interval Δt . Similarly, for the product B having concentration $[B]$, its corresponding rate [13] is defined as

$$\text{Rate} := +\frac{\Delta[B]}{\Delta t} \quad (3)$$

It is worth mentioning that the above equilibrium is not immediately achieved. In practice, it could be attained in a few micro to milli seconds. An optimized formation of such equilibria is the subject matter of this research. Notice that the above rate law can be generalized to arbitrary chemical reaction having finitely many reactants and products, as well. Namely, given the most general chemical reaction



taking place at a constant temperature, its corresponding rate [13] reads as per the power law

$$\text{Rate} = k[A]^m[B]^n \dots, \quad (5)$$

where the constant k is termed as the rate constant of the reaction, exponents $\{m, n, \dots\}$ represent respective orders and $\{a, b, c, d, \dots\}$ are the stoichiometric coefficients corresponding the constituents $\{A, B, \dots\}$. Various chemical reactions have different rates, such as a faster reaction proceeds with a higher rate; however, a slower reaction has a lower rate. First, it is worth emphasizing that a higher rate is attained due to sudden decrease in the concentration of reactants, whereas a lower rate arises due to a slow decrease of their concentrations. For a given chemical reaction, there are mainly four factors that control its rate, viz. the (i) concentration of the reactants, (ii) their physical state, (iii) reaction temperature and (iv) use of catalysts. As mentioned before, the number of collisions of the molecules is directly proportional to the concentration of reactants [1,2]. In general, when more collisions of the molecules occur, an increase in the rate of the reaction takes place. Thus, the concentration of reactants plays an important role in happening of a chemical reaction.

Secondly, the physical state of a reaction depends on the collision frequency, which decides how straightforwardly the reactants can combine. In a given phase of reactants, their molecules are brought into contact by the random thermal motion whereby they get mixed to form a new state. If the phases of reactants are different, the contact between them takes place only at the interface of the phases.

Hence, there is a less possibility of the happening of the reaction. Quantum mechanically, it follows that a vigorous stirring or grinding is needed for a fast happening of the reaction. In addition, the surface area of reactants emerges as an essential quantity in determining the rate of the reaction. It is worth mentioning that finer and smaller solid or liquid reactants—having a greater surface area—create possible active sites for a reactant to interact with others. This leads a faster occurrence of the reaction.

Thus, the temperature plays an important role in enhancing the reaction rate, viz. it increases the frequency of colliding molecules [1]. Namely, an increase in the frequency increases the interaction between the participating molecules, whereby a boost takes place in the rate of the reaction. As the kinetic energy of the molecules depended on their speed, therefore it increases as we increase the temperature of the reaction. As a result, when larger number of molecules collide, we find an increase in the chemical rate. Consequently, the rate of a chemical reaction is measured by changes in the concentration of reactants or that of the products per unit time.

2.2. Fluctuation Theory

In this subsection, we focus on the behavior of the chemical rate as in Equation (5) with respect to the concentrations $\{c_1, c_2\}$. To discuss the most general binary component chemical reaction, we consider the formation of an equilibrium for the reaction as in Equation (4). As per this formulation, given a pair of reactants $\{A, B\}$ with their active concentrations $\{[A], [B]\}$ and orders m and n respectively, the forward rate r_{dir} varies as the power law as given by Equation (5) with respect to $\{[A], [B]\}$. Notice further that the orders $\{m, n\}$ remain fixed in a given chemical experiment. With reference to the above observation that $\{c_1, c_2\}$ plays an important role, we investigate the formation of an equilibrium as depicted in Equation (4).

To address the question how the reactants $\{A, B\}$ form an equilibrium, we need to optimize the corresponding rate under infinitesimal variations of $\{c_1, c_2\}$. Namely, at a given time $t = t_0$, with their respective concentrations as $[A] = c_1$ and $[B] = c_2$, from Equation (5), it follows [13] that we have the following reaction rate

$$r(c_1, c_2) = kc_1^m c_2^n \quad (6)$$

Depending upon the state of the reacting species, the concentrations $\{c_1, c_2\}$, when taken as (i) the mass concentration, are measured in kg/m^3 , (ii) the molar concentration, are measured in mol/m^3 , and (iii) the volume concentration, are dimensionless. Furthermore, it is worth mentioning that the unit of the rate constant k depend upon the global order of a chosen reaction [4,13]. Namely, when the concentrations $\{c_1, c_2\}$ are measured in the units of mol/L , then for the above-mentioned chemical reaction of the order $(m + n)$, the rate constant k has units of $\text{mol}^{1-(m+n)} \text{L}^{(m+n)-1} \text{s}^{-1}$. Thus, from Equation (6), it follows that the rate $r(c_1, c_2)$ has the unit $\text{mol}/\text{L}/\text{s}$.

In due course of the above reaction, when the concentration of only one of reactants varies and that of the other is held fixed, we have the following transformations

$$\begin{aligned} c_1 &\longrightarrow c_1 + \delta c_1 \text{ with a modified rate } r(c_1 + \delta c_1, c_2) \\ c_2 &\longrightarrow c_2 + \delta c_2 \text{ with a modified rate } r(c_1, c_2 + \delta c_2) \end{aligned} \quad (7)$$

When both the concentrations $\{c_1, c_2\}$ simultaneously change to $\{c_1 + \delta c_1, c_2 + \delta c_2\}$, the rate $r(c_1, c_2)$ as in Equation (6) changes as

$$r \longrightarrow r(c_1 + \delta c_1, c_2 + \delta c_2) = r' \quad (8)$$

In the limit of $r \approx r'$, the chemical equilibrium is formed. That is, the equilibrium is formed at the fixed point of the rate $r(c_1, c_2)$ as in Equation (6). As per the fluctuation theory analysis [17–22], the local nature of the chemical equilibrium depends on the sign of the chemical concentration capacities, which are defined as the pure second derivatives of $r(c_1, c_2)$ with respect to $\{c_1, c_2\}$ respectively.

The corresponding global nature of the equilibrium is characterized by the sign of the determinant of fluctuation matrix of the rate $r(c_1, c_2)$. Before proceeding further, let us consider a first-order reaction with $m = 1$ and $n = 1$ as per the equilibrium



In general, the equilibrium between the reactants A, B of their orders $\{m, n\}$ and C, D of their orders $\{p, q\}$ is achieved when the rate of the forward reaction becomes same as that of the reverse reaction. As mentioned before, up to a constant factor, the rate of the forward reaction varies as the product of concentrations of the reactants as in Equation (5), viz. for two components $\{A, B\}$ we have the following power law

$$r_{dir} = k_{dir}[A]^m[B]^n, \quad (10)$$

where the constant factor k_{dir} is termed as the rate constant of the forward reaction [13]. Similarly, let k_{inv} be the rate constant of the backward reaction. Then, the corresponding rate modulates as per the product of concentrations of the products $\{C, D\}$ as

$$r_{inv} = k_{inv}[C]^p[D]^q, \quad (11)$$

where $[C]$ and $[D]$ are their respective concentrations. Thus, it is understood that the law of mass action arises as per the equality $r_{dir} = r_{inv}$. From the above equations, we find the equilibrium constant K reads as the ratio of the rate constants of the forward reaction r_{dir} to that of the backward reaction r_{inv} . Thus, in the light of chemical affinity [12], we have the following equilibrium constant

$$K = \frac{[C]^p[D]^q}{[A]^m[B]^n} \quad (12)$$

Having determined the fluctuation properties of the forward reaction about the equilibrium from Equation (12), we can also estimate that of the backward reactions, as well. Namely, for a given equilibrium constant K , our present investigation helps in understanding the nature of a chemical equilibrium formation as fluctuations over the law of mass action. Therefore, it is worth emphasizing that a chemical reaction never proceeds till its end, but it rather attains an equilibrium state [26], which exclusively depends upon the available number of reactants participating in the reaction [13]. It is important to note that a reaction in its equilibrium retains its dynamic characteristics; however, its forward and reverse directions eventually both possess the same rate. This gives an impression of the termination of a chemical reaction. For example, such an equilibrium formation is supported by the following titration



In this setup, a reaction can proceed in forward or backward direction depending upon external conditions and catalysts present in the reaction. Indeed, in the light of various physiochemical investigations [29], an equilibrium formation happens via the donation of a proton H^+ , whose concentration $[H^+]$ defines the pH values of the solution as

$$pH = -\ln[H^+] \quad (14)$$

Concerning the equilibrium formation, the pH value plays an important role. Historically, the term pH represents the potential of hydrogen which corresponds to a numerical value indicating the acidity or the basicity of a given aqueous solution. In short, the pH value of a solution is defined as the negative logarithm of hydrogen ions concentration $[H^+]$ as in Equation (14). It is worth mentioning that the value of pH ranges from 0 to 14 with the classification that its values less than 7 indicating an acidic

solution, greater than 7, as a basic solution, and equal to 7 as the neutral [13]. Indeed, for non-aqueous solutions, the *pH* measurement is realized by a different scale than its aqueous counterparts as above in Equation (14), viz. the acidity functions, see [30]. Namely, the corresponding *pH* of a solvent as the hydrogen ion activity depends on the chemical potential, state and the temperature governing the system.

Subsequently, *pH* value emerges as an important conception in various studies including the chemical equilibria, acid-base pairs, titration reactions, donor-acceptor and strong base formation. Following the same, in Section 6, we provide the below statistical fundamentals behind the reaction mechanism and chemical equilibrium formation for various chemical reactions that pave path for industrial developments.

3. Chemical Equilibrium Formation

In this section, we commence by describing binary component chemical reactions and their equilibrium formation [30]. Here, by following the above-mentioned fluctuation theory perspective, we examine equilibrium formation for binary component chemical reactions, their associated flow components, capacities, and fluctuation quantities regarding the local and global chemical stabilities as below.

In this work, we mainly focus on the behavior of the above rate as in Equation (6) with respect to fluctuations of the concentrations $\{c_1, c_2\}$. To address the question how the reactants $\{A, B\}$ form an equilibrium, we need to determine an optimized rate $r(c_1, c_2)$ under infinitesimal variations of $\{c_1, c_2\}$. Before proceeding further, let us emphasize that we offer an equilibrium formation via an intrinsic perspective of the fluctuation theory.

3.1. Flow Components

Given two reactants $\{A, B\}$ with their concentrations $\{c_1, c_2\}$, the associated rate $r(c_1, c_2)$ takes a power law of the form as in Equation (6). In this context, the *i*th flow component is defined as the first partial derivative of the chemical rate $r(c_i)$ with respect to the concentration c_i . Herewith, under fluctuations of $\{c_1, c_2\}$, we have the following flow components

$$r_1 = \frac{\partial r}{\partial c_1} = kmc_1^{m-1}c_2^n \quad (15)$$

with respect to c_1 , and that of the other with respect to c_2 as

$$r_2 = \frac{\partial r}{\partial c_2} = knc_1^m c_2^{n-1} \quad (16)$$

Thus, it follows that an equilibrium—defined as the simultaneous roots of flows equations $r_1 = 0 = r_2$ as in Equations (15) and (16)—is formed when either one of the orders $\{m, n\}$ vanishes or one of the concentrations $\{c_1, c_2\}$ vanishes. More precisely, the reaction attains its steady state when we have either (i) $m = 0$ and $n = 0$ or (ii) $c_1 = 0$, or (iii) $c_2 = 0$.

3.2. Concentration Capacity

As per the above fluctuation theory analysis [17–22], the chemical concentration capacity of the components *A* takes the following power law form

$$r_{11} = \frac{\partial^2 r}{\partial c_1^2} = km(m-1)c_1^{m-2}c_2^n \quad (17)$$

For all non-zero concentrations $\{c_1, c_2\}$, we see that r_{11} (representing the local stability of the chemical system with respect to fluctuations in the concentration of the component *A*) vanishes identically whenever we have either $m = 0$ or $m = 1$. Similarly, the chemical concentration capacity of the components *B* simplifies as

$$r_{22} = \frac{\partial^2 r}{\partial c_2^2} = kn(n-1)c_1^m c_2^{n-2} \tag{18}$$

Herewith, for all non-zero concentrations $\{c_1, c_2\}$, r_{22} (representing the local stability of the chemical system with respect to fluctuations in the concentration of the component B) vanishes whenever it is of the zero or unit orders, viz. $n = 0, 1$.

3.3. Concentration Correlation

It follows that the correlation between the components A and B is given by

$$r_{12} = \frac{\partial^2 r}{\partial c_1 \partial c_2} = knm c_1^{m-1} c_2^{n-1} \tag{19}$$

Please note that r_{12} signifying simultaneous fluctuations of the components A and B vanishes only when either one of them is of zeroth order at non-vanishing concentrations $\{c_1, c_2\}$. Thus, the corresponding rate $r(c_1, c_2)$ becomes independent of either c_1 or c_2 .

3.4. Equilibrium Stability

To study the stability of the equilibrium [17–22], let us define the fluctuation matrix as

$$H = \begin{bmatrix} r_{11} & r_{12} \\ r_{12} & r_{22} \end{bmatrix} \tag{20}$$

Thus, from the above evaluation of the chemical capacities $\{r_{11}, r_{22}\}$ as in Equations (17) and (18) and the associated correlation r_{12} as in Equation (19), we have the following fluctuation matrix

$$H = kc_1^{m-2} c_2^{n-2} \begin{bmatrix} m(m-1)c_2^2 & mnc_1c_2 \\ mnc_1c_2 & n(n-1)c_1^2 \end{bmatrix} \tag{21}$$

Consequently, it is direct to see that the determinant $\Delta := r_{11}r_{22} - r_{12}^2$ of H simplifies as

$$\Delta = k^2 mn(1-m-n)c_1^{2m-2} c_2^{2n-2} \tag{22}$$

Herewith, we see that the determinant Δ vanishes identically when one of the concentrations (c_1, c_2) vanishes or one of the reactants is of the zero order or the sum of orders of the reactants is unity. In particular, it is worth mentioning that we have $\Delta = 0$ along the line $m + n = 1$. For example, such an equilibrium arises for the chemical reaction with an equal order of reactants $\{A, B\}$ with its rate $r = k\sqrt{c_1 c_2}$. Furthermore, from Equation (22), it follows that the determinant Δ is identically zero for all pair of reactants $\{A, B\}$ with their respective orders as $\{m, 1 - m\}$.

3.4.1. Local Stability

It is interesting to note that the local chemical equilibrium stability requires a positive value of either $m(m-1)$ or $n(n-1)$. This results into the condition that the orders m and n should either be negative or larger than unity. In other words, the system is locally unstable for an arbitrary pair of reactants $\{A, B\}$ with their orders $m, n \in (0, 1)$.

3.4.2. Global Stability

From Equation (22), we see that the global stability of the chemical equilibrium requires the positivity of a cubic factor $mn(1-m-n)$ under variations of $\{m, n\}$. This happens for the orders $\{m, n\}$ such that (i) $1 > m + n$ with m and n having the same signatures, and (ii) $1 < m + n$ with m and n having the opposite signatures.

Furthermore, concerning the chemical fluctuation invariants, another interesting quantity is the trace $tr(H) := r_{11} + r_{22}$ of the fluctuation matrix H . From Equation (21), the concentrations $\{1/c_1, 1/c_2\}$ lie on a conic section whenever the ratio of the trace $tr(H)$ and the chemical rate $r(c_1, c_2)$ as in Equation (6) takes a constant value. In this case, it follows that $\{c_1, c_2\}$ satisfy

$$\frac{m(m-1)}{c_1^2} + \frac{n(n-1)}{c_2^2} = k_e, \tag{23}$$

where $k_e = tr(H)/kc_1^{-m}c_2^{-n}$. In the sequel, for various values of the orders $\{m, n\}$, we offer qualitative features of the fluctuations quantities $\{r, r_1, r_2, r_{11}, r_{22}, r_{12}, \Delta, tr(H)\}$ under variations of the concentrations $\{c_1, c_2\}$. Notice also that all the other fluctuation quantities vanish identically for a zeroth-order chemical reaction, except its rate $r(c_1, c_2)$. In the next section, the above fluctuations quantities are plotted for a set of typical orders (m, n) as

$$\mathcal{C} := \{(-1, -1), (-1, 1/2), (-1, 2), (1/2, 1/2), (1/2, 2), (2, 2)\} \tag{24}$$

It is worth noticing that the set \mathcal{C} includes all the types of possibilities concerning a stable chemical equilibrium formation for the reactants $\{A, B\}$.

4. Discussion of the Results

Below, for the above-mentioned typical orders (m, n) as in Equation (24), we provide qualitative discussion of the fluctuation quantities. Namely, we highlight the qualitative features of the fluctuation theory analysis by varying the rate in the concentration plane of the reactants. As mentioned before, the concentrations are measured in mol/L and the corresponding rate $r(c_1, c_2)$ is measured in the unit of mol/L/s. With reference to the Figures 1–6, the X-axis and Y-axis denote the concentrations c_1 and c_2 respectively.

4.1. Chemical Reactions with Orders $(-1, -1)$

For chemical reactions with the reactants $\{A, B\}$ of their respective orders as $m = -1$ and $n = -1$, we give qualitative behavior of the rate $r(c_1, c_2)$ in the Figure 1a. In this case, we see that r has four peaks of fluctuations where the two them have a positive amplitude of the order 0.2, while the other two have a negative amplitude of the same order. Furthermore, for given concentration of the reactants, we observe that there are fluctuations solely along the limiting lines $c_2 \rightarrow 0$ and $c_1 \rightarrow 0$. As we approach the origin $(0, 0)$ in the concentration plane, the equilibrium is achieved as a long-term effect, i.e., r takes a constant value.

From the Figure 1b, we find that the rate of change of $r_1(c_1, c_2)$ has a negative amplitude of the order -0.1 for a positive value of the concentration c_2 of the reactant B . However, for the other case $c_2 < 0$, we observe symmetrical fluctuations of the same order of the positive amplitude. Furthermore, we notice a satellite peak for decreasing concentration c_2 with an alternating spike while approaching the concentration axis $c_2 = 0$.

From Figure 1c, we see an analogous behavior of the rate of change of the flow component $r_1(c_1, c_2)$ with a right-angle rotation of the concentration of the reactants $\{A, B\}$. Interestingly, the amplitude of fluctuations of $r_1(c_1, c_2)$ remains the same and only the axes are being exchanged in the interval of $-50 < c_1, c_2 < 50$.

With the above observations of $\{r_1, r_2\}$, we notice from Figure 1d that the same number of four peaks of fluctuations in the capacity $r_{11}(c_1, c_2)$ occurs around the origin $(0, 0)$. On the other hand, for $c_1 \rightarrow 0$, a constant positive capacity r_{11} is maintained along the negative c_2 -axis. Furthermore, a constant negative capacity r_{11} is followed along the positive c_2 -axis.

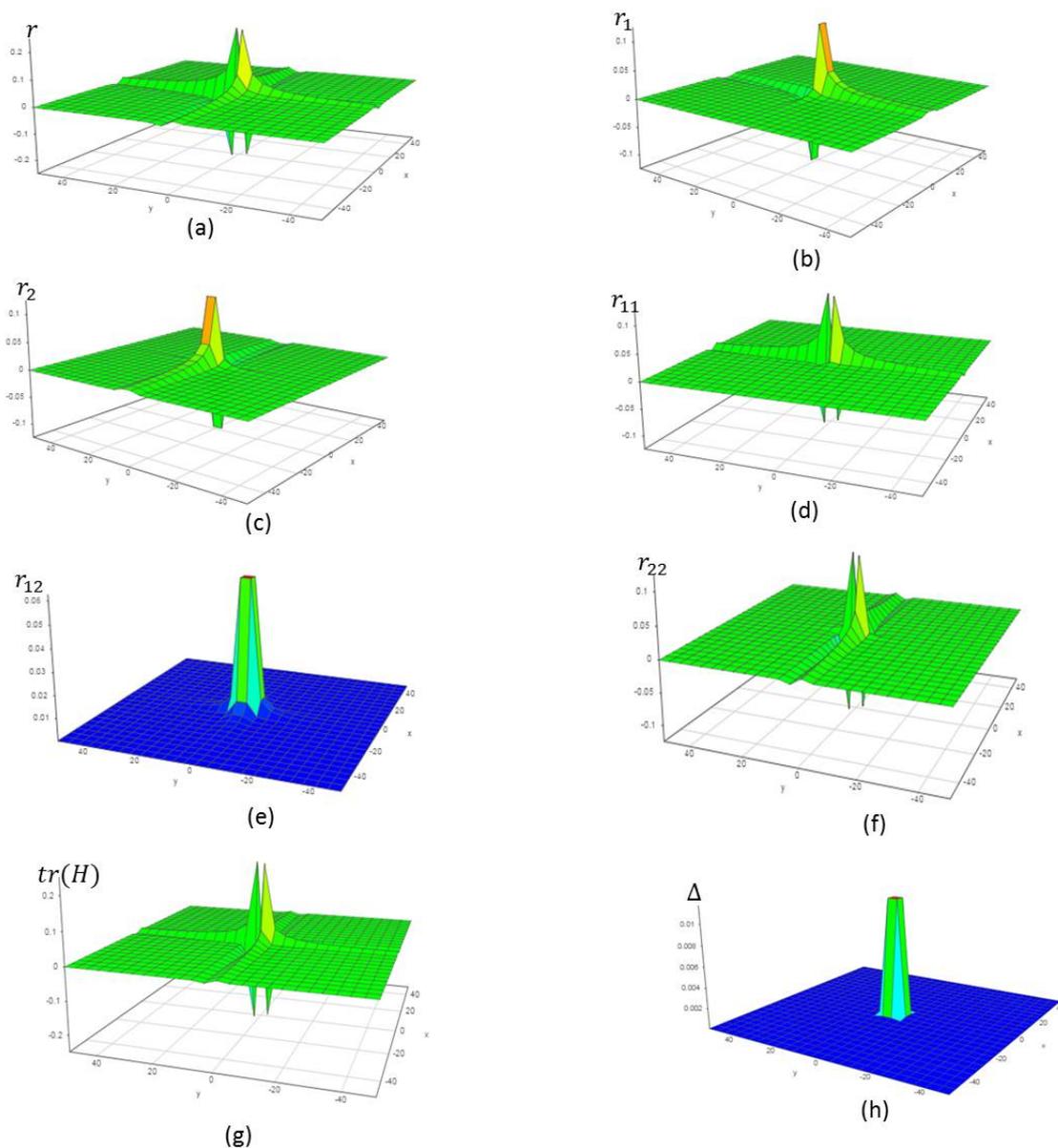


Figure 1. The fluctuation quantities as a function of the chemical concentrations $\{c_1, c_2\}$ for $m = -1$ and $n = -1$ plotted in the interval $-50 \leq c_1, c_2 \leq 50$ against (a) the rate $r(c_1, c_2)$, (b) flow $r_1(c_1, c_2)$, (c) flow $r_2(c_1, c_2)$, (d) capacity $r_{11}(c_1, c_2)$, (e) correlation $r_{12}(c_1, c_2)$, (f) capacity $r_{22}(c_1, c_2)$, (g) trace $tr(H)$ and (h) determinant $\Delta(c_1, c_2)$. (Note: with c_1, c_2 measured in mol/L on X and Y axis respectively, the other quantities on Z-axis are measured in the units as: $r \rightarrow \text{mol/L/s}$; $r_1, r_2 \rightarrow \text{s}^{-1}$; $r_{11}, r_{12}, r_{22}, tr(H) \rightarrow \text{mol}^{-1} \text{L s}^{-1}$; $\Delta \rightarrow \text{mol}^{-2} \text{L}^2 \text{s}^{-2}$).

From the above Figure 1e, it is evident that the cross-correlation $r_{12}(c_1, c_2)$ of the rate of the reaction takes a positive value for any $\{c_1, c_2\}$ with a maximum amplitude of 0.06. For a given pair of concentrations $\{c_1, c_2\}$, the cross-correlation r_{12} increases steeply as we approach the origin (0,0) in the concentration plane. Interestingly, we find that the chemical equilibrium is uniformly maintained between A and B throughout the concentration plane, except the origin (0,0).

Figure 1f depicts the variation of the capacity $r_{22}(c_1, c_2)$ as a function of the concentrations $-50 < c_1, c_2 < 50$. It could be analyzed thus that there are symmetrical fluctuations in r_{22} taking place around the origin (0,0) with a reduced amplitude in comparison to the rate r as in Figure 1a. We see a pair of pulse-like oscillations in r_{22} both in the positive and negative directions about the origin.

In addition, fluctuations along the c_1 -axis are notably observed as $c_2 \rightarrow 0$. A uniform and constant capacity r_{22} of a positive amplitude is maintained along the negative c_1 -axis, whereas the capacity r_{22} possesses a constant negative amplitude along the positive c_1 -axis.

The above Figure 1g represents common characteristics at the origin as mentioned in the previous observations. Thus, we notice steady and equal oscillations in the value of the trace $tr(H)$ of the fluctuation matrix H of the rate of the reaction. Similarly, a constant dip in $tr(H)$ is observed along the c_1 axis as $c_2 \rightarrow 0$. In contrast to the above, viz. as $x \rightarrow 0$, a constant positive trace is found along c_2 axis under fluctuations of $\{c_1, c_2\}$.

Figure 1h shows a similar behavior for the determinant $\Delta(c_1, c_2)$ of the fluctuation matrix of the chemical rate to the cross-correlation r_{12} as depicted above in Figure 1e. It follows that Δ and r_{12} both have positive amplitudes of fluctuations for any values of $\{c_1, c_2\}$. In contrast to the chemical correlation r_{12} , we find that Δ possesses a smaller amplitude of fluctuations with its maximum value of the order 0.01. For a given pair of concentrations $\{c_1, c_2\}$, it is observed that Δ equally increases steeply as $\{c_1, c_2\}$ approach the origin. Concerning the quest of a global stability, it follows that the equilibrium is uniformly maintained between the reactants $\{A, B\}$ as long as the concentrations $\{c_1, c_2\}$ take non-zero values.

4.2. Chemical Reactions with Orders $(-1, \frac{1}{2})$

We depict below the characteristics of the chemical fluctuations in Figure 2 for various chemical concentrations $\{c_1, c_2\}$ of the reactants A and B of their order $m = -1$ and $n = 1/2$ respectively.

For $c_2 > 0$, there are fluctuations in the rate $r(c_1, c_2)$ for $m = -1$ and $n = 1/2$ for the reactants A and B . Namely, from Figure 2a it follows that the rate has fluctuations with the maximum amplitude of 3 when c_1 approaches the origin from its small positive value. On the other hand, for c_1 approaching the origin from its small negative value, there is a dip in the rate with its maximum negative value -3 . Furthermore, the fluctuations in $r(c_1, c_2)$ are asymmetric about the line $c_1 = 0$. In contrast to the above, the rate remains constant for $c_2 < 0$. The same observation holds for $c_2 > 0$ with a large positive or negative value of c_1 .

From Figure 2b, along the concentration line $c_1 = 0$, we see that the flow component $r_1(c_1, c_2)$ has a valley as c_2 increases from the origin, which emerges symmetrically as we approach $c_1 = 0$ from its corresponding small positive and negative values. The amplitude of r_1 increases as we increase c_2 , namely, we find that r_1 has the maximum amplitude of -2.0 at $c_2 = 50$ and it declines as c_2 reaches the origin. Furthermore, there are no fluctuations in r_1 for any value of c_1 with $c_2 < 0$. Also, r_1 remains constant far away from the region $c_1 = 0$ and $c_2 > 0$.

From the Figure 2c, it follows that the amplitude of $r_2(c_1, c_2)$ decreases as either c_1 or c_2 increases from the origin. There is a small positive damping uphill in r_2 with an amplitude 0.15 as we approach the concentration $c_2 = 0$ with an increasing value of $c_1 > 0$. Similarly, there is an uphill in r_2 in the region $c_1 = 0$ as c_2 approaches the origin from its positive values. In the region $c_1 < 0$ and $c_2 > 0$, we see that there is an asymmetric peak of the negative amplitude -0.5 as we approach the regions (i) $c_1 = 0$ for $c_2 > 0$ and (ii) $c_2 = 0$ for $c_1 < 0$. Furthermore, for all value of c_1 , we notice that r_2 remains constant for $c_2 < 0$.

From the Figure 2d, it is observed that the capacity $r_{11}(c_1, c_2)$ has fluctuations for $c_2 > 0$, for species of A and B of the orders $m = -1$ and $n = 1/2$ respectively. In contrast to the rate of the reaction $r(c_1, c_2)$, the capacity has the maximum amplitude 1.5 when c_1 approaches the origin from its small positive values with $c_2 > 0$. When c_1 approaches the origin from its small negative values, we find a crest of negative amplitude -1.5 . Moreover, we see that the capacity r_{11} fluctuates asymmetrically about the region $c_1 = 0$ and $c_2 > 0$. In this case, we find that r_{11} takes a small constant value for any c_1 with $c_2 < 0$. Furthermore, r_{11} a small constant value for $c_2 > 0$ with a large value of $|c_1|$.

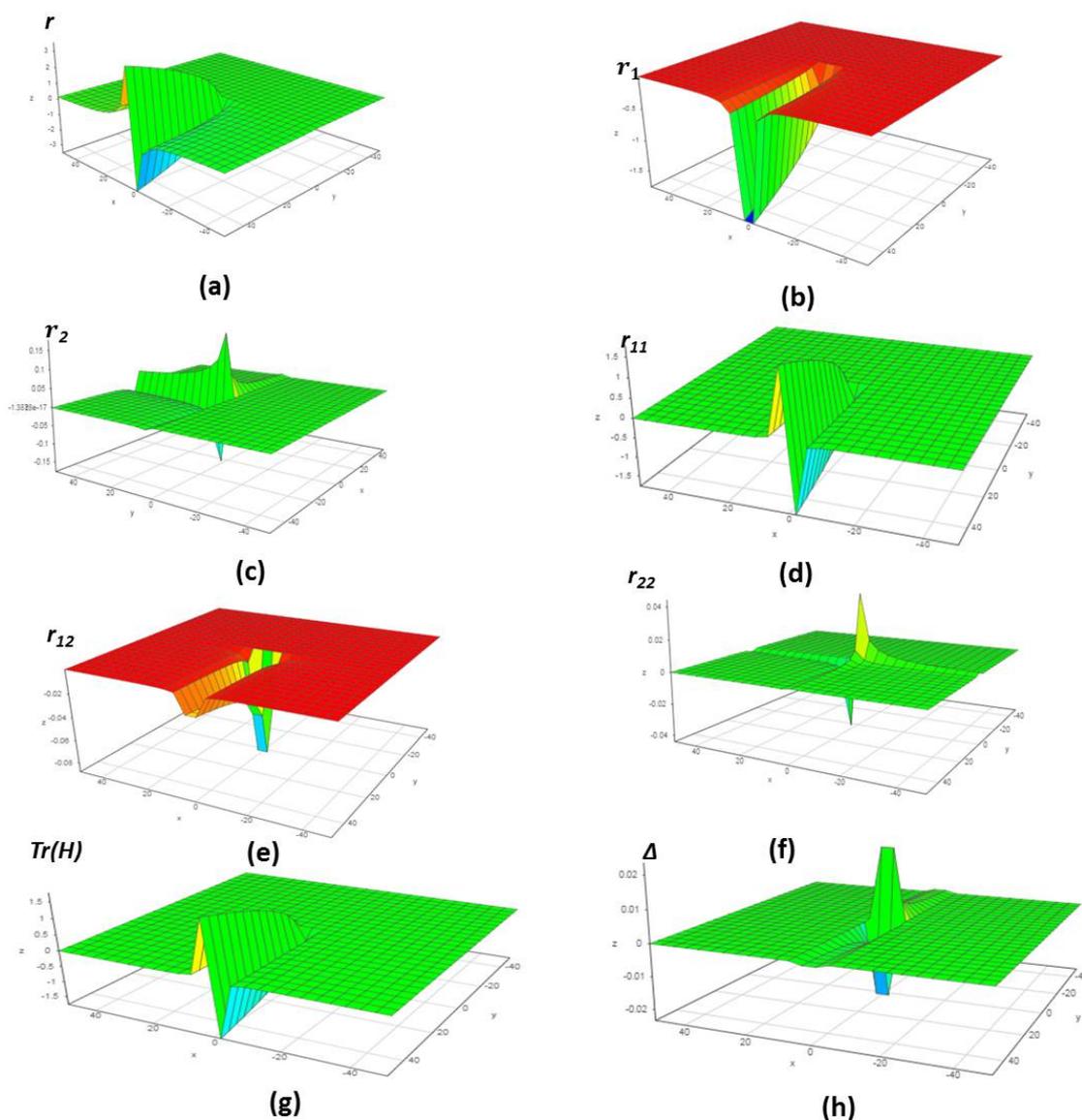


Figure 2. The fluctuation quantities as a function of the chemical concentrations $\{c_1, c_2\}$ for $m = -1$ and $n = \frac{1}{2}$ plotted in the interval $-50 \leq c_1, c_2 \leq 50$ against (a) the rate $r(c_1, c_2)$, (b) flow $r_1(c_1, c_2)$, (c) flow $r_2(c_1, c_2)$, (d) capacity $r_{11}(c_1, c_2)$, (e) correlation $r_{12}(c_1, c_2)$, (f) capacity $r_{22}(c_1, c_2)$, (g) trace $tr(H)$ and (h) determinant $\Delta(c_1, c_2)$. (Note: with c_1, c_2 measured in mol/L on X and Y axis respectively, the other quantities on Z-axis are measured in the units as: $r \rightarrow \text{mol/L/s}$; $r_1, r_2 \rightarrow \text{s}^{-1}$; $r_{11}, r_{12}, r_{22}, tr(H) \rightarrow \text{mol}^{-1} \text{L s}^{-1}$; $\Delta \rightarrow \text{mol}^{-2} \text{L}^2 \text{s}^{-2}$).

As depicted in Figure 2e, we find that there are no fluctuations in the correlation $r_{12}(c_1, c_2)$ for any value of c_1 with $c_2 < 0$. On the other hand, for all positive values of c_2 , we notice a valley in the region $c_1 = 0$. At the origin, it follows that r_{12} has a negative peak with the amplitude 0.08. Furthermore, there are small non-vanishing fluctuations in r_{12} in the concentration region $c_2 = 0$ within the limit $-20 < c_1 < 20$. For all other values of c_1 and c_2 , there are no fluctuations in the cross-correlation.

The capacity $r_{22}(c_1, c_2)$ is plotted in Figure 2f for various values of the concentrations $\{c_1, c_2\}$ with orders $m = -1$ and $n = 1/2$ of the reactants A and B respectively. In this case, we see that there are fluctuations of positive amplitude of the order 0.04 for small negative values of c_1 with a positive value of c_2 . On the other hand, for $c_1 > 0$, we notice a downhill in r_{22} along the concentration axis $c_2 = 0$. Furthermore, in the region $c_1 = 0$, there exists an uphill in the capacity r_{22} as we approach the line $c_2 = 0$ from a positive value. In the region $c_1 < 0$ and $c_2 > 0$, we observe an asymmetric peak of

negative amplitude 0.04. In short, the capacity r_{22} has fluctuations in the region (i) $c_1 = 0$ for $c_2 > 0$ and (ii) $c_2 = 0$ for $c_1 < 0$. Furthermore, it remains constant for all value of c_1 with concentration $c_2 < 0$.

In the above Figure 2g, we provide qualitative behavior of the trace $tr(c_1, c_2)$ of fluctuations of the reactants $\{A, B\}$ with their orders $m = -1$ and $n = 1/2$. Specifically, we find that $tr(H)$ takes a similar fluctuation property to that of the capacity r_{11} with its maximum amplitude 1.5 when the concentration c_1 approaches the origin from a positive value of c_2 . For c_1 approaching the origin from a negative value, the trace $tr(H)$ shows a negative value of the amplitude 1.5. In the region $c_2 > 0$, we observe that tr has asymmetric fluctuations around $c_1 = 0$. For the orders $m = -1$ and $n = 1/2$, for various values of c_1 , from the Figure 2g, it follows that tr vanishes for all $c_2 < 0$. In this case, it is worth mentioning that tr disappears for $c_2 > 0$ and $|c_1| > 20$.

The Figure 2h depicts qualitative feature of the determinant $\Delta(c_1, c_2)$ of the fluctuation matrix of the rate of reaction with orders $m = -1$ and $n = 1/2$. In this case, we observe that the reaction could become unstable only along $c_1 = 0$. In particular, for $c_2 > 0$, we see a negative value of the determinant Δ . In the limit of $c_1 \rightarrow 0$ with $c_2 > 0$, we find the amplitude of -0.02 for $\Delta(c_1, c_2)$. For the negative value of c_2 , we find a positive uphill in Δ along the line $c_1 = 0$ with its maximum amplitude of 0.02 around the origin. In the remaining part of the reaction plane, viz. for large values of c_1 , we notice that $\Delta(c_1, c_2)$ vanishes identically for all values of c_2 .

4.3. Chemical Reactions with Orders $(-1, 2)$

In Figure 3a, we give qualitative behavior of the rate $r(c_1, c_2)$ for the orders $m = -1$ and $n = 2$ of the reactants $\{A, B\}$. We see that the rate r possess an asymmetric nature about the line $c_1 = 0$ and has symmetric fluctuations about the concentration axis $c_2 = 0$. Namely, for a large positive c_2 , the rate r has a negative amplitude of the order 1000 when we approach the axis $c_1 = 0$ from its small negative values. On the other hand, for $c_2 > 0$, we observe a positive amplitude of the order 1000 for the rate r while approaching $c_1 = 0$ from its positive values. Similarly, for $c_2 < 0$, it is observed that r takes the same negative amplitude of 1000 while one approaches $c_1 = 0$ from its negative end. Indeed, as we approach $c_1 = 0$ from a negative value, the rate r receives a positive value of 1000 for $c_2 < 0$. Furthermore, for all other values of c_2 , there are no fluctuations in r for a large $|c_1| > 20$.

For $m = -1$ and $n = 2$, the flow component $r_1(c_1, c_2)$ as plotted in Figure 3b shows that we have large negative fluctuations about the concentration axis $c_1 = 0$ for extreme positive and negative values of c_2 . Namely, for $c_2 = \pm 50$, the rate r_1 takes a negative value of 600. Furthermore, the behavior of r_1 remains symmetric about the axes $c_1 = 0$ and $c_2 = 0$. Indeed, there are no fluctuations in r_1 far away from axis $c_1 = 0$.

The variations in the flow component $r_2(c_1, c_2)$ with chemical concentration $\{c_1, c_2\}$ at orders -1 and 2 of the reactants A and B are demonstrated in Figure 3c. The graph shows that r_2 gradually increases from its minimum value of -40 to its maximum value of 40 when c_2 varies from 50 to -50 while approaching $c_1 = 0$ from its negative values. When approaching $c_1 = 0$ from its positive values, r_2 decreases from its maximum value of 40 to its minimum -40 as c_2 decreases from $+50$ to -50 . Consequently, we find a dual characteristic of r_2 along the axis $c_1 = 0$. Interestingly, we see that there are no fluctuations in r_2 for large absolute values of c_1 .

In Figure 3d, we provide the local stability properties of a chemical system for the reactant A and B of their orders $m = -1$ and $n = 2$ respectively. In particular, we see that the capacity $r_{11}(c_1, c_2)$ is symmetric about the axis $c_2 = 0$. Namely, it follows that r_{11} takes large negative value of the order 600 as we approach $c_1 = 0$ from its negative values. In contrast, r_{11} receives a large positive amplitude of the order 600 as we approach $c_1 = 0$ from its positive values. Thus, we see a saddle behavior in r_{11} along the axis $c_1 = 0$. As in the previous cases, there are no fluctuations in r_{11} for $|c_1| > 20$.

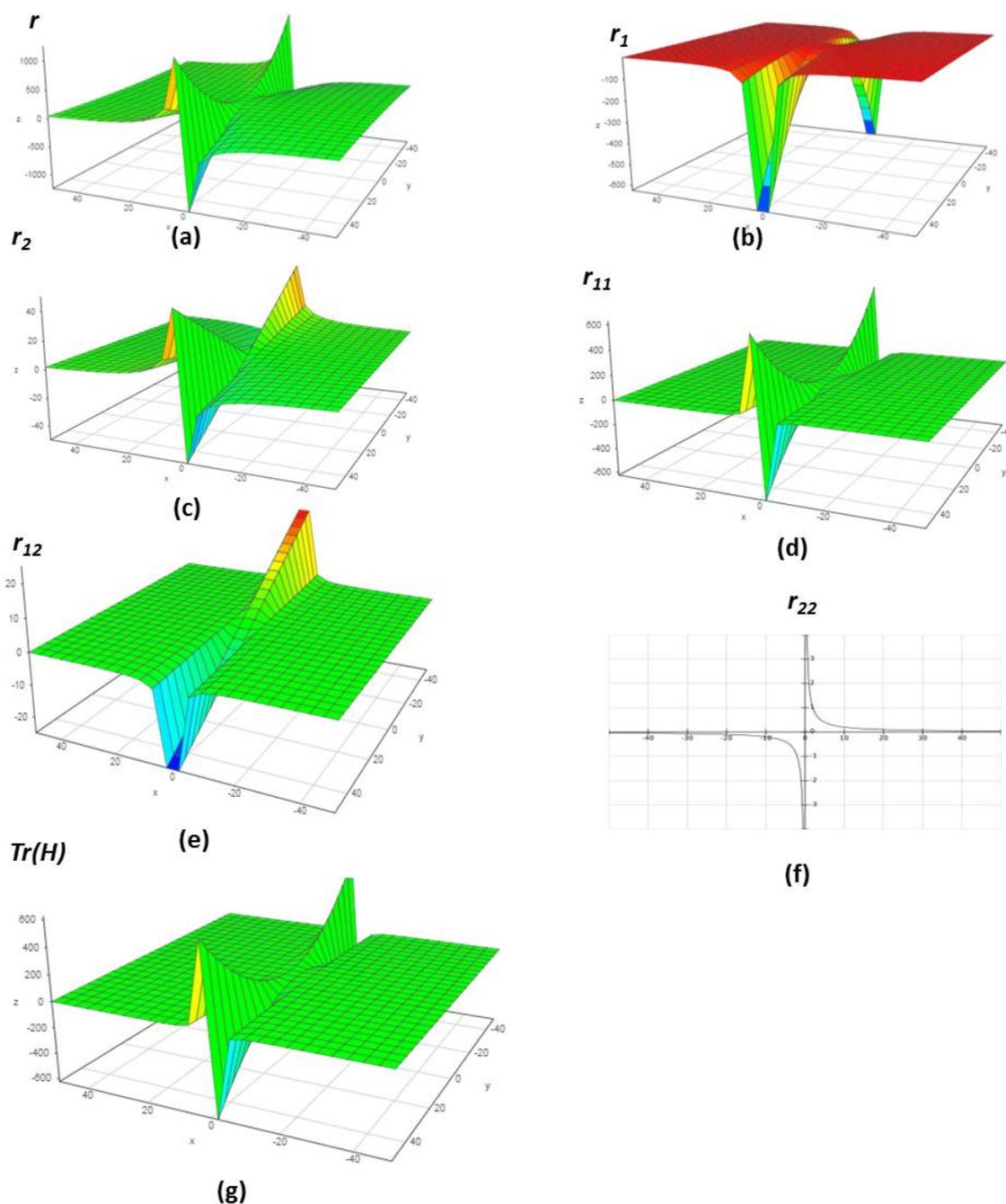


Figure 3. The fluctuation quantities as a function of the chemical concentrations $\{c_1, c_2\}$ for $m = -1$ and $n = 2$ plotted in the interval $-50 < c_1, c_2 < 50$ against (a) the rate $r(c_1, c_2)$, (b) flow $r_1(c_1, c_2)$, (c) flow $r_2(c_1, c_2)$, (d) capacity $r_{11}(c_1, c_2)$, (e) correlation $r_{12}(c_1, c_2)$, (f) capacity $r_{22}(c_1, c_2)$ and (g) trace $tr(H)$. (Note: with c_1, c_2 measured in mol/L on X and Y axis respectively, the other quantities on Z-axis are measured in the units as: $r \rightarrow \text{mol/L/s}$; $r_1, r_2 \rightarrow \text{s}^{-1}$; $r_{11}, r_{12}, r_{22}, tr(H) \rightarrow \text{mol}^{-1} \text{L s}^{-1}$; $\Delta \rightarrow \text{mol}^{-2} \text{L}^2 \text{s}^{-2}$).

From the Figure 3e, we see that the cross-correlation $r_{12}(c_1, c_2)$ increases along the axis $c_1 = 0$ as the concentration c_2 decreases from 50 to -50 . In particular, there is a negative peak of fluctuations of the order 20 in r_{12} for large positive values of c_2 along the axis $c_1 = 0$. On the other hand, we find that r_{12} has a positive amplitude of the order 20 for large negative values of c_2 . Furthermore, we observe

symmetric fluctuations in r_{12} along $c_1 = 0$ for all values of c_2 . In this case, for all values of c_2 , the cross-correlation r_{12} vanishes identically for a large $|c_1| > 20$.

In Figure 3f, it is shown that the capacity $r_{22}(c_1, c_2)$ becomes independent of c_2 , and therefore it displays a rectangular hyperbolic behavior with c_1 , viz. we have $c_1 r_{22}(c_1, c_2) = 2$. Herewith, the capacity r_{22} increases indefinitely as c_1 approaches the origin from its positive values. Similarly, it tends to a large negative value while c_1 approaches the origin from its negative values. Namely, the reaction happens only for positive value of c_1 , whereby its intensity decreases as c_1 increases further. Physically, we see that the chemical system is not stable in initial stages of the reaction.

From Figure 3g, we find that trace $tr(c_1, c_2)$ possess a symmetric behavior about the line $c_2 = 0$ for the orders $m = -1$ and $n = 2$ of the reactants A and B respectively. In this case, it is observed that the trace tr has a large negative peak of the amplitude 600 as we approach the axis $c_1 = 0$ from its negative values. On the other hand, we observe that $tr(H)$ takes a positive value of the order 600 while approaching $c_1 = 0$ from its positive values. As in the case of r_{11} , it follows that $tr(H)$ has a saddle point behavior along the concentration axis $c_1 = 0$. Furthermore, it is worth mentioning that $tr(H)$ differs from the capacity r_{11} largely in the limit of small values of c_1 . It is observed for $m = -1$ and $n = 2$ that $tr(H)$ of the fluctuation matrix H vanishes for $|c_1| > 20$.

4.4. Chemical Reactions with Orders $(\frac{1}{2}, \frac{1}{2})$

The Figure 4 represent the fluctuation quantities as a function of the chemical concentrations $\{c_1, c_2\}$ for $m = \frac{1}{2}$ and $n = \frac{1}{2}$ of the reactants $\{A, B\}$ plotted in the interval $-50 < c_1, c_2 < 50$. Namely, from Figure 4a, we see that the rate $r(c_1, c_2)$ shoots up as both the active chemical concentrations $\{c_1, c_2\}$ increase. On the other hand, it remains constant for both an increasing value of c_1 and decreasing c_2 , or vice-versa. Moreover, it follows that r falls off for decreasing values of $\{c_1, c_2\}$.

The flow component $r_1(c_1, c_2)$ as the rate of change of the $r(c_1, c_2)$ with respect to c_1 as shown in Figure 4b increases in the second quadrant as c_1 decrease from 50 to 0 and c_2 increases from 0 to 50. The same behavior of r_1 is found in the fourth quadrant when c_1 increases from -50 to 0 and c_2 decreases from 0 to -50 . In the limit of $c_1 \rightarrow 0$, two extreme values of the amplitude 2.5 of r_1 are achieved as c_2 takes it maximum and minimum values. However, in the first and third quadrants, we notice no fluctuations in r_1 under variations of $\{c_1, c_2\}$.

From Figure 4c, we find that the flow component $r_2(c_1, c_2)$ shows an inverse behavior of the component $r_1(c_1, c_2)$ as depicted in Figure 4b. Specifically, it follows that r_2 increases when we have either an increasing $c_1 \in (0, 50)$ and decreasing $c_2 \in (0, 50)$, or an increasing $c_2 \in (-50, 0)$ and decreasing $c_1 \in (0, -50)$. In this case, an extreme value of $r_2 = 2.5$ is found for the maximum and minimum values of c_1 in the limit $c_2 \rightarrow 0$. Moreover, there are no changes in r_2 whenever c_1 and c_2 have contrasting variations.

From the above Figure 4d, it is interesting to note that the capacity $r_{11}(c_1, c_2)$ decreases in the first quadrant to its minimum value -0.6 as c_2 approaches to the origin from its small positive values along the axis $c_1 = 0$. Also, r_{11} increases to its maximum value 0.60 in 3rd quadrant along $c_1 = 0$ when c_2 approaches the origin from its small negative values. In the intermediate quadrants 2 and 4, we observe that r_{11} remain constant with a vanishingly small negative value.

As c_1 and c_2 decrease in the first quadrant, from Figure 4e, we see that the cross-correlation $r_{12}(c_1, c_2)$ increases to its maximum value of 0.1 in the absence of the reactants. Furthermore, we find that r_{12} attains its minimum value of -0.1 as (c_1, c_2) approaches the origin from their small negative values. It is noteworthy that the behavior of r_{12} in 3rd quadrant is asymmetrical in its nature to that of the 1st quadrant. In this representation, there is no cross-correlation r_{12} in the 2nd and 4th quadrants, i.e., when (c_1, c_2) take their values with an opposite signature.

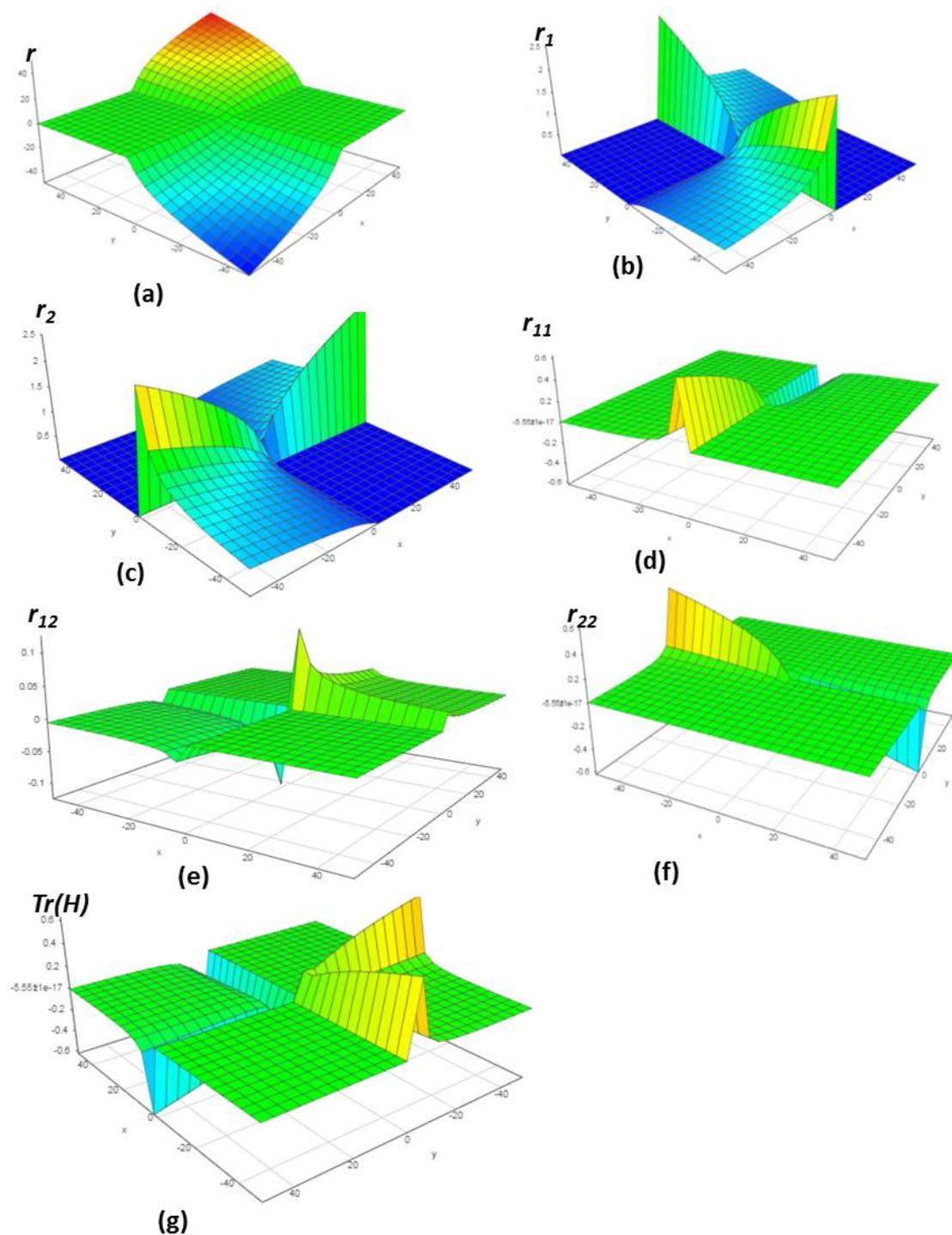


Figure 4. The fluctuation quantities as a function of the chemical concentrations $\{c_1, c_2\}$ for $m = \frac{1}{2}$ and $n = \frac{1}{2}$ plotted in the interval $-50 < c_1, c_2 < 50$ against (a) the rate $r(c_1, c_2)$, (b) flow $r_1(c_1, c_2)$, (c) flow $r_2(c_1, c_2)$, (d) capacity $r_{11}(c_1, c_2)$, (e) correlation $r_{12}(c_1, c_2)$, (f) capacity $r_{22}(c_1, c_2)$, and (g) trace $tr(H)$. (Note: with c_1, c_2 measured in mol/L on X and Y axis respectively, the other quantities on Z-axis are measured in the units as: $r \rightarrow \text{mol/L/s}$; $r_1, r_2 \rightarrow \text{s}^{-1}$; $r_{11}, r_{12}, r_{22}, tr(H) \rightarrow \text{mol}^{-1} \text{L s}^{-1}$; $\Delta \rightarrow \text{mol}^{-2} \text{L}^2 \text{s}^{-2}$).

Figure 4f provides a qualitative behavior of the capacity $r_{22}(c_1, c_2)$. Here, we find that it decreases in the first quadrant to its minimum value of -0.6 as c_1 approaches to its extreme value along the $c_2 = 0$. As observed in the case of the capacity $r_{11}(c_1, c_2)$, in this case we notice that r_{22} takes its

maximum value 0.6 in 3rd quadrant along the axis $c_2 = 0$ when c_1 decreases from the origin to its large negative values. In this case, we also see that r_{22} takes a small negative value in 2nd and 4th quadrants of the concentration plane.

From Figure 4g, the trace $tr(c_1, c_2)$ increases for decreasing value of c_1 for $c_2 = 0$ and it again increase for decreasing values of c_2 along the axis $c_1 = 0$. Similarly, in the 3rd quadrant, along the axis $c_1 = 0$, it decreases for increasing values of c_2 . Furthermore, it decreases along the line $c_2 = 0$ for increasing values of c_1 . Interestingly, the amplitude of the maximum and minimum values of the tr takes a constant value of 0.6. In the 2nd and 4th quadrants, there are no fluctuations in the tr for all non-zero values of c_1 and c_2 .

4.5. Chemical Reactions with Orders $(\frac{1}{2}, 2)$

In Figure 5a, it is demonstrated that the rate $r(c_1, c_2)$ varies largely for the concentration $c_1 > 0$ away from the axis $c_2 = 0$ for the orders $m = \frac{1}{2}$ and $n = 2$ of the reactants A and B respectively. Namely, as we move away from line $c_2 = 0$, it shows a parabolic behavior for a large c_1 with an amplitude of the order 2000. For a small c_1 , the rate r also shows a semi-parabolic behavior as a function of non-vanishing c_2 about the axis $c_1 = 0$. On the other hand, there are no real fluctuations in r for a negative value of c_1 . Indeed, it follows that r has a symmetric behavior about the line $c_2 = 0$.

In the above Figure 5b, we depict qualitative behavior of the flow component $r_1(c_1, c_2)$ for the order $m = \frac{1}{2}$ and $n = 2$ of the reactants $\{A, B\}$. For large positive or negative values of c_2 , we find that r_1 has a large amplitude of the order 800 about the axis $c_1 = 0$. Notice further that it has a symmetrical behavior along $c_2 = 0$, namely, it is a parabolic function of c_2 for a given value of c_1 . At a large absolute value of c_2 , it follows that r_1 attains a minimum value of 200 as c_1 reaches to its extreme positive and negative values. For all values of c_2 , there are no real fluctuations in r_1 for $c_1 < 0$. Furthermore, as we augment the absolute value of the concentration c_2 , the intensity of r_1 increases at any given $c_1 > 0$.

From Figure 5c, we find that the flow component $r_2(c_1, c_2)$ decreases as c_2 decreases in the interval $(-50, 50)$ while c_1 increases in the interval $(0, 50)$. For a large positive value of c_1 , the amplitude of r_2 takes a maximum value of 600 at $c_2 = 50$, while it takes a minimum value of -600 at $c_2 = -50$. For a large positive c_2 , it worth noticing that r_2 displays a semi-parabolic behavior along the line $c_2 = 50$ with a positive c_1 . However, for all $c_1 > 0$, we have an oppositely vertex parabola along the line $c_2 = -50$. In this case, as a real valued function, r_2 remains constant for all negative values of c_1 .

The variations of capacity $r_{11}(c_1, c_2)$ with various concentrations $\{c_1, c_2\}$ are plotted in Figure 5d for orders $1/2$ and 2 of the reactants A and B respectively. In this case, we see that r_{11} has a symmetric behavior about the line $c_2 = 0$. For the extreme values of c_2 , r_{11} takes a large negative amplitude of the order 200. Furthermore, it follows that r_{11} vanishes identically along the line $c_2 = 0$ for any values of c_1 . Moreover, for all values of c_2 , there are no fluctuations in r_{11} far away from the concentration axis $c_1 = 0$.

For given orders of $m = 1/2$ and $n = 2$ of the reactants A and B , the cross-correlation $r_{12}(c_1, c_2)$ of the chemical rate $r(c_1, c_2)$ is depicted in Figure 5e as a function of the concentrations c_1 and c_2 . Thus, for all c_1 , we see that r_{12} vanishes identically along the axis $c_2 = 0$. For $c_2 < 0$, we find that r_{12} takes negative values with its amplitude of the order 30 as c_1 approaches zero from its positive values. On the other hand, we observe a sudden fall in r_{12} for $c_1, c_2 < 0$. Similarly, in the region $c_2 > 0$, we notice a positive peak of the amplitude 30 in r_{12} . Interestingly, we see an amplitude of the order 20 corresponding to the sub-leading fluctuations in $r_{12}(x, y)$. Indeed, from Figure 5e, it is evident that there are no cross correlations far away from the axis $c_1 = 0$.

The capacity $r_{22}(c_1, c_2)$ plotted in Figure 5f for the products A and B of their orders $m = 1/2$ and $n = 2$. Thus, we see that r_{22} solely depends on c_1 . Here, we have a parabola with its vertex at $c_1 = 0$. As c_1 increases, we see that r_{22} indefinitely increases as well. It is clear that there are no possibilities of the occurrence of such a reaction for the concentration $c_1 < 0$ at this order.

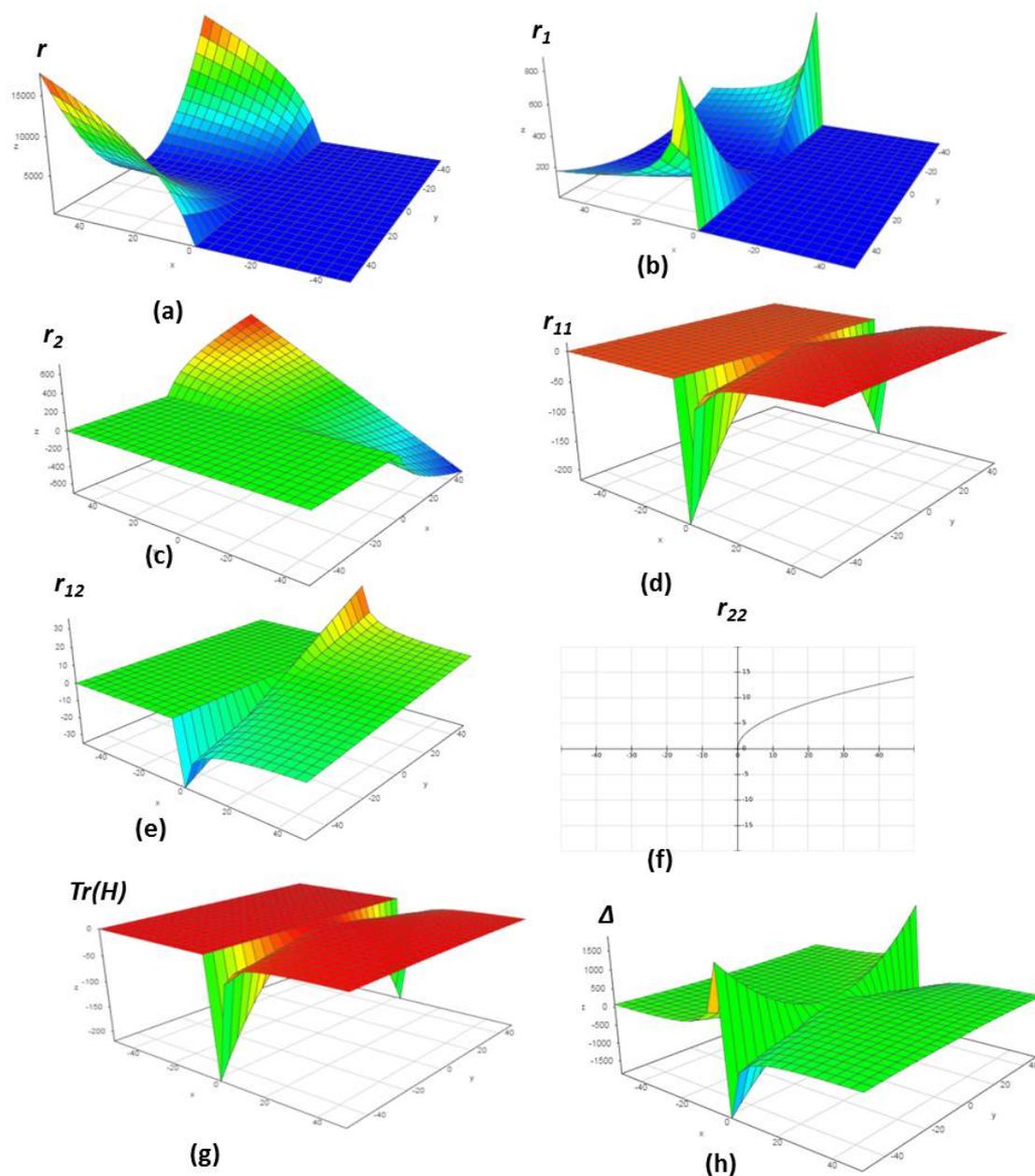


Figure 5. The fluctuation quantities as a function of the chemical concentrations $\{c_1, c_2\}$ for $m = \frac{1}{2}$ and $n = 2$ plotted in the interval $-50 < c_1, c_2 < 50$ against (a) the rate $r(c_1, c_2)$, (b) flow $r_1(c_1, c_2)$, (c) flow $r_2(c_1, c_2)$, (d) capacity $r_{11}(c_1, c_2)$, (e) correlation $r_{12}(c_1, c_2)$, (f) capacity $r_{22}(c_1, c_2)$, (g) trace $tr(H)$ and (h) determinant $\Delta(c_1, c_2)$. (Note: with c_1, c_2 measured in mol/L on X and Y axis respectively, the other quantities on Z-axis are measured in the units as: $r \rightarrow \text{mol/L/s}$; $r_1, r_2 \rightarrow \text{s}^{-1}$; $r_{11}, r_{12}, r_{22}, tr(H) \rightarrow \text{mol}^{-1} \text{L s}^{-1}$; $\Delta \rightarrow \text{mol}^{-2} \text{L}^2 \text{s}^{-2}$).

Figure 5g provides a qualitative behavior of the trace $tr(c_1, c_2)$ of the fluctuation matrix H for orders $m = 1/2$ and $n = 2$ of the species as a function of $\{c_1, c_2\}$. The trace appears to possess a similar qualitative behavior to the capacity r_{11} . Along the axis $c_1 = 0$, it has fluctuations of a negative amplitude of the order 200 for large positive and negative values of c_2 . For the all values of c_1 , $tr(H)$ has a symmetric behavior along the line $c_2 = 0$. There are no real fluctuations in $tr(H)$ for $c_1 < 0$. For all value of c_2 as c_1 increases, the trace $tr(H)$ increase from its large negative value to the order 200. Finally, it follows that $tr(H)$ vanishes asymptotically as c_1 takes a large value.

In Figure 5h, we depict the characteristic feature of the determinant $\Delta(c_1, c_2)$ of the fluctuation matrix with the orders $m = 1/2$ and $n = 2$. As a function of the concentrations $\{c_1, c_2\}$, we see that Δ takes a large positive amplitude of the order 1500 as we approach the axis $c_2 = 0$ from its negative values. For $c_1 > 0$, we observe a large negative amplitude of the order 1500 in Δ along $c_1 = 0$. Furthermore, for all values of c_1 , we find that Δ remains symmetric along the line $c_2 = 0$. Notice further that at a given value of $c_1 < 0$, the amplitude of Δ increases as we increase the value of $|c_2|$. In contrast to above, for all values of $c_1 > 0$, it follows that Δ decreases as we increase $|c_2|$. In addition, for all values of c_2 , the fluctuations in Δ of a given chemical reaction remains constant for all concentrations $\{c_1, c_2\}$ far away from the axis $c_1 = 0$.

4.6. Chemical Reactions with Orders (2,2)

The rate r of the chemical reaction of reactants A and B of their orders $m = 2$ and $n = 2$ is shown in Figure 6a over the concentrations $\{c_1, c_2\}$ in the rang $(-50, 50)$. In this case, we find an increasing value of r of the order 6×10^6 as c_1 and c_2 increase to large positive or negative values. We find that it remains symmetric about both axes $c_1 = 0$ and $c_2 = 0$ with its vanishing amplitude at the point $(0, 0)$. For a given value of c_1 or c_2 , the rate r emerges as parabola in either c_1 or c_2 respectively.

In Figure 6b, we demonstrate qualitative behavior of the flow component $r_1(c_1, c_2)$ as a function of the concentrations $\{c_1, c_2\}$ for the given chemical reaction with the reactants of the order 2. In particular, for a given non-zero c_1 , we find a parabolic behavior of r_1 as a function of c_2 . For a large c_2 , we observe respective positive and negative amplitudes of fluctuations of their orders 2×10^5 in r_1 for large positive and negative values of c_1 . For all $c_1 \neq 0$, it follows from Figure 6b that the fluctuations in r_1 remain symmetric along the axis $c_2 = 0$.

The characteristic behavior of the component $r_2(c_1, c_2)$ is shown in Figure 6c with respect to $\{c_1, c_2\}$ for the reacting species of the order 2. For all values of c_2 , we notice that r_2 has a symmetric behavior along the axis $c_1 = 0$. The maximum amplitude of r_2 is found to be of the order 2.5^5 as c_1 tends to its extreme values ± 50 for the value of $c_2 = 50$. Similarly, its minimum value of the order -2.5^5 is achieved at the concentration line $c_2 = -50$. Given any value of c_1 , it follows that r_2 has positive valued fluctuations for $c_2 > 0$ and negative valued fluctuations for $c_2 < 0$.

Figure 6d represent the capacity $r_{11}(c_1, c_2)$ of the reaction with products $\{A, B\}$ of their orders 2. This condition illustrates parabolic variations as the capacity $r_{11}(c_1, c_2) = 2c_2^2$ remain symmetric about the concentration $c_2 = 0$.

The variation of the cross-correlation $r_{12}(c_1, c_2)$ with respect to the concentrations $\{c_1, c_2\}$ of the species $\{A, B\}$ having orders 2 is shown in Figure 6e. In this case, we observe that r_{12} attained a maximum value of the order 10^4 for large positive values of $\{c_1, c_2\}$ and a minimum value of the order -10^4 for a large positive c_1 and negative c_2 , and vice-versa. Moreover, from Figure 6e, it follows that r_{12} has no variations when either c_1 or c_2 vanishes.

The capacity $r_{22}(c_1, c_2)$ of the products of their orders 2 as a function of the concentrations $\{c_1, c_2\}$ is equally represented by Figure 6d. Namely, the variations in r_{22} are similar to the capacity $r_{11}(c_1, c_2)$ with a replacement of c_2 to c_1 . Thus, we find parabolic variations in the capacity r_{22} with respect to the concentration c_1 , viz. we have a symmetric capacity $r_{22} = 2c_1^2$. In this case, it follows that r_{22} vanishes identically in the limit of $c_1 = 0$.

Figure 6f represents the qualitative nature of the trace $tr(c_1, c_2)$ over the concentrations c_1 and c_2 of species of the orders 2. Herewith, we observed that $tr(c_1, c_2)$ takes a maximum positive amplitude of the order 10^4 for large positive or negative values of $\{c_1, c_2\}$. As a matter of the fact, there are no fluctuations in the $tr(H)$ in the limit of either $c_1 = 0$ or $c_2 = 0$. Furthermore, at a fixed value of c_1 or c_2 , it follows that $tr(H)$ arises as a shifted parabola in c_2 or c_1 respectively.

In Figure 6g, we depict the determinant $\Delta(c_1, c_2)$ of fluctuations in the rate of the happening of the chemical reaction with products $\{A, B\}$ of their order 2. For given values of $\{c_1, c_2\}$, we find that Δ arises as an inverted image of the rate $r(c_1, c_2)$ with different values of its amplitude of fluctuations. Namely, as c_1 and c_2 take large positive or negative values, we notice that Δ takes a large negative

amplitude of the order 7×10^7 . Thus, there are no fluctuations in Δ when either of the concentration c_1 or c_2 vanishes. Finally, from Figure 6g, it follows that Δ remains symmetric about both the concentration axes $c_1 = 0$ and $c_2 = 0$.

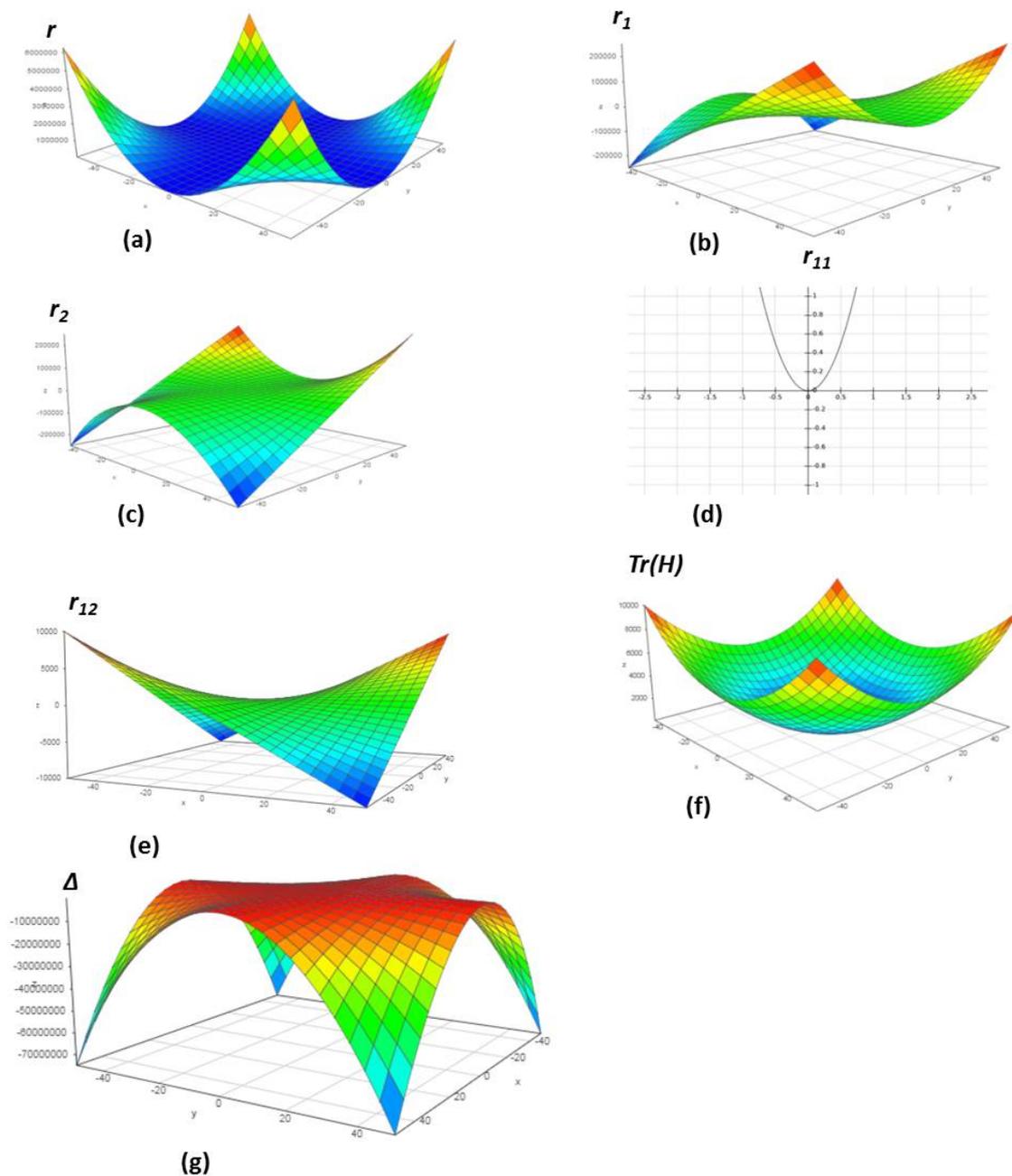


Figure 6. The fluctuation quantities as a function of the chemical concentrations $\{c_1, c_2\}$ for $m = 2$ and $n = 2$ plotted in the interval $-50 < c_1, c_2 < 50$ against (a) the rate $r(c_1, c_2)$, (b) flow $r_1(c_1, c_2)$, (c) flow $r_2(c_1, c_2)$, (d) capacity $r_{11}(c_1, c_2)$ (remains the same for the capacity $r_{22}(c_1, c_2)$ with the replacement of c_1 by c_2), (e) correlation $r_{12}(c_1, c_2)$, (f) trace $tr(H)$ and (g) determinant $\Delta(c_1, c_2)$. (Note: with c_1, c_2 measured in mol/L on X and Y axis respectively, the other quantities on Z-axis are measured in the units as: $r \rightarrow \text{mol/L/s}$; $r_1, r_2 \rightarrow \text{s}^{-1}$; $r_{11}, r_{12}, r_{22}, tr(H) \rightarrow \text{mol}^{-1} \text{L s}^{-1}$; $\Delta \rightarrow \text{mol}^{-2} \text{L}^2 \text{s}^{-2}$).

5. Verification of the Model

In this section, following the fact that the rate of a reaction offers valuable guidelines in modeling chemical interactions [23], we provide fluctuation theory analysis of equilibrium formation under variations of the rate and order of reactants. Namely, given an arbitrary chemical rate r , we discuss equilibrium formation as the function of the concentrations $\{c_1, c_2\}$ and partial orders $\{m, n\}$ of the reactants $\{A, B\}$ respectively. The formation of the chemical equilibrium can be represented as



As per the analysis as in the previous section, for any positive concentrations c_1 and c_2 of the reactants A and B , we see that the stability of the equilibrium largely depends on the partial orders m and n . Namely, we find that the determinant Δ takes a positive value for all m and n satisfying $mn(1 - m - n) > 0$. Similarly, for all m and n , the capacity r_{11} takes a positive value wherever we have $m(m - 1) > 0$. In this concern, a comparative analysis of the equilibrium with the reaction rate r with respect to variations of the orders m and n is summarized in the Table 1.

Table 1. A comparative analysis of the stability of the equilibrium as a function of the rate r with respect to the orders m and n of the reactants.

SN	m	n	$\textcircled{O} = m + n$	Δ	r_{11}
1	0	0	0	0	0
2	1	0	1	0	0
3	0	1	0	0	0
4	1	1	2	-	-
5	1	2	3	-	-
6	2	1	3	-	-
7	2	2	4	-	-
\vdots	\vdots	\vdots	\vdots	\vdots	\vdots

In Table 1, \textcircled{O} is the overall order of the reaction. Thus, for $\Delta > 0$, we find that a stable equilibrium is formed when we have either r_{11} or r_{22} is positive. The equilibrium will be unstable when the rate reaches its maximum, i.e., we have either r_{11} or r_{22} is negative. On the other hand, we need a refined analysis when either r_{11} or r_{22} vanishes identically. As per our analysis, a new matter will be formed when we have $\Delta < 0$. In the case, when m and n are even, the factor $c_1^{2m-2}c_2^{2n-2}$ of Δ does not change its sign. Therefore, when the total order $m + n < 1$, the reaction capacity r_{11} is positive if we have either $m < 0$ or $m > 1$. However, we anticipate an improved analysis for the either of the partial orders $m, n = 0, 1$ of the reactants A and B . It is worth emphasizing that the sign of Δ depends only on the orders of A and B . For the zeroth-order reaction, i.e., $m + n = 0$ the sign of Δ varies as the product of m and n . Further when either of the reactants A or B has order zero, it follows that the determinant Δ vanishes identically. Similarly, for the first-order reaction i.e., when $m + n = 1$, we have $\Delta = 0$. In such cases, we need an improved analysis. Such an investigation we leave open for a future study.

For a second- or higher-order reaction, i.e., when $m + n \geq 2$, we notice that the sign of Δ varies as the negative of the product of the partial orders m and n of the reactants A and B . Thus, for all $m, n \geq 0$, we have a negative Δ , wherefore new products are formed. On the other hand, when either m or n takes a negative value, we have a different result than the above, i.e., a new product is formed when either r_{11} or r_{22} takes a negative value. In this concern, our analysis takes an account of the fractional- and negative-order reactants and their equilibrium formation. This is because our analysis is valid for any real valued concentrations c_1 and c_2 and any real values of the partial orders m and n of the reactants A and B .

In the sequel, we concentrate on the nitrogen-based reactants, organic reactions, and catalytic oxidation of Co-H₂ mixtures.

5.1. An Inorganic Equilibrium Formation

In this subsection, we offer an experimental prediction of our analysis for an inorganic reaction, see [31] in the light of the reaction mechanism and chemical kinetics of inorganic reactions towards the experimental and theoretical studies. To do so, let us consider an equilibrium between ammonium and nitrite ions [31,32] as a nitrogen-based reaction with the reactants as $A = NH_4^+$ and $B = NO_2^-$, i.e., the reaction of ammonium and nitrite ions in water at 25 °C as per the equilibrium



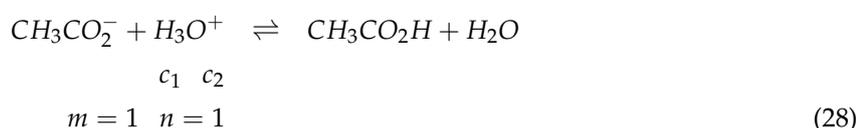
Thus, the rate of the reaction is given by

$$r = [NH_4^+][NO_2^-] \quad (27)$$

In this case, we see that the overall order of the reaction is $m + n = 2$. Thus, for all c_1 and c_2 , we have $\Delta < 0$, and therefore our analysis predicts formation of new products via the reaction of the reactants NH_4^+ and NO_2^- .

5.2. An Organic Equilibrium Formation

To illustrate our analysis for organic reactions let us consider hydrolysis of the CH_3CO_2H molecules. As per the Bronsted-Lowry theory [33,34], this reaction is mediated by the following equilibrium:



Thus, the rate of the above reaction is given by

$$r = [CH_3CO_2^-][H_3O^+] \quad (29)$$

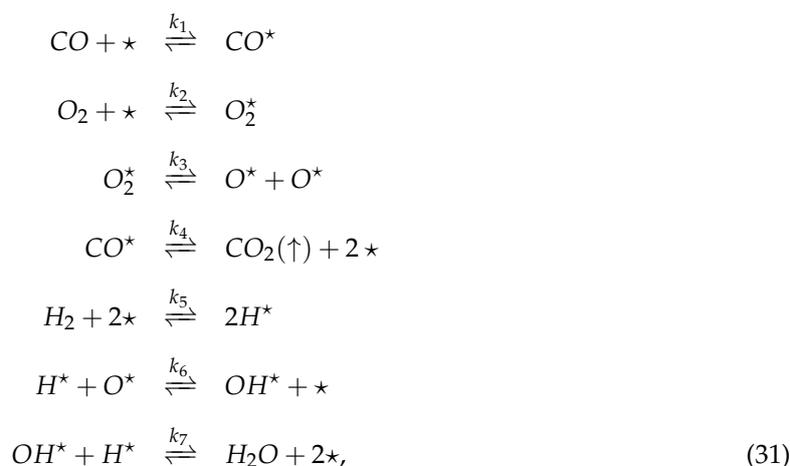
Here, it is known [33,34] that the partial order of the reactants $CH_3CO_2^-$ and H_3O^+ are $m = 1$ and $n = 1$ respectively. Thus, the overall order of the reaction is $m + n = 2$. As in the previous case, in this case also for all c_1 and c_2 , we observe that the determinant Δ takes a negative value, whereby the new products CH_3CO_2H and H_2O are formed. In the sequel, we discuss an oxidation of CO – H₂ mixtures in presence of Pt as the catalyst.

5.3. A Catalytic Oxidation of CO – H₂ Mixtures

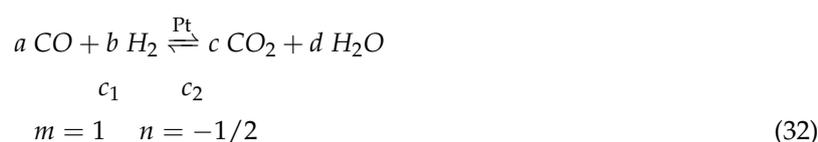
In the sequel, we provide verification of our results for the oxidation of CO – H₂ mixtures, i.e., an equilibrium with catalyst Pt to make the oxidation of CO – H₂ mixtures [35]. Consider the general oxidation of a mole of CO with b mole of H₂ as per the equilibrium



forming c mole of CO₂ and d mole of H₂O. The equilibrium takes place [35] with the following intermediate steps



where the $k_i, i = 1, 2, \dots, 7$ are the respective rate constants of the above intermediate reactions. In this case, it is found [35] that the order of the reactants, viz. CO and H_2 take their respective values as $m = 1$ and $n = -1/2$ respectively. Thus, the oxidation is described as per the equilibrium



Thus, the associated rate of the above oxidation reaction reads as

$$r = [\text{CO}][\text{H}_2]^{-1/2} \tag{33}$$

Therefore, the overall order of the reaction is $m + n = 1/2$. Herewith, we see that the determinant Δ takes a negative value. Thus, in this case, new matters are formed, that is, a catalytic oxidation of $\text{CO} - \text{H}_2$ mixtures in presence of Pt results into the formation of CO_2 and H_2O .

6. Future Scope of the Work

In this section, we offer highlights and applications of the fluctuation theory analysis towards reaction mechanisms, donation of a proton, titration analysis, fall of the proton, Bronsted-Lawry equilibrium, buffer capacity, pH value and the issues of acid raining as below.

6.1. Proton Donor-Acceptor Equilibrium

An optimized formation of the proton donor-acceptor equilibrium plays an important role in various chemical industries, see [36] for molecular interactions and electron donor-acceptor complexes in the light of the proton affinity. Thus, we offer a general method to describe such an acid-base equilibrium of an arbitrary acid HA with its conjugate base A^- . Depending on the nature of A , the electric charges of the reacting species is decided. However, the base A^- always possesses a negative charge comparison to the acid HA . Therefore, an acid-base system consists of at least a pair of species governing the equilibrium of chemical reactions.

To study acid-base equilibrium in a quantitative way, there are two problems that come into picture. Firstly, an inability of the proton to exist independent in a solution is a major issue. Chemically, this makes an inadequate prediction of the acid or base to donate or accept a proton individually. To overcome this situation, the acid-base system must be compared and evaluated up to an extent at which the base and acid compete for combining with the proton. Thus, our proposed fluctuation

theory-based optimization of the chemical rate is anticipated to precisely illustrate the formation of an equilibrium.

The second pitfall is the dual nature of water which exists both as the acid and base, see [37] for the corresponding vibrational spectroscopic evidence. In general, most experiments on the acid-base chemistry involve the presence of aqueous solution. Therefore, for dealing with an acid HA in the aqueous solution, it is necessary to consider an acid with its conjugate base to form an acid-base pair. An optimized formation of such a pair is in the future scope of this work.

6.2. Fall of the Proton

As far as the fall of the proton is concerned, an acid is known as the proton donor with respect to a base that can accept the proton. However, a base accepts a proton, if there exists an acid which can donate a proton in a given aqueous solution. In general, there are energetic conditions that must be fulfilled in order that a base accepts a proton, involves a lowering in its free energy compared to the corresponding acid, see [38]. Thus, a given acid-base reaction takes place, if the proton released from the acid fall to a lower free energy level. Indeed, acids act as a source of the protons, which move to a base acting as a sink.

For the aqueous solutions, the water turns out to be the best sink for an acid, as it normally loses protons to H_2O to form H_3O^+ as the strongest acid [39]. This is termed as the leveling effect which plays an important role in connection with the fall of the protons. All strong acids that are said to be 100% dissociated in an aqueous solution, if they possess a large equilibrium constant, therefore they are bound to endure a fall in the respective free energy. In this concern, various strong acids, e.g., HCl , H_2SO_4 and others encounter H_2O solely via an existence of the H_3O^+ , see [12] for experimental perspectives. Energetically, this follows because there exists a definite capacity of H_2O to act as a proton sink by maintaining a non-vanishing free energy [38].

On the other hand, a weak acid, e.g., HCN does not undergo dissociation sharply without the presence of an energy source. This happens because HCN has a positive free energy, which the proton must attain for its dissociation. Concerning a titration with such weak acids, we know [40] that the hydroxyl ion OH^- can equally act as a proton sink. Namely, upon the addition of a strong base, e.g., $NaOH$, KOH , an acid lowers the free energy of the total configuration as the fall of its protons H^+ from a relatively higher energy state into OH^- of the base according to the reaction



Therefore, a titration could be realized as the mechanism to obtain a lower free energy sink that converts the acid by draining off the protons into their respective conjugate bases. As mentioned before, the pH of an arbitrary solution is generally defined based on the available hydrogen ion concentration on the logarithmic scale. Based on the above energy constraints, the pH scale specifies an accessibility of protons in the solution, which incidentally reflects the capacity of the chosen solution to supply more protons to a base. To illustrate our optimization analysis, we may consider a mixture of weak acid-base systems, e.g., various biological fluids and natural water sources such as ocean, see [41] for the associated protides. In such cases, existing protons jump into the lowest possible free energy state to form a chemical equilibrium.

Initially, this begins by accommodating a lowest energy sink, therefore filling up the succeeding energy levels. This process continues until all the proton vacant sites in a given base are filled with an optimum cutoff energy, which largely depends upon characteristics of the considered acid. This analysis is left open for a future research. Chemically, by various thermal excitations, the highest protonated species donate protons to H_2O to form H_3O^+ whose concentration largely depends on concentrations of different species. In short, an optimized amount of H_3O^+ concentration enables us in defining the equilibrium pH of the corresponding solution. In other words, a pH measurement points out the relative free energy of protons required to preserve the highest protonated species in

their acid forms [12,38]. Herewith, it is worth emphasizing that our discussion can be applied for the determination of the proton free energy by *pH* scale measurements.

6.3. Buffer Capacity

In the light of quantitative treatments of chemical equilibria, we focus on acid-base phenomena arising from the hydronium ion [39]. In this aspect, a titration can happen in non-aqueous solvents, as well. Such acid-base systems came into the existence by independent investigations of Bronsted and Lowry in 1923, see [39] for related fundamentals and their historical accounts. Subsequently, in both the aqueous and non-aqueous solvents, an acid can be regarded as the species that can donate a proton and the corresponding base as the species that can accept it. Examples of non-aqueous solvents include alcohol, benzene, ether, carbon tetrachloride, acetone, and other organic solvents, while the liquid ammonia, disulfide and sulfuric acid arise in the category of the inorganic solvents. In this regard, for a given acid *HA* and base *B*, our optimization analysis is explained by the following chemical equilibrium.



From the perspective of the Bronsted and Lowry [39], the notion of a chemical equilibrium is based on the proton itself and not on the hydronium ion, whereby one finds a solvent independent of the chemical equilibrium. Specifically, because of an accepting behavior of the proton H^+ of A^- , it acts as a base as above in the first reaction as in Equation (35). However, in the second reaction as in Equation (35), BH^+ behaves as an acid since it donates a proton H^+ to the base *B*. This yields the following Bronsted-Lowry acid-base [39] chemical equilibrium.



Essentially, as per the above acid-base pair having a deficit of the proton H^+ as in Equation (36), an optimized conjugate acid-base pair is anticipated to arise via our fluctuation theory analysis. Indeed, the above-mentioned Bronsted-Lowry definition of the acid-base pair does not state the type of the charges present in either of the acid or base, i.e., the chemical equilibrium formation has nothing to do with electronic charges of the species and it is rather independent of their ionization properties [39]. In short, we may recite the formation of an acid-base equilibrium by stating that an acid has one more positive charge than its corresponding conjugate base. This offers a perspective application of our proposal to pharmaceutical systems and their thermodynamic characterization. In the highlight of the same, it is worth anticipating that an optimized chemical equilibrium is formed by the acid CH_3CH_2COOH with its conjugate base $CH_3CH_2COO^-$ by exchanging a proton H^+ .

To perform chemical composition analysis [42], the titration offers a conventional laboratory tool to calculate unknown concentration of a set of given chemical species. Thus, among various types of titration methods, we focus on an optimized acid-base titration, which anticipated to emerge as an important topic of current research. Namely, in a given solution, our proposition involves the concept of an optimal neutralization of an acid-base pair. Here, the concentration of the chosen acid or base is calculated by the addition of the respective base or acid with their known concentrations. In this case, we can add a *pH* indicator to the solution to determine the optimal point of the solution by observing a change in its color.

Therefore, our method support that the buffer capacity arises as the resistance to *pH* change of a solution. Namely, given an acid with its conjugate base, the buffer capacity plays a vital role in determining the relative dissociation, which follows via Châtelier principle [43,44]. In general, an aqueous solution consists of a weak acid and its conjugate base or vice-versa, therefore the formation of a buffer solution. One of the main characteristics of buffer solutions is to maintain a steady *pH* value upon an addition of a strong acid or base. Thus, the *pH* buffers arise as the best alternatives to

maintain a constant pH value of chemical solutions. In the setup of Bronsted and Lowry theory, viz. Equation (36), buffer solutions acquire an optimized resistance to pH change due to the formation of a chemical equilibrium between the weak acid HA and its conjugate base A^- . Thus, for a given buffer solution, its buffer capacity yields a quantitative measurement for determining the optimal resistance of pH change [12,38] upon an addition of hydroxide ions. Such issues we leave open for future research and developments.

6.4. Acid Raining

In the sequel, we focus on the nature of an optimized rate via the acid-base chemistry. In general, we are interested in chemical reactions which are optimally formulated in the light of the acid-base chemistry. Acid-base reaction can be described as the reaction between hydrogen ions with other electrically charged species or neutral ones. The reaction between acid and base is considered to be a reversible reaction. This means, the product obtained could react among themselves to give the reactant back. In the light of acid-base chemistry, this idea is the root cause towards an optimized chemical equilibrium formation [26] in the realism of chemical kinetics.

Various environmental problems arise because of the acid raining, see [45] for environmental problems and their existing remedies. Notice that acid rain refers to presence of acid in the rain water due to effects of pollutants exhausted into the atmosphere such as automobiles and factories. In this regard, sulfur dioxide and nitrogen oxides accounts for the main pollutants responsible for the cause. When such gaseous species react with the water and oxygen molecules present in the atmosphere, it results in the formation of acids such as sulfuric acid and nitric acid in rain water. Thus, acid rain creates various damage such as corrosion of metals and their salt hydrates [46], damage to buildings [47], etc. Thus, one finds diverse effects of CO_2 water. It is reported that the amount of CO_2 in the atmosphere is increasing day by day due to the burning of fossil fuels in the presence of oxygen. The above-mentioned CO_2 tend to dissolve in the ocean water by forming carbonic acid. Thus, to safeguard the natural resources, an optimized emission of CO_2 -based species falls in the domain of the future scope of this research.

7. Summary and Conclusions

In the present research, we have thoroughly examined the optimized formation of chemical equilibria via the fluctuation theory. Our consideration was based on the formation of an intermediate state of products whose energy crosses the potential barrier to form the final state. Various concentrations of reacting species in a given chemical reaction can fluctuate. At a constant temperature, fluctuations in the rate are characterized by a weighted product of concentrations of the reacting species with different orders. We observed that the stability of the equilibrium depends mainly on these parameters of the reactants.

As far as the fluctuation theory is concerned, our analysis is based on the statistical and thermodynamic factors that determine the characteristic properties of a given chemical reaction. We have provided fluctuation theory perspective towards the formation of chemical equilibria of arbitrary orders. Here, the progress of a chemical reaction is governed by a step by step infinitesimal modification of the law of mass action. This is realized by varying the reaction rate governing the changes in a given chemical reaction. It is worth mentioning that the above equilibrium is not immediately achieved, but it arises as a collective phenomenon. An apt formation of such equilibria is the subject matter of this research.

Given a binary component chemical reaction, we have computed the flow components, chemical capacities, chemical correlation, and associated fluctuation quantities concerning the global stability of an equilibrium. Under fluctuations of the reactant's concentrations, we find that the equilibrium is formed when either one of the orders of the reactants vanishes or either of their concentrations vanishes. The chemical concentration capacities of the components are calculated to describe the local stabilities of the equilibrium. The correlation between the components is obtained as the mixed

second-order derivative of the rate with respect to the concentrations. To be precise, we find that the local system stability requires the order of the reactants to be either negative or larger than the unity.

On the other hand, for a binary component reaction, the global stability analysis is performed by introducing a symmetric matrix with its diagonal components as the chemical capacities and off-diagonal components as the chemical correlation. The global stability of the system requires the positivity of a factor over the orders of the reactants that we have examined both quantitatively and qualitatively. For reactants of the order less than two, we infer from our observations that the fluctuations are mostly originating at the points where either of the concentration approaches zero value. However, for the reactants of second orders, we find a global instability as the corresponding determinant of the fluctuation matrix takes a large negative value of the order 10^7 . In addition, for a pair of reactants of their orders of the same sign, the reaction is globally stable when the sum of their orders is less than unity. This well coincides with the observations for the reactions of the orders $(-1, -1)$ as in Figure 1. The instability gets introduced as the orders gradually change to their values $(-1, 1/2)$, $(-1, 2)$, $(1/2, 1/2)$, $(1/2, 2)$ and $(2, 2)$ as depicted in Figures 2–6 respectively.

Subsequently, we have offered verification of our model. Following the above theory, we focus on stability structures of the chemical equilibrium formation of the carbon materials under variations of concentrations of the participating species while the other parameters of the reaction are held fixed. To understand the formation of a chemical equilibrium as a statistical sample, we have introduced simultaneous fluctuations over active masses, i.e., the concentrations of reacting species with the associated rate as an embedding function. This offers the optimization properties of a given chemical equilibrium and thus the formation of products. Thus, we have discussed the stability of chemical equilibria and formation of products involving carbon materials such as an organic reaction and a catalytic oxidation of $CO - H_2$ mixtures in presence of Pt and other inorganic reactions, as well.

Our proposition can be understood based on macroscopic observations governing the forward and reverse reactions. Namely, a chemical equilibrium arises as an average of the microscopic concept that takes place when a given amount of chemical species remains same. The global stability of an equilibrium originates via collisions between the molecules, therefore the dissociation of the reacting species. Furthermore, in the vicinity of equilibrium, the fluctuation analysis can be exploited by varying either the forward rate over the concentration of the reactants, or the backward rate of the products. This is because the equilibrium constant reads as the ratio of the rate constants of the forward reaction to that of the backward reaction. It is evident from our observations that a chemical reaction never proceeds until its end; instead, it attends an equilibrium state when the available amount of participating species in the reaction does not fluctuate. From the above perspectives, we find that all the fluctuation quantities vanish identically for a zeroth-order chemical reaction, except its rate. In addition, we have classified all possibilities concerning the stability of the equilibrium formed by a given pair of reacting species with different orders.

In general, the fluctuation theory-based chemical equilibrium can equally depend on the temperature, pressure, volume, and chemical compositions of the reacting species, as well. This can provide further possibilities for research. Indeed, our proposal can be generalized for arbitrary chemical reactions with finitely many reactants and products, as well. Other directions include unification of the fluctuation theory analysis with the physical state of the reacting species, reaction temperature and use of a catalyst. This depends on the collision frequency, phase of reactants and random thermal motion of molecules to form a new state. Also, the temperature variations enhance the reaction rate, namely, they increase the collision frequency between the molecules of interacting species.

Finally, we anticipate future scope of our work in the light of the acid-base chemistry, fall of the protons, thermal excitations, formation of hydronium ions, buffer capacity as well as industrial implications towards the thermodynamic properties of pharmaceutical configurations, formation of buffer solutions, corrosion of metals, protection of building, environment and ecosystems, and pollutant exhaust management for automobiles and factories. Moreover, it worth mentioning that a

chemical equilibrium requires an understanding of the electron affinity and reactivity of the species, as well. Such investigations we leave open for future research and developments.

Author Contributions: Conceptualization, B.N.T. and S.C.K.; Data curation, B.N.T.; Formal analysis, B.N.T.; Investigation, B.N.T., S.C.K., N.M. and S.B.; Methodology, B.N.T. and S.B.; Project administration, N.M.; Resources, S.C.K. and N.M.; Supervision, S.B.; Validation, B.N.T. and S.C.K.; Visualization, B.N.T., S.C.K. and S.B.; Writing—original draft, B.N.T. and S.C.K.; Writing—review & editing, B.N.T., S.C.K., N.M. and S.B.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

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