THE STEADY STATE IN CHEMICAL KINETICS: CHARACTERIZATION IN TERMS OF THE FIRST AND SECOND STEADY STATE RATE LAWS

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ABSTRACT

Chemical reaction rate laws facilitate the design and control of chemical processes. In turn rate laws are often arrived at after assumption of the steady state approximation, whereby the steady state is characterized by the First State Rate Law, defined for reactions involving very reactive intermediates, by assuming that the concentrations of the chemical species, involved as very reactive intermediates can be eliminated by equaling their rate of formation to their rate of disappearance, in which case the concentration of the intermediate can be assumed to be constant. In this communication theoretical evidence, as well as experimental evidence from the literature, is presented showing that the steady state can also be characterized by the Second Steady Rate Law based on pseudo-zero order kinetics. In addition, equations are derived showing that the concentration of the steady state intermediate can be expressed in terms of the initial concentration of the reactant, and that the steady state approximation is valid within the kinetic limits bounded by truly first (or second) order rate laws and the truly equilibrium rate law. The article has the following highlights: 1. The steady state in chemical kinetics is defined by the First Steady State Rate Law in terms of the constancy of the concentration of the reaction intermediate, and by the Second Steady State Rate Law in terms of the constancy of the rate of reaction. 2. Both First and Second Steady State Rate Laws can be used as bases for assuming the steady state approximation. 3. The limits of the validity of the steady state approximation are defined. *[African Journal of Chemical Education—AJCE 14(1), January 2024]*

INTRODUCTION

Knowledge about chemical kinetics enables us to understand, design, and control chemical reactions in the laboratory, to understand and explain the actions of enzymes in biochemical systems including the human body, to design and control chemical processes in oil refineries and other chemical industries [1-3], as well as to describe drug absorption and metabolism in the human body [4]. The most important parameter in the study of kinetics of chemical reactions is the rate law or rate equation, from which we can infer the rate constant and the stoichiometry of the reaction [1]. In the derivation of the rate law corresponding to the mechanism of a complex chemical reaction it is necessary to express the concentrations of all intermediates in terms of the concentrations of the primary reactants, because intermediates are transient.

This often requires making some assumptions [5-11]. One of the most commonly employed assumption is the steady-state approximation [5-11], first proposed by Bodenstein, and independently by Chapman and Underhill in 1913 for the photochemical gas phase reaction between chlorine and hydrogen [12-14]. The resulting stationary-state method was further developed by Christiansen, Herzfeld and Polanyi [15-19]. According to the stationary-state method, the concentrations of the chemical species, involved as very reactive intermediates (I) can be eliminated by equaling their rate of formation to their rate of disappearance, in which case the concentration of the intermediate can be assumed to be constant [15], and hence:

$$\frac{dI}{dt} = 0 \tag{1}$$

Equation 1 holds for reactions involving very reactive intermediates, since for very reactive intermediates, the rate limiting step is the formation of the intermediate, hence the rate of disappearance of the intermediate is necessarily equal to the rate of its formation, in which case the concentration of the intermediate should remain constant. Thus, in this case, *Equation 1 rigorously defines the steady state in chemical kinetics* with respect to the constancy of the concentration of very reactive intermediates and constitutes the *first steady state rate law*. Thus, the *steady state approximation,* as proposed by Bodenstein and by Chapman and Underhill [12-14], assumes the *first steady state rate law.*

The steady state approximation is invoked when an overall chemical reaction consists of a series of consecutive elementary steps. Such reactions are encountered in several chemical kinetic systems, well-known examples of which include acid-base catalysis, enzyme catalysis, nucleophilic and electrophilic substitution reactions, quasi-unimolecular reactions, and free radical reaction [6]. The steady state approximation is also used in many cases for which the first steady state rate law is not applicable, which is often difficult to justify. Although the validity of the steady state approximation in such cases has been the subject of debate since it was first proposed by Bodenstein and Chapman and Underhill in 1913 [12-14], and has been discussed by several authors [7-11,20-27], there is no consensus as to the conditions for a steady state in chemical kinetics, the validity of the steady state assumption, its applicable time regime, or its accuracy [10,23,27,28], It is therefore important that students of chemistry, especially at undergraduate level, understand (a) what is meant by the *steady state* in chemical kinetics, (b) the *steady state approximation* and its validity, its time regime of application and the central role it plays in chemical kinetics.

This paper addresses the difficulties currently encountered with respect to the conditions for a steady state in chemical kinetics, the validity of the steady state assumption, and its applicable time regime. It is shown that (a) the steady state can also be characterized in terms of the *second steady state rate law* based on pseudo zero-order kinetics, (b) the steady state concentration of the intermediate can be expressed in terms of the initial concentration of the reactant, and (c) the steady state approximation is applicable within the kinetic limits represented by the truly first (or second) order rate law and the truly equilibrium rate law. Empirical evidence from the literature is presented in support of the validity of the *second steady state rate law*.

THEORETICAL

Consider the reaction:

$$A \leftrightarrows A^{‡} \rightarrow P \qquad (2)$$

The elementary steps for this reaction are shown in Table I:

Table I. Elementary steps for a first order reaction

Step	Elementary reaction	Rate constant	Transformation
1	$A \rightarrow A^{‡}$	k_1	Activation ($A^{‡}$ = activated complex)
2	$A^{‡} \rightarrow A$	k_{-1}	De-activation
3	$A^{‡} \rightarrow P$	k_2	Reaction (P = products)

The rate of formation of $A^{‡}$ is given by:

$$\frac{d[A^{‡}]}{dt} = k_1[A] \qquad (3)$$

The rate of disappearance of $A^{‡}$ is:

$$-\frac{d[A^{‡}]}{dt} = [A^{‡}](k_2 + k_{-1}) \qquad (4)$$

If $-\frac{d[A^{‡}]}{dt} = \frac{d[A^{‡}]}{dt}$

$$[A^{‡}] = \left(\frac{k_1}{k_{-1}+k_2}\right)[A] \qquad (5)$$

Substituting Equation 5 into Equation 1,

$$\frac{d[A^{\ddagger}]}{dt} = \frac{d}{dt}\left(\frac{k_1}{k_{-1}+k_2}\right)[A] = 0 \qquad (6)$$

Equation. 6 is only possible if [A] is constant. This is only true for equilibrium reactions at equilibrium and can only be approximately obeyed for other reactions. The question to be answered is: Under what circumstances, other than equilibrium conditions, is Equation 6 valid?

Note, $[A] = [A]_o - \Delta[A]_t$, where $[A]_o$ = initial concentration of A, and $\Delta[A]_t$ is the change in the concentration of A at any time t. When t = 1, i.e., in unity time of reaction,

$$[A]_{t=1} = [A]_o - \Delta[A]_{t=1}$$

When $[A]_o \ll \Delta[A]_{t=1}$

$[A]_{t=1} = [A]_o$, a constant. (7)

From TABLE I,

$$\frac{dP}{dt} = k_2[A^{\ddagger}] \qquad (8)$$

In terms of $[A]_{t=1}$ and $[A]_o$, Equation 5 becomes

$$[A^{\ddagger}] = \left(\frac{k_1}{k_{-1}+k_2}\right)[A]_{t=1} = \left(\frac{k_1}{k_{-1}+k_2}\right)[A]_o \qquad (9)$$

Substituting for $[A^{\ddagger}]$ in Equation 8:

$$\frac{dP}{dt} = \left(\frac{k_1 k_2}{k_{-1} + k_2}\right)[A]_o = k_o, a\ constant \qquad (10)$$

where k_o is a zero-order rate constant.

A zero-order reaction implies a constant or linear rate of reaction, and under these conditions,

$$\Delta[A]_{t=1} = rate\ of\ reaction.$$

i.e., the steady state as defined by Equation 6 obtains when $\Delta[A]_{t=1} \ll [A]_o$, and is defined for the constancy of the rate of reaction or formation of reaction products. Equation 10 constitutes the *second steady state rate law* and obtains when the numerical value of the rate of reaction is insignificant compared to, or significantly smaller than, the numerical value of the initial concentration of the reactant. Thus, in essence the Second Steady State Rale law is in effect the Stationary-state hypothesis applied to the rate of reaction, i.e., the rate of reaction is “at all times much less than the numerical value of the concentrations of the reactants and products” [15]. This situation is most likely to be encountered with extremely slow reactions as measured by the rate of disappearance of the reactant.

Note Equation 10 can be written as

$$\frac{dP}{dt} = \left(\frac{k_1 k_2}{k_{-1} + k_2}\right)[A]_o = k_o = k_2 A^{\ddagger} \qquad (10)$$

Therefore

$$A^{\ddagger} = \frac{k_0}{k_2} = \left(\frac{k_1}{k_{-1}+k_2}\right)[A]_o \qquad (11)$$

i.e., $A^{\ddagger}$ is a constant related to $[A]_o$ by Equation 11.

Equation 11 limiting cases:

Limiting Case I: $k_{-1} \gg k_2$, i.e., the Second Steady State Rate Law limit:

$$A^{\ddagger} = K_{(A \rightleftharpoons A^{\ddagger})}[A]_o \qquad (12)$$

where $K_{(A \rightleftharpoons A^{\ddagger})}$ is the equilibrium constant for the $A \rightleftharpoons A^{\ddagger}$ reaction. Thus, beyond Limiting Case I, the reaction becomes an equilibrium reaction.

Limiting Case II: $k_2 \gg k_{-1}$, i.e., i.e., the First Steady State Rate Law limit.

$$A^{\ddagger} = \left(\frac{k_1}{k_2}\right)[A]_o \qquad (13),$$

Or

$$k_1[A]_o = k_2 A^{\ddagger} \qquad (14\ ),$$

i.e., rate of formation of the intermediate is equal to its rate of disappearance as proposed by Bodenstein [12,13] [9,10], and Chapman and Underhill [14] in 1913.

Equation 14 is a First order reaction.

In between Limiting cases I and II, $A^{\ddagger}$ is given by Equations. 9 and 11.

Differentiation of Equations 11, 12 and Equation 13 lead to the First Steady State Rate Law thus:

$$\frac{dA^{\ddagger}}{dt} = 0 \qquad (1)$$

The only assumptions made in arriving at Equations 10 to 11 are that

1. The rate of formation of reaction intermediates is equal to the rate of their disappearance as proposed in 1913 by Bodenstein [9,10] and Chapman and Underhill [14],
2. $\Delta[A]_{t=1} \ll [A]_o$, i.e., the numerical value of the rate of reaction is insignificant compared to, or significantly smaller than, the numerical value of the initial concentration of the reactant, consistent with the Stationary-state hypothesis for chain reactions [15].

EXPERIMENTAL APPROACH

While it is difficult to demonstrate the First Steady State Rate Law experimentally, the Second Steady State Rate Law is easily demonstrated experimentally by measuring the rate of disappearance of the reactant or the rate of formation of reaction product, which should be zero order. The resulting regression curve should exhibit high linearity confirmed by a high regression coefficient. Experimental evidence for the Second Steady State Rate Law is available in the literature as discussed below.

RESULTS AND DISCUSSION

Chemical degradation of organic substances

Linear rates of reaction were confirmed experimentally in the case of chemical degradation of organic compounds (e.g., hydrolysis) by Zaranyika et al. [29-31], when aqueous solutions of tetracycline, oxytetracycline, doxycycline and chlortetracycline were studied under dark conditions and the residual concentrations of the antibiotics monitored as a function of time.

Photochemical degradation of organic substances

The existence of linear rates of reaction have also been confirmed experimentally in the case of photochemical degradation of organic compounds by Collin et al. [32]. Collin et al. obtained linear rates of photochemical degradation when aqueous suspensions of particulate black carbon (BC) and aqueous solutions of BC derived from arctic biomass were exposed to sunlight, and the partial or complete mineralization was quantified as photochemical CO_2 emission and O_2 consumption relative to dark controls. Similarly, linear rates of photochemical degradation were also confirmed experimentally when aqueous solutions of tetracycline, oxytetracycline, doxycycline and chlortetracycline were exposed under natural sunlight conditions and the residual concentrations of the antibiotics monitored as a function of time relative to dark controls (by Zaranyika et al. [29-31].

Microbial degradation of organic substances

The existence of linear rates of reaction were confirmed experimentally in the case of microbial degradation of pesticides by Schmidt et al. [33]. Schmidt et al. conducted microbial degradation experiments with different initial pesticide concentrations and microbial populations and showed that the degradation was zero-order with respect to pesticide concentration.

Multi-phase pseudo-zero order rate law

Current formalism for the dissipation of persistent organic pollutants in the terrestrial environment assumes that dissipation follows first order kinetics, although Edwards in 1966 had observed that the dissipation of DDT in the environment rarely conforms to first order kinetics and proposed that the dissipation is instead composed of 2 to 4 linear portions [34]. The existence of multi-phase linear rates of dissipation has now been demonstrated by Zaranyika et al. [35], who recently showed that the dissipation curves of DDT in several tropical soil environments can be resolved into biphasic or triphasic linear dissipation profiles and attributed this to the existence of different speciation forms of the insecticide in the medium. Several other incidences of the existence of multi-phase linear rates of dissipation have been reported in the literature for other organic environmental pollutants including organochlorine insecticides (endosulfan I and II) [36], organophosphate herbicides (glyphosate and dimethoate) [37,38], and tetracycline antibiotics (oxytetracycline, doxycycline, chlortetracycline and tetracycline) [29-31]. The assumption of the steady state pseudo zero-order rate law in such cases is therefore fully justified. A generalized multi-phase pseudo zero-order rate law which governs the dissipation of persistent organic compounds in the soil and aquatic environments has since been proposed to account for such dissipation curves [30], the criteria for conformance to the multi-phase pseudo-zero order rate law being: (a) each linear phase should exhibit high linearity, and (b) the slopes of the different linear phases should differ significantly.

The steady state approximation

The steady state approximation is commonly used quoting the *first steady state rate law* [7,8,11,25,26]. The use of the steady state approximation on the basis of the *second steady state rate law*, though currently not common, is fully justified. In addition, as indicated above, in between the First and Second Steady State Rate Law limits, the steady state approximation is applicable based on Equation 11. Outside these limits, the reactions follow the truly equilibrium rate law or truly first (or second) order rate laws, although in terms of the Activated Complex or Transition State theories, truly first (or second) order rate laws are extremely rare if at all possible.

CONCLUSIONS

From the foregoing discussion, the following conclusions can be made: (a) The steady state in chemical kinetics is characterized by the *first steady state rate law*, $dI/dt = 0$, for reactions involving very reactive intermediates (I), and by the *second steady state rate law*, $dP/dt = k$, for very slow reactions as measured by the rate of formation of products (P), or by $-dA/dt = k$, the rate of disappearance of the reactant (A). (b) Both steady state rate laws can be cited as bases for assuming the steady state approximation. (c) In both cases, the concentration of the steady state intermediate can be expressed in terms of the concentration of the initial concentration of the reactant. (d) The steady state approximation is applicable within the limits represented by truly first (or second) order rate law and the truly equilibrium rate law.

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