*Article*

# Integral Characteristic of Complex Catalytic Reaction Accompanied by Deactivation

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**Abstract:** New theoretical relationships for a complex catalytic reaction accompanied by deactivation are obtained, using as an example the two-step catalytic mechanism (Temkin–Boudart mechanism) with irreversible reactions and irreversible deactivation. In the domain of small concentrations, $A_{\lim} = N_S \frac{k_1 C_A}{k_d}$, where $A_{\lim}$ is the limit of the integral consumption of the gas substance, $N_S$ is the number of active sites per unit of catalyst surface; $k_1$ and $k_d$, are kinetic coefficients which relate to two reactions which compete for the free active site Z. $C_A$ is the gas concentration. One reaction belongs to the catalytic cycle. The other reaction with kinetic coefficient $k_d$ is irreversible deactivation. The catalyst lifetime, $\tau_{\text{cat}} = \frac{1}{C'_Z} \frac{1}{k_d}$, where $C'_Z$ is the dimensionless steady-state concentration of free active sites. The main conclusion was formulated as follows: the catalyst lifetime can be enhanced by decreasing the steady-state (quasi-steady-state) concentration of free active sites. In some domains of parameters, it can also be achieved by increasing the steady-state (quasi-steady-state) reaction rate of the fresh catalyst. We can express this conclusion as follows: under some conditions, an elevated fresh catalyst activity protects the catalyst from deactivation. These theoretical results are illustrated with the use of computer simulations.

**Keywords:** catalyst deactivation; catalytic cycle; integral consumption; catalyst lifetime

## 1. Introduction

Catalyst deactivation is a complex, non-steady-state process governed by a variety of phenomena that are influenced by many physicochemical factors.

In the literature, different types of kinetic models of catalytic reactions with deactivation were proposed, i.e., phenomenological models, detailed kinetic models, and semi-phenomenological models.

### 1.1. Phenomenological Models

In phenomenological models of 'gas-solid' catalytic reactions, the main characteristic of the catalytic process, the reaction rate ($r$), is presented as a function of the concentrations of the reactants ($C = C_1, C_2, \ldots$), the temperature ($T$), and catalyst activity ($a$),

$$r = f(C, T, a). \tag{1}$$

The catalyst activity $a$ is considered a function of the reaction conditions, here $C$ and $T$, and its change can be called 'catalyst deactivation'.

The first kinetic phenomenological model was formulated by Szépe and Levenspiel [1].

$$r(t) = R_0 a(t) \tag{2}$$

$$\frac{da}{dt} = f(C, T) a^d \tag{3}$$

where $R_0$ is the reaction rate over the non-deactivated ('fresh') catalyst and $d$ is an empirical parameter.

These models are called *separable* because the reaction kinetics and deactivation kinetics are assumed to be separate, see papers by Corella et al. [2,3] as well.

Froment and Bischoff [4,5] introduced the activity parameter

$$\Phi = \frac{k}{k_0} \tag{4}$$

(that is the ratio of the reaction rate constants of the deactivated $k$ and of the 'fresh' catalyst $k_0$) and considered it as a function of coke concentration. They proposed three functions:

$$\text{linear:} \quad \Phi_1 = 1 - \gamma C_c, \tag{5}$$

$$\text{exponential:} \quad \Phi_2 = \exp(-\gamma C_c), \tag{6}$$

$$\text{hyperbolic:} \quad \Phi_3 = \frac{1}{1 + \gamma C_c}. \tag{7}$$

Later, these relationships were used in many studies to describe the coking and deactivation of the catalysts in the processes of dehydrogenation, cracking, etc. In these processes, the activity changes rapidly, Therefore, in this case the quasi-steady-state assumption does not make the task easier.

Beeckman, Marin, and Froment [6,7] developed the probabilistic model of catalyst coking that implies coke deposition on the active and coked surface.

In this model, the catalyst activity is the product of two probabilities:

$$a = PS, \tag{8}$$

where $S$ is the probability that an active site is not covered with coke; $P$ is the probability that an active site is not locked as a result of pore blockage.

In reactors with the moving and fluidized bed, the coke concentration measurement becomes as accessible as the reactant concentration measurement (i.e., conversion and activity calculation). Therefore, it becomes important to express activity via coke concentration.

Such dependencies were derived by Ostrovskii based on the multilayer mechanism of coke formations.

Two equations were obtained, corresponding to infinite coke formation and a finite number of layers:

$$\frac{C_c}{C_m} = (1 - \varphi)(1 - a) - \varphi \ln a, \tag{9}$$

$$\frac{C_c}{C_m} = N - a - (N - 1)a^{\varphi}. \tag{10}$$

where $C_m$ is the monolayer coke concentration; $\varphi$ is the ratio of rate constants of poly- and monolayer coking; $N$ is the number of coke layers.

### 1.2. Detailed Kinetic Models

In detailed models (micro-kinetic or mechanistic models), the model is based on the mechanism, i.e., the set of steps that include reactants and products of the overall reactions as well as catalytic intermediates.

A detailed kinetic model was presented in [8] with a description of two different periods of irreversible deactivation. However, even presently, 50 years later, the number of papers with detailed kinetic models of catalyst deactivation is limited, since the information on the evolution of the surface composition is in short supply.

### 1.3. Semi-Phenomenological Models

In the catalytic literature, many models have been presented combining phenomenology with some mechanistic considerations of deactivation, e.g., power-law kinetic dependencies and Langmuir–Hinshelwood–Hougen–Watson relationships based on the concept of adsorption equilibrium, see Butt [9] and Bartholomew [10]. In our paper [11], such models are called semi-phenomenological.

In 1989, Ostrovskii and Yablonskii [12] proposed the semi-phenomenological model of single-route catalytic reactions assuming two types of catalyst deactivation, i.e., reversible and irreversible ('aging'). In deriving this model, the known principle of quasi-steady-state (QSS) concentrations was used to obtain the concentration of the catalytic intermediate, which deactivates during the process. This concentration was presented as a function of the QSS reaction rate and other kinetic parameters. Later, Ostrovskii developed this approach further in the monograph [13] and paper [14].

In our paper [11], the same approach was presented for the rigorous derivation of the kinetic equation of the $n$-step single-route catalytic reaction accompanied by two processes of catalytic deactivation, one reversible and the other irreversible. Here the term "reversible deactivation" refers to the fact that the deactivation step includes two reactions, a forward, and a reverse one.

This catalytic process was described by the three-building-block scheme (Figure 1). There we considered a linear mechanism for the catalytic cycle, i.e., only one 'molecule' of the catalytic intermediate, including the active center, participates in each reaction.
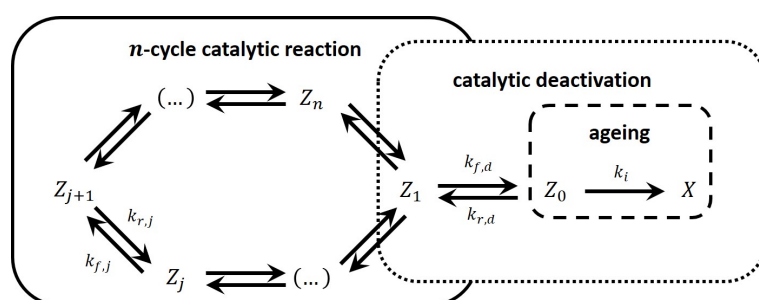


**Figure 1.** The three-building-block scheme approach to phenomenological modeling for a linear catalytic reaction accompanied by linear catalyst deactivation. Block one is a $n$-step linear catalytic reaction. Block two is a linear reversible catalyst deactivation. Block three is aging, i.e., linear irreversible catalyst deactivation.

Applying the new, more convenient form of the rate equation for the single-route catalytic reaction with the linear mechanism [15], resulted in the three-factor kinetic equation of deactivation [11] for this complex process.

$$R(t) = N_S^0 R_{\text{fresh}} \psi_{r,d} \psi_{i,d}, \tag{11}$$

$$\psi_{r,d} = \underbrace{\frac{1 + \alpha K_d R_{\text{fresh}} \exp(-(1 + \alpha K_d R_{\text{fresh}}) k_{r,d} t)}{1 + \alpha K_d R_{\text{fresh}}}}_{\text{reversible deactivation factor}}, \tag{12}$$

$$\psi_{i,d} = \underbrace{\exp\left(-\frac{\alpha K_d R_{\text{fresh}}}{1 + \alpha K_d R_{\text{fresh}}} k_i t\right)}_{\text{irreversible deactivation factor}}, \tag{13}$$

where $N_S^0$ is the initial number of active sites per unit of catalyst surface; $R_{\text{fresh}}$ is the 'fresh' rate of the main catalyst cycle; $\alpha R_{\text{fresh}} = C'_{Z,\text{fresh}}$ is the 'fresh' concentration of free catalyst active site Z and where $\alpha$ is a special parameter described in [11]; $K_d$ is the equilibrium constant of the reversible deactivation reaction; and $k_i$ is the rate constant of the irreversible deactivation reaction.

This deactivation equation with some simplifications will be used in this paper for different purposes. As mentioned, the quasi-steady-state hypothesis (QSSH) was applied as a tool for the derivation of this deactivation equation. The status of the QSSH in our problems should be discussed in more detail.

This model is an advantageous simplification of the mechanistic model. It is based on the idea of a cyclic catalytic mechanism, and its constituents are the concept of active sites and assumptions on fast and slow parameters considering the quasi-steady-state principle. In comparison with the recent all-component-model, e.g., Cordero-Lanzac et al. [16], and detailed multi-step and multi-route models [17,18] see also Cordero-Lanzac's dissertation, the semi-phenomenological model used in this paper has obvious advantages:

1. the number of parameters is much smaller;
2. this model allows the derivation of interesting analytical results, as will be demonstrated in this paper;
3. potentially, this simpler model can be useful for the design of catalytic reactors with deactivation and optimization of industrial regimes.

One of the main ideas of chemical kinetics is a hierarchy, i.e., the time scale separation, based on the large difference in magnitude of the parameters of the kinetic model. This hierarchy determines a variety of different cases and regimes, e.g., quasi-equilibrium (QE), quasi-steady-state (QSS), limiting step (LS), assumptions on most abundant reactive intermediates (mari) or surface intermediates (masi), and, finally, lumping.

The quasi-steady-state (QSS) approximation is the central one among all these simplifications. The QSS-principle regarding kinetic intermediates of a complex chemical reaction is typically attributed to Bodenstein [19] and sometimes to Chapman [20,21] as well, see the historical information [22,23].

It was based on the idea of fast intermediates, i.e., the kinetic parameters related to some intermediates are much larger than the kinetic parameters related to stable molecules.

In the pioneering paper by Michaelis–Menten [24], two hierarchies were considered:

1. a large difference in kinetic parameters
2. a large difference between the total amounts of main reactants and the total amount of intermediates. For the 'gas-solid' catalytic reaction, the latter corresponds to the case when the total number of active catalytic centers is much smaller than the total number of reactant and product molecules, see [22] (Chapter 3).

Gorban and Shahzad [25] theoretically revisited and generalized the Michaelis–Menten approach. It was shown that, rigorously speaking, the Michaelis–Menten kinetics, as we refer to it presently, should be attributed to Briggs and Haldane [26].

In accordance with the QSS method, the derivatives of the chemical intermediates are replaced by 'zeros', and the corresponding differential equations transform to algebraic ones.

This 'trick' became an extremely popular tool in the theoretical study of complex chemical reactions, both homogeneous and heterogeneous.

However, for a period of 50-plus years after the time of Bodenstein and Michaelis–Menten, the mathematical status of the QSS method was very unclear, there was no understanding of why the derivatives of 'fast' intermediates are replaced by zero. Only starting from the 1950s, a rigorous mathematical concept for QSS was created based on the theory of singularly perturbed ordinary differential equations (ODEs). This theory was developed by Tikhonov and his colleagues [27–30], and the central point of this theory was the concept of a so-called 'small parameter'.

In 1955 Sayasov and Vasil'eva published the first pioneering paper [28] on the mathematical status of the QSS using a radical gas chain reaction with fast intermediates as an example. The small parameter was chosen as the ratio of kinetic parameters. A similar point of view was expressed in 1963 by Bowen, Acrivos, and Oppenheim [31].

In 1963, Heineken, Tsuchiya, and Aris (HTA) published a paper [32] on the mathematical status of the QSS for the Michaelis–Menten two-step mechanism. The small parameter

used by HTA was the ratio of two numbers, the number of enzyme active sites and the number of substrate molecules. A similar small parameter, i.e., the ratio of the total amount of surface intermediates, mole, to the total amount of reacting components, mole, was used in monographs [22,23] for obtaining general results in catalytic kinetics (see also the early monograph [33]).

The general methodology in studying hierarchical kinetics, see "Asymptotology" by Gorban et al., [34–36] as well.

## 2. Goal of the Paper: General Problems and Specific Problems of This Paper

The goal of this paper is to present the integral characteristic $A$ (mol cm$_{cat}^{-2}$) of complex 'gas-solid' catalytic reactions accompanied by deactivation, i.e.,

$$A = \int_0^\tau R(t)\, dt, \tag{14}$$

where $R(t)$ is the consumption rate of the gas reactant, or the rate of release of the gas product. It will be presented for some regimes as an analytical expression and will be illustrated using computational results.

Our goal will also be to estimate the catalyst lifetime by relating the value of $A$ to the value of the quasi-steady-state (QSS) rate of the 'fresh' (non-deactivated) catalyst.

Our model of a complex catalytic reaction accompanied by deactivation includes two small parameters

1.　the small parameter which is caused by the difference between the number of catalyst active sites and the number of gaseous molecules ("the first small parameter")
2.　the small parameter caused by the difference between the deactivation parameters and kinetic coefficients of the main catalytic cycle ("the second small parameter")

In this paper, we are going to start the systematic application of our three-factor kinetic equation proposed in [11] to different problems of catalytic kinetics. The program of our studies will include different cases and scenarios. It is reasonable to expect that the results of our studies will depend on the type of the kinetic device and its kinetic model, on the analyzed chemical mechanisms and corresponding models, and the conditions of the process reversibility, i.e., whether deactivation is reversible or irreversible, whether the chemical catalytic cycle is reversible or irreversible etc.

Generally, we are planning to analyze the following cases:

1.　Kinetic models of the batch reactor (BR) and continuously stirred tank reactor (CSTR).
2.　Kinetic models of typical heterogeneous catalytic mechanisms:

　　(a)　The $n$-step single-route complex catalytic reaction with a linear mechanism.
　　(b)　The two-step catalytic mechanism (Temkin–Boudart mechanism) as a basic mechanism of theoretical chemical kinetics of heterogeneous catalysis [37–39].

3.　Models with reversible and irreversible steps in the catalytic cycle.
4.　Models with reversible and irreversible deactivation process.

In this paper, we will study the kinetic behavior of a batch reactor in which catalytic reactions are accompanied by deactivation. As an example the simplest two-step catalytic mechanism (Temkin–Boudart mechanism) is chosen with irreversible deactivation. It is the simplest mechanism of the ones mentioned above.

Different scenarios of the transient interplay between the main cycle relaxation and deactivation dynamics will be described, and different temporal and parametric domains will be distinguished:

1.　The initial non-steady-state kinetic regime caused by the intrinsic catalytic cycle.
2.　The quasi-steady-state regime regarding the catalytic intermediates with insignificant deactivation ('no deactivation' regime). This regime is caused by the difference between the number of catalyst active sites and the number of gaseous molecules ("the first small parameter").

3. The quasi-steady-state regime regarding the intermediates in which the deactivation process is significant. Within this domain, the total number of active sites is decreased, and the quasi-steady-state regime becomes more pronounced.

Under concrete values of parameters, some domains can be negligible. Different questions will be answered:

1. In which domain will the catalyst composition be nearly constant, i.e., despite the change in the number of active sites the relative concentrations of catalytic intermediates are remaining approximately the same?
2. How to analyze the long-term behavior of the catalytic system with deactivation based on its integral characteristic?
3. What is the best strategy for the increase of catalytic efficiency based on the kinetic description?

**3. Theoretical Analysis**

Our strategy is to first analyze the full model, i.e., the two-step irreversible catalytic cycle with irreversible deactivation, and then to analyze the three reduced models, two of which have "no" deactivation and are known in the literature, i.e.,

- Only the main catalytic cycle model; the non-steady-state case.
- Only the main catalytic cycle model; the quasi-steady-state case.

In our opinion, it is necessary to study these models to build a strong foundation and systematic framework on which to continue the analysis of more complex cases related to deactivation. We expect these simple models can be used as asymptotics for the more complex ones. This content will also help us to understand the final results for both the mathematical and chemical engineering communities.

*3.1. The Full Model of the Two-Step Irreversible Catalytic Cycle with Irreversible Deactivation*

We use the two-step catalytic mechanism of an isomerization reaction with irreversible steps,

$$\text{A} + \text{Z} \xrightarrow{k_1} \text{AZ}$$
$$\text{and AZ} \xrightarrow{k_2} \text{B} + \text{Z}$$
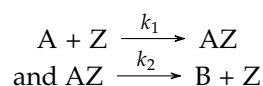
accompanied by a (possible) deactivation step,

$$\text{Z} \xrightarrow{k_d} \text{X}.$$
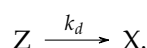
The rate equations corresponding to these reactions are,

$$r_1 = k_1 C_A C_Z, \tag{15}$$
$$r_2 = k_2 C_{AZ}, \tag{16}$$
$$\text{and } r_d = k_d C_Z, \tag{17}$$

where $r_1$, $r_2$ and $r_d$ are rate equations in $\text{mol}\,\text{cm}_{\text{cat}}^{-2}\,\text{s}^{-1}$; $k_1$ is a reaction rate constant in $\text{cm}_{\text{gas}}^3\,\text{mol}^{-1}\,\text{s}^{-1}$; $k_2$ and $k_d$ are reaction rate constants in $\text{s}^{-1}$; $C_A$ is the concentration of gas reactant A in $\text{mol}\,\text{cm}_{\text{gas}}^{-3}$; and $C_Z$ and $C_{AZ}$ are concentrations of active catalyst sites, also referred to as catalyst intermediates, in $\text{mol}\,\text{cm}_{\text{cat}}^{-2}$.

The kinetic equations for the gas reactant and product are,

$$\frac{dC_A}{dt} = -\frac{S_{\text{cat}}}{V_{\text{gas}}} r_1,$$
$$= -\frac{S_{\text{cat}}}{V_{\text{gas}}} k_1 C_A (N_S - C_{AZ}), \tag{18}$$

$$C_B = N_V - C_A - \frac{S_{\text{cat}}}{V_{\text{gas}}} C_{AZ}, \tag{19}$$

where $C_B$ is the concentration of the gas product and $\frac{S_{\text{cat}}}{V_{\text{gas}}}$ is a factor consisting of ratio of the catalyst surface area $S_{\text{cat}}$ (cm$^2_{\text{cat}}$) to the gas volume (cm$^3_{\text{gas}}$). Equation (19) is derived from the law of mass conservation for element A where $N_V$ is the total concentration of gas (mol cm$^{-3}_{\text{gas}}$).

The kinetic equations for the catalytic intermediates are,

$$
\begin{aligned}
\frac{dC_{AZ}}{dt} &= r_1 - r_2, \\
&= k_1 C_A (N_S - C_{AZ}) - k_2 C_{AZ},
\end{aligned} \tag{20}
$$

$$
\begin{aligned}
\frac{dN_S}{dt} &= -r_d, \\
&= k_d (N_S - C_{AZ}),
\end{aligned} \tag{21}
$$

$$
C_Z = N_S - C_{AZ}, \tag{22}
$$

where $N_S$ is the total concentration of active catalyst sites in mol cm$^{-2}_{\text{cat}}$. Equation (22) is derived from the law of mass conservation for the catalyst sites.

Equations (18)–(22) represent the dimensional system of equations for the full model. There are three differential equations, two non-linear (18), (20) and one linear (21), and two linear algebraic Equations (19) and (22).

In our analysis, we wish to differentiate between slow and fast behavior. To do this, we must first identify a small parameter. In some cases, one small parameter is enough. However, we will highlight two different small parameters for this specific work.

The first small parameter, $\varepsilon_1$, is defined as the ratio of the number of catalyst sites to the number of gas molecules. At time zero, the number of catalyst sites is equal to the number of active catalyst sites. If there is deactivation, this equality will not hold anymore. This is why we use the initial ('fresh') number of active sites in our definition.

**Small Parameter 1.** *The ratio of the total number of 'fresh' active sites to the total number of gas molecules,*

$$
\varepsilon_1 = \frac{S_{cat} N_S^0}{V_{gas} N_V}.
$$

*The parameters $S_{cat}$, $V_{gas}$, $N_S^0$ and $N_V$ are the catalyst surface (cm$^2_{\text{cat}}$), gas volume (cm$^3_{\text{gas}}$), the 'fresh' concentration of active sites, i.e., the concentration of active sites (mol cm$^{-2}_{\text{cat}}$) at time zero, $N_S^0 = N_S(0)$ and the total concentration of gas (mol cm$^{-3}_{\text{gas}}$), respectively.*

The second small parameter, $\varepsilon_2$, is defined as the ratio of the deactivation parameter to a kinetic rate coefficient of the main catalytic cycle. The deactivation rate constant $k_d$ is assumed to be much smaller than the rate constants of the catalytic cycle $k_1 N_V$ and $k_2$, i.e., $k_d \ll k_1 N_V, k_2$. Our second small parameter can be interpreted as a dimensionless deactivation rate constant. We achieve this by either scaling with respect to $k_1 N_V$ or $k_2$. We chose $k_1 N_V$ here because the term reappears in several of the system equations.

**Small Parameter 2.** *The dimensionless deactivation rate constant,*

$$
\varepsilon_2 = \frac{k_d}{k_1 N_V}.
$$

*The parameters $k_d$, $k_1$ and $N_V$ are the deactivation rate constant (s$^{-1}$), the reaction rate constant of reaction 1 (cm$^3_{\text{gas}}$ mol$^{-1}$ s$^{-1}$) and the total concentration of gas (mol cm$^{-3}_{\text{gas}}$), respectively.*

Implementing the small parameter into the kinetic equations for the reactant, product, and catalytic intermediates, we rewrite the equations for the full system (18)–(22). It now includes the two small parameters, $\varepsilon_1$ and $\varepsilon_2$,

$$\frac{dC_A}{dt} = -\varepsilon_1 \frac{k_1 N_V}{N_S^0} C_A (N_S - C_{AZ}), \tag{23}$$

$$C_B = N_V - C_A - \varepsilon_1 \frac{N_V}{N_S^0} C_{AZ}, \tag{24}$$

$$\frac{dC_{AZ}}{dt} = k_1 C_A (N_S - C_{AZ}) - k_2 C_{AZ}, \tag{25}$$

$$\frac{dN_S}{dt} = \varepsilon_2 k_1 N_V (N_S - C_{AZ}), \tag{26}$$

$$C_Z = N_S - C_{AZ}. \tag{27}$$

Mathematically, there is a benefit to working with dimensionless variables and parameters, as this can simplify the equations significantly. We therefore introduce the dimensionless concentrations $C_i' = \frac{C_i}{N_V}$ with $i = A, B$, $C_j' = \frac{C_j}{N_S^0}$ with $j = Z, AZ$ and $N_S' = \frac{N_S}{N_S^0}$.

Physically, there is a benefit to working with real dimensional variables and parameters, as this helps in physical interpretation. In this case, we use dimensional time.

The set of equations for the system of dimensionless concentrations is given by,

$$\frac{dC_A'}{dt} = -\varepsilon_1 k_1 N_V C_A' (N_S' - C_{AZ}'), \tag{28}$$

$$C_B' = 1 - C_A' - \varepsilon_1 C_{AZ}', \tag{29}$$

$$\frac{dC_{AZ}'}{dt} = k_1 N_V C_A' (N_S' - C_{AZ}') - k_2 C_{AZ}', \tag{30}$$

$$\frac{dN_S'}{dt} = -\varepsilon_2 k_1 N_V (N_S' - C_{AZ}') \tag{31}$$

$$C_Z' = N_S' - C_{AZ}'. \tag{32}$$

We will continue to study this set of Equations (28)–(32). This mathematical model of the whole process is a non-linear system containing three differential equations for the dimensionless concentrations, of the gas reactant A (28), of the intermediate AZ of the catalytic cycle (30) and the active catalytic sites (31). The model further contains two linear algebraic equations for the dimensionless concentrations of the gas product B (29) and of the other intermediate of the catalytic cycle Z (32).

*3.2. The Initial Non-Steady-State Domain; Gas Concentration Is Abundant, and Deactivation Is Negligible*

Above we have introduced the full system of equations that will be studied further. We will first start with the implication of the two small parameters. If the small parameters

are close to zero, i.e., $\varepsilon_1, \varepsilon_2 \approx 0$ (or in the case of no deactivation $\varepsilon_1 \approx 0$ and $\varepsilon_2 = 0$), then for small $t$ we find that Equations (28) and (31) are approximately zero.

$$\frac{dC'_{AZ}}{dt} = k_1 N_V C'_A (N'_S - C'_{AZ}) - k_2 C'_{AZ}, \tag{33}$$

$$\frac{dN'_S}{dt} = 0, \tag{34}$$

$$C'_Z = N'_S - C'_{AZ}, \tag{35}$$

$$\frac{dC'_A}{dt} = 0, \tag{36}$$

$$C'_B = 1 - C'_A. \tag{37}$$

If the change in active sites is approximately zero, this means there is almost no deactivation. On a certain domain where $t$ is small we may claim there to be no deactivation. For the change in gas reactant A to be small, it has to be small compared to its absolute value. The change in A is insignificant because it is in abundance.

In this domain, for the full model, the changes in both substances (reactant A and active sites N) happen so slowly they cannot be observed, and thus are deemed insignificant. The fast behavior is dominating the slow one. Resulting in the following exact solution for the approximate model in the fast domain,

$$N'_S(t) = N'_S(0) = 1, \tag{38}$$

$$C'_A(t) = C'_A(0) = 1, \tag{39}$$

$$C'_B(t) = C'_B(0) = 0, \tag{40}$$

$$C'_{AZ}(t) = \frac{k_1 N_V}{k_1 N_V + k_2} (1 - \exp(-(k_1 N_V + k_2)t), \tag{41}$$

$$C'_Z(t) = \frac{k_2}{k_1 N_V + k_2} + \frac{k_1 N_V}{k_1 N_V + k_2} \exp(-(k_1 N_V + k_2)t). \tag{42}$$

$$\frac{C'_{AZ}}{C'_Z} = \frac{k_1 N_V - k_1 N_V \exp(-(k_1 N_V + k_2)t)}{k_2 + k_1 N_V \exp(-(k_1 N_V + k_2)t)} \tag{43}$$

The fast domain, also referred to as the non-steady-state (NSS) domain, is the time frame in which the above solutions are good estimates for the exact solutions. It is governed by the main catalytic cycle with "no" deactivation and under the assumption that the gas concentration is abundant.

### 3.3. The Quasi-Steady-State Domain; Deactivation Is Absent

When we go outside the fast or non-steady-state (NSS) domain, the same assumptions don't hold as in the previous section. Here we need to differentiate whether deactivation is truly absent or not. We first look at the case where deactivation is absent, i.e., $\varepsilon_2 = 0$.

In this slow domain, we introduce the new time $\tau = \varepsilon_1 t$. The main result of introducing the time $\tau$ with small parameter $\varepsilon_1$ is the following equations for the catalytic intermediates,

$$\varepsilon_1 \frac{dC'_{AZ}}{d\tau} = k_1 N_V \left( C'_A (N'_S - C'_{AZ}) - \frac{k_2}{k_1 N_V} C'_{AZ} \right), \tag{44}$$

$$C'_Z = N'_S - C'_{AZ}. \tag{45}$$

Since $\varepsilon_1 \approx 0$, we can replace Equation (44) with the algebraic equation,

$$k_1 N_V \left( C'_A (N'_S - C'_{AZ}) - \frac{k_2}{k_1 N_V} C'_{AZ} \right) = 0. \tag{46}$$

This is our quasi-steady-state (QSS) assumption, and we identify this domain as the QSS domain. The QSS intermediate concentrations are calculated as,

$$C'_{AZ} = \frac{k_1 N_V C'_A}{k_1 N_V C'_A + k_2} N'_S, \tag{47}$$

$$C'_Z = \frac{k_2}{k_1 N_V C'_A + k_2} N'_S. \tag{48}$$

If we substitute the values of $C'_A$ and $N'_S$ with their respective 'fresh' values $C'_{A,fresh} = C'_A(0)$ and $N'_{S,fresh} = N'_S(0)$ these solutions are equivalent to the steady-state (SS) values of Equation (41) and Equation (42) respectively.

At the beginning of the QSS domain, the concentration $C_A$ is changing insignificantly and the relative ratio composition of the active catalyst sites,

$$\frac{C'_{AZ}}{C'_Z} = \frac{k_1 N_V C'_A}{k_2}, \tag{49}$$

appears constant. However, as time increases the change in $C_A$ will increase, and thus the ratio will not remain constant. As we will see in later sections this is not the case when deactivation is present.

### 3.3.1. Introduction to the Lambert W function

To recap, in the absence of deactivation, we have the following set of equations for the dimensionless concentrations,

$$\varepsilon_1 \frac{dC'_{AZ}}{d\tau} = k_1 N_V C'_A (N'_S - C'_{AZ}) - k_2 C'_{AZ}, \tag{50}$$

$$C'_Z = N'_S - C'_{AZ}, \tag{51}$$

$$\frac{dC'_A}{d\tau} = -k_1 N_V C'_A (N'_S - C'_{AZ}), \tag{52}$$

$$C'_B = 1 - C'_A - \varepsilon_1 C'_{AZ}. \tag{53}$$

There are two nonlinear differential equations, (50) and (52), and two linear algebraic equations, (51) and (53). Making use of the small parameter and the quasi-steady-state (QSS) assumption, see Equations (46)–(48), this set of equations reduce to one nonlinear differential equation, (56), and three algebraic equations, (54), (55) and (57).

$$C'_{AZ} = \frac{k_1 N_V C'_A}{k_1 N_V C'_A + k_2} N'_S, \tag{54}$$

$$C'_Z = \frac{k_2}{k_1 N_V C'_A + k_2} N'_S, \tag{55}$$

$$\frac{dC'_A}{d\tau} = -\frac{k_1 k_2 N_V C'_A}{k_1 N_V C'_A + k_2} N'_S, \tag{56}$$

$$C'_B = 1 - C'_A - \varepsilon_1 \frac{k_1 N_V C'_A}{k_1 N_V C'_A + k_2} N'_S. \tag{57}$$

This specific set of equations is well-known in the literature. However, to our knowledge, an exact analytical expression for the concentration of A has yet to be presented.

To this end, we would like to introduce the Lambert $W$ function [40], which calculates the converse (inverse) relation of the function

$$f(w) = we^w,$$

with $w \in \mathbb{C}$.

We now have a way to express the solution of ordinary differential Equation (56),

$$C'_A(\tau) = \exp\left(-\text{LambertW}\left(\frac{1}{\eta}\exp\left(-\frac{1}{\eta}(k_2 N'_S t - 1)\right)\right) - \frac{1}{\eta}(k_2 N'_S t - 1)\right), \quad (58)$$

$$\eta = \frac{k_2}{k_1 N_V}. \quad (59)$$

Remember because there is no deactivation $N_S$ will be constant and $N'_S = 1$ for all time. By extension of the above equation we now also have analytical expressions for the remaining concentrations,

$$C'_{AZ}(\tau) = \frac{k_1 N_V C'_A(\tau)}{k_1 N_V C'_A(\tau) + k_2} \quad (60)$$

$$C'_Z(\tau) = \frac{k_2}{k_1 N_V C'_A(\tau) + k_2} \quad (61)$$

$$C'_B(\tau) = 1 - C_A(\tau)\left(1 - \varepsilon_1 \frac{k_1 N_V}{k_1 N_V C'_A(\tau) + k_2}\right) \quad (62)$$

$$R(\tau) = k_2 C_{AZ} = k_2 C'_{AZ} N_S = N_S \frac{k_1 k_2 N_V C'_A(\tau)}{k_1 N_V C'_A(\tau) + k_2} \quad (63)$$

Using Equation (58), one can obtain the expression for half decay time, $\tau_{1/2}$, which is traditional in chemical kinetics. It is the time during which half of the reactant is transformed into the product.

As known, for the first order reaction A $\xrightarrow{k}$ B,

$$\tau_{1/2} = \frac{\ln(2)}{k}$$

where $k$ is the kinetic rate coefficient of the reaction. For our two-step mechanism (Temkin–Boudart mechanism), based on Equation (58),

$$\tau_{1/2} = \frac{\ln(2)}{k_1 N_V} + \frac{1}{2k_2} \quad (64)$$

Clearly, the half decay time is decreased with the rise of both kinetic coefficients $k_1 N_V$ and $k2$. If $k_2$ is much bigger then $k_1 N_V$,

$$\tau_{1/2} = \frac{\ln(2)}{k_1 N_V}, \quad (65)$$

it is identical to the expression for the first-order reaction. In contrast, if $k_1 N_V$ is much bigger than $k_2$ then,

$$\tau_{1/2} = \frac{1}{2k_2}. \quad (66)$$

If $k_1 N_V = k_2 = k$,

$$\tau_{1/2} = \frac{1/2 + \ln(2)}{k} \approx \frac{1.19}{k}. \quad (67)$$

This expression can be used as a rough estimate of the parameter.

Based on Equation (64) it is possible to recognize the deviation of the Temkin–Boudart non-steady-state kinetic dependence from the first-order (linear) one.

### 3.4. The Quasi-Steady-State Domain of the Cyclic Reaction Accompanied by Deactivation

In this domain, applying the quasi-steady-state assumption, the kinetic model is given by:

$$C'_{AZ} = \frac{k_1 N_V C'_A}{k_1 N_V C'_A + k_2} N'_S, \tag{68}$$

$$C'_Z = \frac{k_2}{k_1 N_V C'_A + k_2} N'_S, \tag{69}$$

$$\frac{dN'_S}{d\tau} = -\frac{\varepsilon_2}{\varepsilon_1} \frac{k_1 k_2 N_V}{k_1 N_V C'_A + k_2} N'_S, \tag{70}$$

$$\frac{dC'_A}{d\tau} = -\frac{k_1 k_2 N_V C'_A}{k_1 N_V C'_A + k_2} N'_S, \tag{71}$$

$$C'_B = 1 - C'_A - \varepsilon_1 \frac{k_1 N_V C'_A}{k_1 N_V C'_A + k_2} N'_S. \tag{72}$$

This system of equations consists out of two nonlinear differential equations, (70) and (71), and three algebraic equations, (68), (69) and (72).

We can rewrite the two differential equations above into one nonlinear differential equation,

$$\frac{dN'_S}{dC'_A} = \frac{\varepsilon_2}{\varepsilon_1 C'_A}. \tag{73}$$

The analytical solution to Equation (73) is found to be

$$N'_S(C'_A) = \frac{\varepsilon_2}{\varepsilon_1} \ln(C'_A). \tag{74}$$

This equation, while correct, does not give much information about the progression of the dimensionless concentration of active sites $N'_S$. The three-factor kinetic equation, (11) as it is presented in [11], can be adapted for models without reversible deactivation by setting $\varphi_{r,d} = 1$ and $K_d = 1$ (Appendix A describes the conditions under which we may use the three-factor rate equation). This results in the following rate equation for this domain,

$$
\begin{aligned}
R(\tau) &= k_2 C_{AZ} = k_2 C'_{AZ} N^0_S, \\
&\approx N^0_S R_{\text{fresh}} \varphi_{i,d}, \\
&= \frac{k_1 k_2 N_V C'_{A,fresh}}{k_1 N_V C'_{A,fresh} + k_2} N^0_S \exp\left(-\frac{\varepsilon_2}{\varepsilon_1} \frac{k_1 k_2 N_V}{k_1 N_V C'_{A,fresh} + k_2} \tau\right).
\end{aligned}
\tag{75}
$$

First, we simplify the terms inside the exponential as follows,

$$C'_{Z,\text{fresh}} = \frac{k_2}{k_1 N_V C_{A,fresh} + k_2}, \tag{76}$$

$$\varepsilon_2 = \frac{k_d}{k_1 N_V}, \tag{77}$$

$$R(\tau) = \frac{k_1 k_2 N_V C'_{A,fresh}}{k_1 N_V C'_{A,fresh} + k_2} N^0_S \exp\left(-\frac{k_d}{\varepsilon_1} C'_{Z,\text{fresh}} \tau\right). \tag{78}$$

Now we shift our time out of the "slow" time $\tau$ domain to the "fast" time $t$ one, which results in the final expression for the rate equation,

$$\tau = \varepsilon_1 t, \tag{79}$$

$$R(t) = \frac{k_1 k_2 N_V C'_{A,fresh}}{k_1 N_V C'_{A,fresh} + k_2} N_S^0 \exp\left(-k_d C'_{Z,fresh} t\right). \tag{80}$$

Obviously, $k_d C'_{Z,fresh}$ is the rate of deactivation for the fresh catalyst. Therefore, the phenomenological equation can be written as,

$$R(t) = R_{fresh} e^{-R_d t}, \tag{81}$$

where $R_d = k_d C'_{Z,fresh}$ is the rate of deactivation of the fresh catalyst.

*3.5. Integral Consumption*

The integral consumption of the reactant which we are going to obtain and analyze is expressed as,

$$A(t) = \int_0^t R(x)\, dx,$$

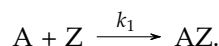$$A(t) = N_S^0 \frac{k_1 N_V C'_A(t)}{k_d}\left(1 - \exp\left(-k_d C'_{Z,fresh} t\right)\right). \tag{82}$$

Experimentally, in the quasi-steady-state domain the dependence of $A(t)$ can be measured by the change of concentrations in time of reactant A ($\Delta C_A$) or product B ($\Delta C_B$) multiplied by the factor ($\frac{V_{gas}}{S_{cat}}$). In our case, where the change in the reactant concentration is insignificant, the product concentrations are more convenient for calculating the values of $A(t)$.

There are two extreme cases for the integral consumption equation:

1.  The limit of the integral consumption as time goes to infinity, $t \to \infty$,

$$A_{lim} = N_S^0 \frac{k_1 N_V C'_A}{k_d}. \tag{83}$$

We find the limit of integral consumption is equal to the product of the number of active sites for the fresh catalyst multiplied by the ratio of the kinetic coefficients of the two reactions competing for the free active site Z. One reaction belongs to the catalytic cycle,

$$\text{A} + \text{Z} \xrightarrow{k_1} \text{AZ}.$$

The other reaction belongs to the irreversible deactivation step,

$$\text{Z} \xrightarrow{k_d} \text{X}.$$
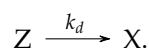
2.  The Taylor approximation for $A(t)$ at small values of $k_d t$. If the term $k_d t$ is very small, i.e., $k_d t \ll 1$, the Taylor approximation of $A(t)$ will be

$$A(t) = N_S^0 \frac{k_1 N_V C'_A}{k_d}\left(1 - \left(1 - k_d C'_{Z,fresh} t\right)\right) + \mathcal{O}(k_d t),$$

$$\approx R_{fresh} t. \tag{84}$$

### 3.6. Combining the Integral Consumption and the Quasi-Steady-State Equation Rate

Comparing the equations for the limit of the integral consumption (83) and the equation for the quasi-steady-state rate, we obtain

$$\frac{A_{\text{lim}}}{R_{\text{fresh}}} = \frac{1}{C'_{Z,\text{fresh}}} \frac{1}{k_d}. \tag{85}$$

This ratio $\frac{A_{\text{lim}}}{R_{\text{fresh}}}$ can be interpreted as the catalyst lifetime for the catalytic reaction with deactivation,

$$\tau_{\text{cat}} = \frac{A_{\text{lim}}}{R_{\text{fresh}}}. \tag{86}$$

If $k_1 N_V C'_A \gg k_2$ then

$$\tau_{\text{cat}} \approx \frac{k_1 N_V C'_A}{k_2} \frac{1}{k_d}.$$

If $k_1 N_V C'_A \ll k_2$ then

$$\tau_{\text{cat}} \approx \frac{1}{k_d}.$$

## 4. Computations

Figure 2 shows the evolution of the concentration of free active sites which first dramatically decreases, then exhibits a plateau, and finally decreases gradually to zero.
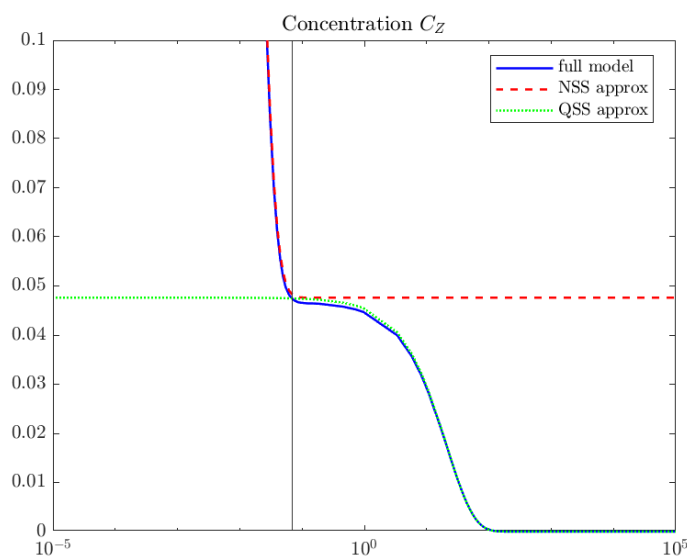


**Figure 2.** Concentration of Z.

Interestingly, this whole model is characterized by a temporal turning point. Left of this turning point, the whole model can easily be approximated by the NSS no-deactivation model. Regarding this point, the QSS model with deactivation (not without) is an excellent approximation of the whole model.

This turning point corresponds to the 'fresh' catalyst, which is characterized by the QSS surface composition.

Under the values of our parameters, the concentration of reactants changes insignificantly in all temporal intervals (the case of small conversion). The concentration of product B is presented in Figure 3.
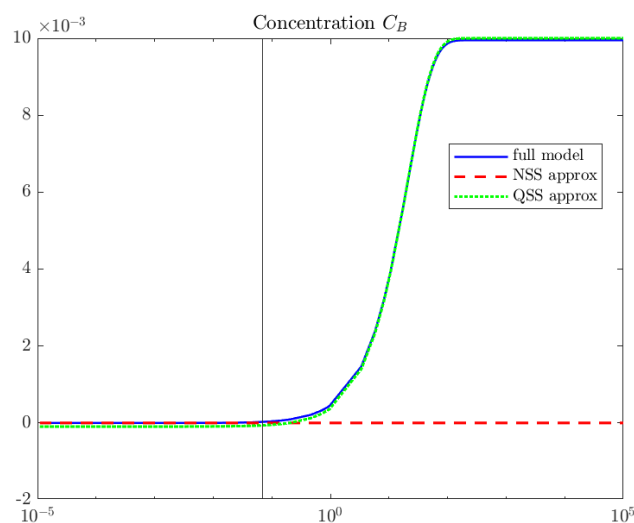
**Figure 3.** Concentration of B.

In our case, the non-steady-state (NSS) domain with deactivation is characterized by the insignificant contribution of reactant A. Furthermore, the effect of deactivation on the concentration of the intermediate is insignificant as well in this domain. The NSS with the no-deactivation domain is indistinguishable from the domain with deactivation.

As for the QSS domain, the main catalytic cycle is accompanied by deactivation from the very beginning of this domain.

Figures 4 and 5 illustrate the main theoretical result of our paper: that if we increase the rate coefficient $k_1$, this will result in a decrease of the QSS concentration of free active sites $C_Z$. Consequently, the integral consumption of reactant A and its limit $A_{\text{lim}}$ will increase, where $A_{\text{lim}}$'s increase will be proportional to the increase in the rate coefficient $k_1$. Hence, the lifetime of the catalyst $\tau_{\text{cat}}$ will increase as well.
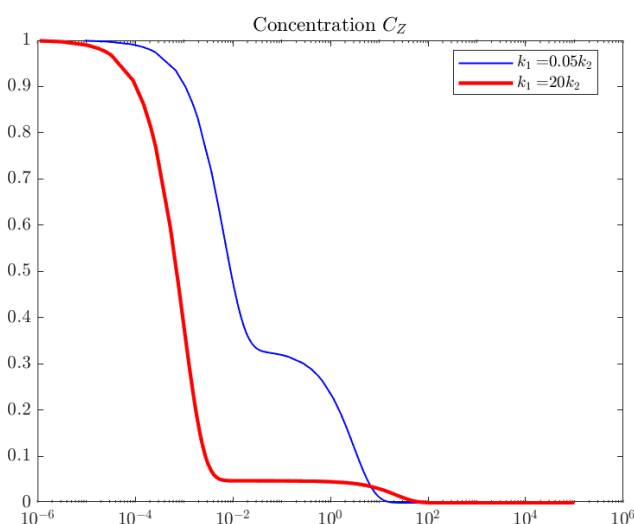


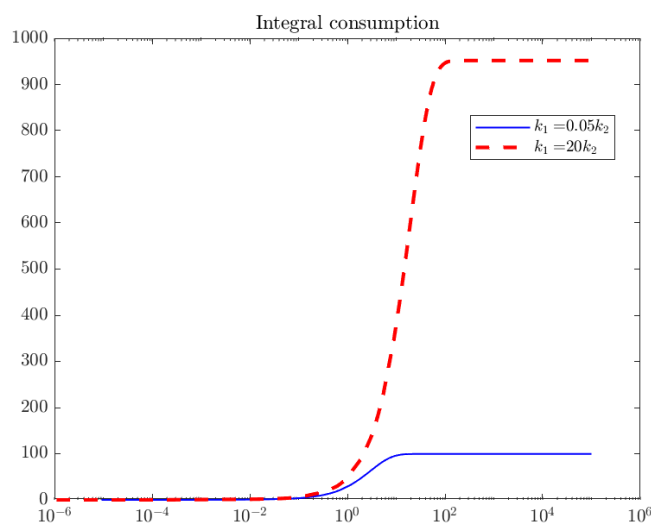**Figure 4.** Concentration $C_Z$ for different $k_1$.

**Figure 5.** Integral consumption for different $k_1$.

## 5. Interpretation and Discussion

The concept of the integral reactant consumption for the catalytic cyclic reaction accompanied by deactivation became the basis for deriving the corresponding analytical expressions.

These expressions, i.e., the integral reactant assumption and catalyst lifetime as a function of reaction parameters, are important for formulating a new general strategy in the optimization of these reactions or processes.

Equations (83) and (86) propose the following recipe for intensifying the catalytic process and extending the catalyst life. The concentration of free active sites (so to say, the deactivated catalytic intermediate) must be kept as low as possible.

It can be achieved by increasing the reactant concentration $C_A$ which reacts with the intermediate Z (free active site). In our case, this is reactant A.

It has arisen a reasonable question: "What about the justification of this recommendation?"

In the monograph "Homogeneous Catalysis with Metal Complexes: Kinetic Aspects and Mechanisms" by O.N. Temkin and P.P. Pozdeev [41], there is a special section devoted to this problem "5.3.5. Protecting active centers by catalytic process from destruction" pp. 492–493. The pioneering paper by Kagan et al. [42] was referred. The observed phenomenon is described as follows: in the reaction of hydroformylation of olefines catalyzed by Rh complexes, the high rate of transformation of the active complex, [HRh(CO$_3$)], leads to the decrease in the steady-state concentration of this complex. As result, the deactivation of this complex by the cluster generation is hindered. So, we can consider this publication as an experimental justification of the phenomenon, i.e., an enhancement of the catalyst lifetime by the decrease of the steady-state concentration of the free active sites. However, the theoretical analysis related to this phenomenon was still not done, and its corresponding relationships are absent.

## 6. Conclusions and Perspectives

In this paper, for the basic catalytic two-step mechanism (Temkin–Boudart mechanism) with irreversible reactions and irreversible deactivation, two analytical results have been obtained, i.e., the expression for the integral consumption of the gas substance and the expression for the catalyst lifetime. These results became a basis for distinguishing the new phenomenon, the enhancement of the catalytic reaction with deactivation via the regime with the small steady-state concentration of free active sites. In some domain of parameters, it can be achieved by increasing the steady-state (quasi-steady-state) reaction rate of the fresh catalyst. We can express this conclusion as follows: under some conditions,

the elevated fresh catalyst activity protects the catalyst from deactivation. These analytical results are illustrated by computer calculations.

We consider these results as prototypes of analogous results for similar models mentioned in the introduction of this paper, i.e., two-step mechanism and *n*-step single route linear mechanism with reversible steps, models with reversible deactivation, and models of reactions in the CSTR. For some of these models, we already have preliminary results and are going to develop them more applying this approach to the description of the experimental kinetic data with catalyst deactivation.

On the other side, the idea of "protecting active centers from deactivation by catalytic process" can be used heuristically for the intensification of the catalytic process.

**Abbreviations**

The following abbreviations are used in this manuscript:

QSS    quasi-steady state
NSS    non-steady state
SS      steady-state

**Appendix A. Epsilon Analysis**

In this section we give a mathematical implications of having small parameters $\varepsilon$. For this analysis we stick to the quasi-steady state domain of the system.

As derived in Section 3.4, the set of equations that hold in this domain look as follows,

$$C'_{AZ} = \frac{k_1 N_V C'_A}{k_1 N_V C'_A + k_2} N'_S, \tag{A1}$$

$$C'_Z = \frac{k_2}{k_1 N_V C'_A + k_2} N'_S, \tag{A2}$$

$$\frac{dN'_S}{d\tau} = -\frac{\varepsilon_2}{\varepsilon_1} \frac{k_1 k_2 N_V}{k_1 N_V C'_A + k_2} N'_S, \tag{A3}$$

$$\frac{dC'_A}{d\tau} = -\frac{k_1 k_2 N_V C'_A}{k_1 N_V C'_A + k_2} N'_S, \tag{A4}$$

$$C'_B = 1 - C'_A - \varepsilon_1 \frac{k_1 N_V C'_A}{k_1 N_V C'_A + k_2} N'_S. \tag{A5}$$

Note that if there is no deactivation Equation (A3) will be equal to zero, and we find the equations as presented in Section 3.3.1.

We have separated our analysis of the small parameters into two cases:

1. Only one small parameter is present, i.e., $\varepsilon_1 > 0$ and $\varepsilon_2 = 0$. As a result there is no deactivation and $N_S(t) = N_S^0$ or equivalently $N'_S(t) = 1$.
2. Two small parameters are present, i.e., $\varepsilon_1, \varepsilon_2 > 0$.

    (a)    $\varepsilon_1 \gg \varepsilon_2$
    (b)    $\varepsilon_1 \ll \varepsilon_2$
    (c)    $\varepsilon_1 \approx \varepsilon_2$

Case 1 is worked out in detail in Section 3.3.1. Case 2 makes use of the hierarchy of small parameters.

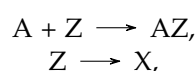*Appendix A.1. Case 2a: Two Small Parameters and $\varepsilon_1 \gg \varepsilon_2$*

In the following case, the hierarchy of small parameters is $\varepsilon_1 \gg \varepsilon_2$. As such the factor $\frac{\varepsilon_2}{\varepsilon_1}$ in Equation (A3) is approximately zero.

$$\frac{dN'_S}{d\tau} \approx 0 \tag{A6}$$

Replacing Equation (A3) with (A6) will result in a set of equations equivalent to those presented in Section 3.3.1.

We see that the solutions presented in Section 3.3.1 are a good approximation for this case. But only for a limited time.

As $C'_A$ becomes zero the effect of deactivation becomes prevelent again.
The two reactions

$$A + Z \longrightarrow AZ,$$
$$Z \longrightarrow X,$$

will no longer be in competition when $C'_A \approx 0$.

*Appendix A.2. Case 2b: There Are Two Small Parameters $\varepsilon_1 \ll \varepsilon_2$*

In the following case, the hierarchy of small parameters is $\varepsilon_1 \ll \varepsilon_2$. As such the factor $\frac{\varepsilon_2}{\varepsilon_1}$ in Equation (A3) is going to infinity.

To combat this, we introduce the following time scaling,

$$C'_{AZ} = \frac{k_1 N_V C'_A}{k_1 N_V C'_A + k_2} N'_S, \tag{A7}$$

$$C'_Z = \frac{k_2}{k_1 N_V C'_A + k_2} N'_S, \tag{A8}$$

$$\frac{dN'_S}{d\tau_\varepsilon} = -\frac{k_1 k_2 N_V}{k_1 N_V C'_A + k_2} N'_S, \tag{A9}$$

$$\frac{dC'_A}{d\tau_\varepsilon} = -\frac{\varepsilon_1}{\varepsilon_2} \frac{k_1 k_2 N_V C'_A}{k_1 N_V C'_A + k_2} N'_S, \tag{A10}$$

$$C'_B = 1 - C'_A - \varepsilon_1 \frac{k_1 N_V C'_A}{k_1 N_V C'_A + k_2} N'_S. \tag{A11}$$

where $\tau_\varepsilon = \frac{\varepsilon_2}{\varepsilon_1} \tau = \varepsilon_2 t$. Now $\frac{\varepsilon_1}{\varepsilon_2}$ is approximately zero and by extension $\frac{dC'_A}{d\tau_\varepsilon} \approx 0$.
We solve the system,

$$C'_{AZ} = \frac{k_1 N_V C'_A}{k_1 N_V C'_A + k_2} N'_S, \tag{A12}$$

$$C'_Z = \frac{k_2}{k_1 N_V C'_A + k_2} N'_S, \tag{A13}$$

$$\frac{dN'_S}{d\tau_\varepsilon} = -\frac{k_1 k_2 N_V}{k_1 N_V C'_A + k_2} N'_S, \tag{A14}$$

$$\frac{dC'_A}{d\tau_\varepsilon} = 0, \tag{A15}$$

$$C'_B = 1 - C'_A - \varepsilon_1 \frac{k_1 N_V C'_A}{k_1 N_V C'_A + k_2} N'_S, \tag{A16}$$

analytically and find,

$$C_A = C'_A(0) = C'_{A,fresh'} \tag{A17}$$

$$N'_S(\tau) = \exp\left(-\frac{\varepsilon_2}{\varepsilon_1} \frac{k_1 k_2 N_V}{k_1 N_V C'_{A,fresh} + k_2} \tau\right), \tag{A18}$$

$$C_{AZ}(\tau) = \frac{k_1 N_V C'_{A,fresh}}{k_1 N_V C'_{A,fresh} + k_2} \exp\left(-\frac{\varepsilon_2}{\varepsilon_1} \frac{k_1 k_2 N_V}{k_1 N_V C'_{A,fresh} + k_2} \tau\right), \tag{A19}$$

$$C_Z(\tau) = \frac{k_2}{k_1 N_V C'_{A,fresh} + k_2} \exp\left(-\frac{\varepsilon_2}{\varepsilon_1} \frac{k_1 k_2 N_V}{k_1 N_V C'_{A,fresh} + k_2} \tau\right), \tag{A20}$$

$$C_B(\tau) = 1 - C'_{A,fresh} - \varepsilon_1 \frac{k_1 N_V C'_{A,fresh}}{k_1 N_V C'_{A,fresh} + k_2} \exp\left(-\frac{\varepsilon_2}{\varepsilon_1} \frac{k_1 k_2 N_V}{k_1 N_V C'_{A,fresh} + k_2} \tau\right). \tag{A21}$$

If we determine the rate equation for this system,

$$\begin{aligned} R(\tau) &= k_2 C_{AZ} = k_2 C'_{AZ} N^0_S, \\ &= \frac{k_1 k_2 N_V C'_{A,fresh}}{k_1 N_V C'_{A,fresh} + k_2} N^0_S \exp\left(-\frac{\varepsilon_2}{\varepsilon_1} \frac{k_1 k_2 N_V}{k_1 N_V C'_{A,fresh} + k_2} \tau\right). \end{aligned} \tag{A22}$$

This rate equation coincides with the three-factor rate Equation (11) presented in [11], specifically for the case where there is no reversible deactivation.

*Appendix A.3. Case 2c: There Are Two Small Parameters $\varepsilon_1 \approx \varepsilon_2$*

In this case the system of equations are given by,

$$C'_{AZ} = \frac{k_1 N_V C'_A}{k_1 N_V C'_A + k_2} N'_{S'} \tag{A23}$$

$$C'_Z = \frac{k_2}{k_1 N_V C'_A + k_2} N'_{S'} \tag{A24}$$

$$\frac{dN'_S}{d\tau} = -\frac{\varepsilon_2}{\varepsilon_1} \frac{k_1 k_2 N_V}{k_1 N_V C'_A + k_2} N'_{S'} \tag{A25}$$

$$\frac{dC'_A}{d\tau} = -\frac{k_1 k_2 N_V C'_A}{k_1 N_V C'_A + k_2} N'_{S'} \tag{A26}$$

$$C'_B = 1 - C'_A - \varepsilon_1 \frac{k_1 N_V C'_A}{k_1 N_V C'_A + k_2} N'_S. \tag{A27}$$

Because there is no clear hierarchy in the small parameters we are not able to set one of the derivatives to zero. Instead we introduce the new differential equation,

$$\frac{dN'_S}{dC'_A} = \frac{\varepsilon_2}{\varepsilon_1 C'_A}. \tag{A28}$$

The analytical solution to this equation is found to be

$$N'_S(C'_A) = \frac{\varepsilon_2}{\varepsilon_1} \ln(C'_A). \tag{A29}$$

For this case, to find the time dependency we must refer back to numerical techniques.

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