

# The steady-state kinetics of parallel reaction networks

Saurabh A. Vilekar, Ilie Fishtik, Ravindra Datta\*

Fuel Cell Center, Department of Chemical Engineering, Worcester Polytechnic Institute, Worcester, MA 01609, USA

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## ABSTRACT

The conventional kinetic analysis of an overall reaction (OR) is limited to a single sequential pathway of molecular steps at a time, based either on the general quasi-steady state (QSS) approach of Bodenstein, or on the much simpler but limited Langmuir–Hinshelwood–Hougen–Watson (LHHW) approach based on assuming a single rate-determining step (RDS), the remaining being quasi-equilibrated (QE). We recently described a new algebraic methodology for deriving the QSS rate expression for a reaction sequence, which allowed interpretation of the final result in an Ohm's law form, i.e., OR rate = OR motive force/OR resistance of an equivalent electric circuit, where the consecutive mechanistic steps represent resistors in series. Here, we propose a similar Ohm's law form of QSS rate for a reaction system involving parallel pathways, whose equivalent electrical circuit derives directly from the reaction route (RR) Graph of its mechanism, as proposed earlier by us. The results are exact for a reaction network with mechanistic steps linear in intermediates concentrations, while they are approximate, albeit accurate, for non-linear step kinetics. We further show how the LHHW methodology, combined with the concept of intermediate reaction might be utilized to obtain the step resistances involved. For illustration, we utilize the relatively simple examples of: (1) the gas-phase hydrogen–bromine non-catalytic reaction (non-linear kinetics), and (2) zeolite catalyzed N<sub>2</sub>O decomposition reaction (linear kinetics). However, the approach is useful for more complex non-catalytic, catalytic and enzymatic reactions networks as well.

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## 1. Introduction

Many of the industrially significant reactions involve parallel reaction pathways. A quandary for the reaction engineer has been how to explicitly account for these alternate pathways in describing the overall reaction (OR) rate,  $r_{OR}$ , in terms of the kinetics of the elementary reaction steps, i.e., in determining the so-called OR “rate law” in terms of the known step weights,  $\omega_\rho$  (Christiansen, 1953; Horiuti, 1973; Temkin, 1979; Wagner, 1970), which represent the step mass-action kinetics with the exclusion of the unknown intermediates compositions. The most general approach for this is the quasi-steady state (QSS) approximation of Bodenstein (Christiansen, 1953; Horiuti, 1973; Temkin, 1979; Wagner, 1970), based simply on the assumption of time-invariance of reaction intermediates. However, an explicit QSS rate expression for overall rate  $r_{OR}$  is often unwieldy, or not possible at all when step kinetics are non-linear in intermediates concentrations (Lazman and Yablonskii, 1991), only numerical results then being possible for a given set of reaction conditions.

The Langmuir–Hinshelwood–Hougen–Watson (LHHW) methodology (Hougen and Watson, 1943), on the other hand, does

generally allow the development of simple explicit expressions for  $r_{OR}$ , but it is based on the often arbitrary assumption of a *single* rate-determining step (RDS), the remaining being at quasi-equilibrium (QE). Further, the *a priori* identification of such a RDS in the mechanism, if it exists at all, is not simple. Dumesic (1999) has presented an approach based on De Donder relations for identification of the RDS involving the concept of step reversibility. Thus, the RDS is defined as the step,  $s_\rho$ , whose step reversibility,  $z_\rho$  ( $\equiv \vec{r}_\rho / \overleftarrow{r}_\rho = \exp(-\mathcal{A}_\rho)$ , the ratio of the step rate in the backward, to that in the forward direction), is approximately equal to that of the OR,  $z_{OR} \equiv \vec{r}_{OR} / \overleftarrow{r}_{OR} = \exp(-\mathcal{A}_{OR})$ . Here, the dimensionless De Donder affinity,  $\mathcal{A}_\rho = -\Delta G_\rho / RT$  for the step, and  $\mathcal{A}_{OR} = -\Delta G_{OR} / RT$  for the overall reaction.

Campbell (2001) has, however, pointed out that such a criterion for identifying the RDS is limited, since reversibility of a step represents only its thermodynamic driving force, not containing any information, for instance, on its activation barrier, or kinetics. On the other hand, identification of RDS simply based on activation barriers is fraught with risk as well. In fact, the net step rate involves both kinetics and thermodynamics, i.e.,  $r_\rho = \vec{r}_\rho - \overleftarrow{r}_\rho = \vec{r}_\rho(1 - z_\rho) = \vec{r}_\rho(E_\rho)$ , where  $E_\rho = 1 - \exp(-\mathcal{A}_\rho)$  represents the thermodynamic driving force (Christiansen, 1953), while  $1/\vec{r}_\rho$  represents a kinetic resistance. Campbell's degree of control approach, on the other hand, based on sensitivity analysis to identify the step rate constant(s) that most influence  $r_{OR}$ ,

\* Corresponding author. Tel.: +1 508 831 6036.

E-mail address: [rdatta@wpi.edu](mailto:rdatta@wpi.edu) (R. Datta).

provides a more robust approach for the identification of the RDS. However, it is based on a numerical analysis. The reaction step resistance,  $R_\rho$ , discussed by us below and elsewhere is, in fact, the most convenient criterion for identifying the slow or rate-limiting steps in a sequence. We assume, in fact, that there can, in general, be more than a single rate-limiting step (RLS), the latter being distinct from the rate-determining step (RDS).

Furthermore, given that there are now first-principles and semi-theoretical methods (Heyden, 2005; Heyden et al., 2005; Shustorovich and Sellers, 1998) available that can predict the kinetics of the elementary reaction steps with increasing accuracy, it is now increasingly important that more comprehensive methods for the analysis of reaction networks be developed, which is our objective here, based on an intuitively appealing electrical analogy of reaction networks.

The electrical analogy is, in fact, commonly invoked in a qualitative discussion of reaction mechanism and kinetics (Fogler, 2006), wherein reaction steps are represented by individual resistances, with the current (rate) being driven by an overall motive force. The electrical analogy was, in fact, first proposed by Nernst (1926), who suggested that the rate of a chemical reaction might be represented in analogy to Ohm's law, being equal to a "chemical force" divided by a "chemical resistance." Besides its intuitive appeal, the analogy is useful in visualizing the network, and especially when rationalizing the assumption of a RLS, as one with the highest "resistance" in a sequence. However, it is rarely utilized in a quantitative analysis. This is so, because the relationships of the step resistance and the motive force to the conventional reaction kinetic and thermodynamic quantities have remained unclear, and it is not known how one might draw an appropriate equivalent electric circuit for a complex mechanism.

We have, actually, more recently developed a Reaction Route (RR) graph approach (Fishtik et al., 2004a,b, 2005a, 2006) that puts this analogy on a rigorous footing by: (1) providing the equivalent electrical circuit for a given mechanism adapted directly from its RR graph, and (2), defining the step resistance in terms of step kinetics via the relation  $R_\rho \equiv \ln(\bar{r}_\rho/\tilde{r}_\rho)/(\bar{r}_\rho - \tilde{r}_\rho)$ , and the dimensionless De Donder affinity,  $\mathcal{A}_\rho$ , as the driving force, resulting in Ohm's law form for step kinetics,  $r_\rho = \mathcal{A}_\rho/R_\rho$ . The corresponding overall rate then takes the form  $r_{OR} = \mathcal{A}_{OR}/R_{OR}$ , where  $R_{OR}$  may be obtained in terms of  $R_\rho$  from the RR graph in a manner completely equivalent to that in electrical circuits (Fishtik et al., 2005b). However, only numerical analysis is possible in this manner, since the step rates,  $\bar{r}_\rho$  and  $\tilde{r}_\rho$ , and, hence, the step resistances are not known *a priori*, involving the unknown intermediates concentrations.

In a recent paper (Vilekar et al., 2009), however, we followed an alternate algebraic methodology for the QSS analysis of a reaction sequence, in which the final result was of a form that could be cast into an alternate Ohm's law form, i.e.,  $r_{OR} = E_{OR}/R_{OR}^*$ , where the OR driving force is in the conventional form,  $E_{OR} = 1 - z_{OR} = \{1 - \exp(-\mathcal{A}_{OR})\}$ , and the OR resistance could be expressed as a sum of the step resistances in series,  $R_{OR}^* = \sum_\rho R_\rho^*$ , while the step resistances  $R_\rho^*$  could be determined *a priori* via the LHHW methodology, thus providing a new analytical approach based on the electrical analogy. Here, we show that this new form can be extended readily to parallel reaction networks as well, where  $R_{OR}^*$  relates to step resistances  $R_\rho^*$  in the usual manner of electrical circuits. This approach not only provides an explicit QSS rate expression for a given mechanism in terms of step kinetics, but also affords perceptive insights into the dominant pathways and rate-limiting steps, thus allowing rigorous network pruning.

We first describe how one might use a given molecular mechanism of an OR to construct its RR graph, which depicts reaction steps as branches interconnected at nodes such that all possible reaction pathways for the OR are represented simply as

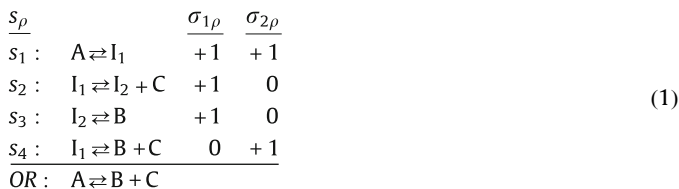
walks on the RR graph. Next, the RR graph is converted into an equivalent circuit by simply replacing the branches by resistors representing the steps, followed by Ohm's law representation of overall rate, with the overall resistance being obtained from the resulting circuit. We show, for the case of linear step kinetics, that the result is exactly the same as that obtained via linear algebra from the conventional QSS analysis. Further, we show that, while approximate, the results are very accurate for non-linear kinetics as well. All the necessary details along with definitions from our previous work are also summarized so that the treatment below is self-contained.

For ease of comprehension, further, the application of our approach to parallel pathway reaction networks is illustrated here for the relatively simple cases of: (1) gas-phase hydrogen-bromine reaction (non-linear kinetics), and (2) zeolite catalyzed  $N_2O$  decomposition reaction (linear kinetics) mechanism, both involving only a handful of steps. Of course, more complex mechanisms are similarly amenable to kinetic analysis.

## 2. Theory

### 2.1. Reaction Routes: basic definitions

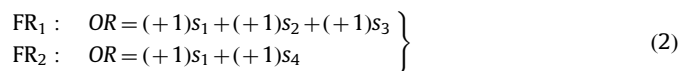
We first consider a simple generic 4-step mechanism with parallel pathways given in Eq. (1), in order to explain the essentials of RR graphs approach, while avoiding the mathematical details (Fishtik et al., 2004a,b, 2005a, 2006).



This mechanism admits two parallel pathways, or reaction routes (RRs), as indicated above by the stoichiometric numbers in the two columns. Thus, steps  $s_1$ ,  $s_2$ , and  $s_3$ , when added, result in a cancellation of the intermediates  $I_1$  and  $I_2$ , resulting in the OR. Similarly,  $s_1 + s_4$  provides the OR, which is a second RR. More formally, thus, we define:

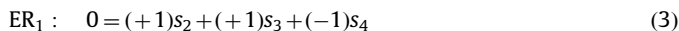
**Reaction Route (RR):** or a reaction pathway, or a reaction sequence, is a linear combination of elementary steps,  $\sum_{\rho=1}^p \sigma_{g\rho} s_\rho$  that eliminates a specified number of intermediate and terminal species to produce a reaction, where  $\sigma_{g\rho}$  is the stoichiometric number (usually, 0,  $\pm 1$  or  $\pm 2$ ) of step  $s_\rho$  in the  $g$ th RR. If all the intermediate species are eliminated the reaction route is called a **Full Route (FR)**.

Thus, for the above example, the two RRs may be written as



On the other hand, an **Empty Route (ER)** or a cycle is a linear combination of the elementary steps such that all of the species, both intermediate and terminal, are cancelled, thus producing the so-called "zero" OR (i.e., the stoichiometric coefficients of all the species are zero).

In fact, since subtracting one FR from the other, e.g.,  $FR_1 - FR_2$ , would eliminate all the species, it can provide an empty route (ER), e.g.,



A negative stoichiometric number, as above, simply indicates that the step in the given RR is followed in the reverse direction to that indicated in Eq. (1). Since all elementary steps are reversible, in

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